Downloaded from rsta.royalsocietypublishing.org

THE PVT Properties of Water I. Liquid Water in the Temperature Range 0 to 150 degrees C and at Pressures up to 1 kb

G. S. Kell and E. Whalley

Phil. Trans. R. Soc. Lond. A 1965 **258**, 565-614
doi: 10.1098/rsta.1965.0051

Email alerting service Receive free email alerts when new articles cite this article - sign up in the box at the top right-hand corner of the article or click here

To subscribe to *Phil. Trans. R. Soc. Lond. A* go to: **http://rsta.royalsocietypublishing.org/subscriptions**

This journal is © 1965 The Royal Society

Downloaded from rsta.royalsocietypublishing.org

THE *PVT* PROPERTIES OF WATER

I. LIQUID WATER IN THE TEMPERATURE RANGE 0 TO 150 °C AND AT PRESSURES UP TO 1 kb*

By G. S. KELL and E. WHALLEY
Division of Applied Chemistry, National Research Council, Ottawa, Canada

(*Communicated by W. G. Schneider, F.R.S.—Received* 20 *April* 1964
—*Revised* 9 *December* 1964)

CONTENTS

PART I. EXPERIMENTAL METHODS

PART II. COMPRESSION AND THERMAL EXPANSION OF WATER

PART III. THE MERCURY COLUMN

---

* N.R.C. No. 7607.

The Royal Society is collaborating with JSTOR to digitize, preserve, and extend access to
Philosophical Transactions of the Royal Society of London. Series A, Mathematical and Physical Sciences.
www.jstor.org

Downloaded from rsta.royalsocietypublishing.org

An apparatus for measuring the *PVT* properties of water with high accuracy up to 1 kb over a wide temperature range is described. A 57 ft. mercury column has been built primarily to calibrate free-piston pressure balances used in this work.

The compression of water relative to mercury has been measured at intervals of 10 degC from 0 to 150 °C and at pressures from 5 to 1026 b, to a reproducibility of 4 to 7 p.p.m. of the volume, and a maximum uncertainty of about 40 p.p.m. at 1000 b. The specific volumes are given in tabular form, and in terms of interpolation equations. The isothermal compressibilities at atmospheric pressure have been obtained with a standard error of about $0{\cdot}03 \times 10^{-6}$ b^{-1}.

The thermal expansion of water relative to mercury at 5·30 b has been measured in the range 80 to 150 °C with an error not more than 5 p.p.m. at 80 °C, 10 p.p.m. at 100 °C, and 20 p.p.m. at 150 °C. The specific volumes, densities, and thermal expansivities have been adjusted to atmospheric pressure and to saturation pressure using the compressions reported here, and are tabulated. A kink reported by Antonoff and Conan in the density of water as a function of temperature near 50·5 °C has been looked for; the density is smooth to 1 p.p.m. over the range 47·5 to 52·0 °C, and the reported kink does not exist.

1. Introduction

The Fourth International Conference on the properties of Steam was convened by the American Society of Mechanical Engineers in Philadelphia in September 1954, primarily for the purpose of encouraging research. A review of the properties of steam that had been measured up to that time was presented by Keyes & Keenan (1955), and the Conference recommended that accurate new measurements were required at temperatures to 800 °C and pressures to 1000 atm. As a contribution to the programme of measurement that resulted from the conference, accurate measurements of the *PVT* properties of water, both as liquid and vapour, were undertaken in these laboratories. The guiding aim of this work is to make the measurements as accurately as is practicable. A survey of previous measurements showed that the density of water under pressures up to 1 kb had not been measured at any temperature to the accuracy that current techniques are capable of. We have, therefore, undertaken measurements on the liquid and vapour starting at 0 °C. The first part of the project has been to determine the specific volume in the liquid region between 0 and 150 °C and up to 1 kb, and the present paper reports the apparatus used and the results of this work. The experimental techniques used in this region are described in part I. The compressions in the range 0 to 150 °C and 5·30 to 1026 b are reported in part II.

At temperatures above 85 °C there are no measurements of the density of water of sufficient accuracy to combine with the compressions reported here. Isotherms were measured at several temperatures for each filling, and it would be possible to use those measurements to determine thermal expansions. Cumulative errors are avoided by measuring the thermal expansions at a relatively low pressure in a separate series of measurements, and we have, therefore, measured the thermal expansion of water up to 150 °C in the same apparatus. Antonoff & Conan (1949) have reported a kink in the density of water as a function of temperature near 50·5 °C. Measurements have been made from 47·5 to 52·0 °C in an attempt to verify this.

The measurement of *PVT* properties requires measurements of mass, volume, pressure, and temperature of a sample of material. Under favourable conditions accuracies of about 10 p.p.m. (parts per million) can be obtained in the measurement of mass, volume, and temperature, in any reasonably well equipped laboratory. The accuracy obtainable in

Downloaded from rsta.royalsocietypublishing.org

measuring pressure is very much less than this, as is demonstrated by the reported vapour pressure of carbon dioxide at the ice-point of water summarized in table 1. This is the only pressure above several bars that has been measured accurately in several laboratories, and the mean value, assuming all points to have the same weight, has a standard error of about 200 p.p.m.

Table 1. Vapour pressure of carbon dioxide at the ice-point

reference	vapour pressure (b)	claimed accuracy	deviation from mean
Bridgeman (1927)	34·8567	0·0013	+0·0083
Meyers & Jessup (1931)	34·8497	0·003–0·006	+0·0013
Roebuck & Cramm (1947)	34·8401	0·003	−0·0083
Michels, Wassenaar, Zweitering & Smits (1950)	34·847	0·001	−0·001
mean	34·848		
standard error of mean if all measurements have same weight	0·007		

Further, high pressures are almost invariably measured accurately by means of a pressure balance, and the gauge constant has nearly always been assumed to be independent of pressure. Simple elastic theory indicates, and recent experiments (Johnson, Cross, Hill & Bowman 1957; Dadson 1958; Bett & Newitt 1963) tend to confirm, that the pressure coefficient of the effective area of typical balances is some parts per 10 million per bar. If this is so, then at a pressure of 1 kb the effective area of a balance deviates from that at zero pressure by some hundreds p.p.m. and this is not usually taken account of. It is evident, therefore, that the pressure is by far the least accurate of the properties mentioned above.

We have, therefore, as part of the present programme, built a differential mercury column for calibrating pressure balances to 3 kb to a high accuracy. It differs in several particulars from previous similar columns (Holborn & Schultze 1915; Keyes & Dewey 1927; Beattie & Edel 1931; Bett, Hayes & Newitt 1956), and only the improvements will be described in detail. This is done in part III.

PART I. EXPERIMENTAL METHODS

2. General description

The principle of the method used is to measure, by means of a calibrated piston, the change of volume of a fixed mass of water with change of temperature or pressure. The method is, of course, well known and has been used, for example (Keyes 1933; Smith & Keyes 1934; Keyes, Smith & Gerry 1935), for measuring the *PVT* properties of water in the range 30 to 450 °C up to 350 b. Our apparatus, which differs from Keyes's in many details, is shown schematically in figure 1. The pressure vessel, whose volume was known, was immersed in a thermostat and was filled with water. The pressure of the water was measured by means of pressure balances, the oil of the balances and the water being separated by mercury in a U tube or in two legs of a Ш tube. The change of mass of water in the pressure vessel due to change of either pressure or temperature was measured by the change of position of the piston of the volumometer. The piston, which was calibrated,

Downloaded from rsta.royalsocietypublishing.org

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

could be advanced into the cylinder by means of a screw thread. To ensure that the elastic deformation of the major parts of the apparatus was hydrostatic only, so as to prevent permanant deformation, the pressure vessel and the cylinder of the volumometer were jacketed by other pressure vessels and were pressurized externally by water at the experimental pressure, and the piston of the volumometer was balanced by a similar piston also subjected to the experimental pressure. In the earlier measurements the balancing pressure was measured by a Bourdon gauge which replaced the connexion to the left-hand leg of the ɯ tube in figure 1. In the later measurements the U tube was replaced by a three-legged or ɯ tube and the equality of pressure of the balancing water and the experimental water was detected by means of this.

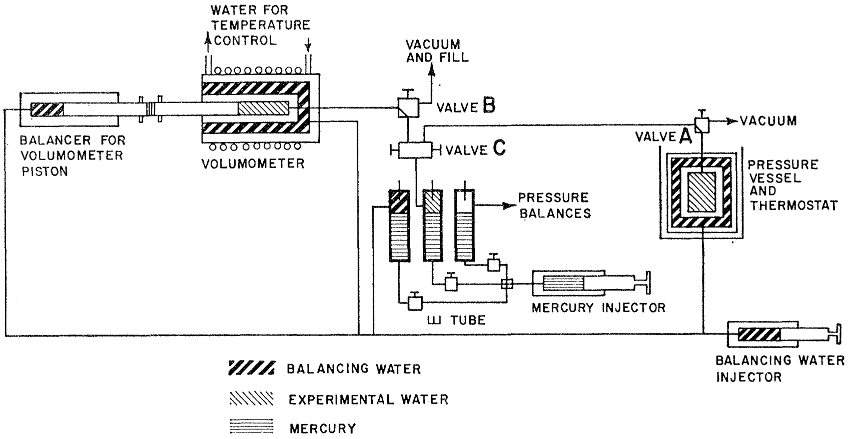

Figure 1. Diagrammatic sketch of the *PVT* apparatus. When the U tube was used the balancing water system was connected to a Bourdon gauge instead of to the ɯ tube.

3. Experimental problems

The aim of this work is to measure the *PVT* properties of liquid and gaseous water to as high an accuracy as practicable. The accuracy required for the different individual measurements that are required depends upon the properties of water, and varies greatly in different regions of pressure and temperature. In the liquid region, say up to 150 °C, an accuracy of the specific volume of about 10 p.p.m. seemed attainable. The compression of water at 1000 b is about 50000 p.p.m. in this range, so that the compression should be measured to at least 200 p.p.m. of its maximum value. The accuracy of the many quantities required to determine compressions should correspond to 70 to 100 p.p.m. of the maximum compression if practicable. If the compressions are measured on 250 $\mathrm{cm^3}$ of water, then changes of volume of 2·5 $\mathrm{mm^3}$ should be readily detectable. A travel of the piston of the volumometer of about 25 cm and a maximum displacement of 50 $\mathrm{cm^3}$ were chosen; a displacement of 2·5 $\mathrm{mm^3}$ then corresponds to a movement of the piston of 12 μm, which should be measurable.

The fractional increase $\delta V/V$ of the volume of a closed-end heavy-walled vessel that is subjected to a pressure p inside and zero outside is, according to the usual theory of elasticity and neglecting end effects,

$$\frac{\delta V}{V}=\frac{p}{E}\,\frac{3(1-2\nu)+2(1+\nu)k^2}{k^2-1},$$

Downloaded from rsta.royalsocietypublishing.org

where ν is Poisson's ratio, E is Young's modulus, and k is the ratio of outside to inside diameters of the vessel. If $E = 2 \times 10^6$ b and $\nu = 0{\cdot}3$, which are typical values for steels, $k = 2$, and $p = 1000$ b, then

$$\delta V/V = 1900 \text{ p.p.m.}$$

Unfortunately, this is too big to calculate accurately, and the calculation would be unrealistic if permanent deformations occurred. Consequently, the vessel should have the same pressure inside and out. Then the inside volume decreases in the proportion $p\kappa_v$, where κ_v is the bulk compressibility of the material of the vessel. If κ_v is $0{\cdot}7 \times 10^{-6}$ b^{-1}, which is a typical value for steel, then the fractional increase of volume at 1000 b is -700 p.p.m. independent of the shape of the vessel. If the specific volume of water is to be determined to 10 p.p.m., then κ_v must be known more accurately than $0{\cdot}01 \times 10^{-6}\ \text{b}^{-1}$. Unfortunately, it is not known to this accuracy, and indeed our vessel is made of stainless steel for which the compressibility is probably not reproducible enough from sample to sample for measurements on another piece, even of the same nominal composition, to be used. The compressibility of the vessel must therefore be measured. This is most easily done relative to a reference substance, and mercury has been used because it is isotropic, it has a low compressibility, and it is easily obtained in a reproducible high purity. Unfortunately, the compression of mercury is uncertain enough in some parts of the range to limit the accuracy of the specific volumes of water. The thermal expansion of the vessel at low pressures is also needed, and this has also been measured relative to mercury in the range 0 to 150 °C.

It is not practicable to pressurize externally the U or ꟺ tube, or all the connecting tubing, valves, junction blocks, etc. If their internal volume, and the stresses in them, are kept low enough, their expansion under pressure should be reproducible enough for our purposes, and can be included in the calibration. The volume of the unpressurized components can be kept to less than 0·01 of the total volume of the system, and so its inelastic deformation should be less than 1000 p.p.m. of this small volume. To ensure that this is so, the maximum stress in the unpressurized components has been kept less than one-half of the tensile yield stress for 0·2 % offset.

The accuracy required of the balancing pressure deserves comment. The fractional change of the inside volume of a vessel due to a difference of pressure δp between inside and outside is

$$\frac{\delta V}{V} = -\frac{\delta p}{E}\,\frac{(5-4\nu)\,k^2}{k^2-1}.$$

If $\delta V/V$ is to be less than 2 to 3 p.p.m. then, with the data given above, the pressure difference should be less than 1 b.

The maximum thermal expansivity of water in the range 0 to 150 °C is about 10^{-3} degC^{-1}. Consequently, the temperature of the main water sample should be controlled to $\pm 0{\cdot}002$ degC. There will inevitably be parts of the system that contain water whose temperature will be difficult to control, such as connecting tubing, valves, junction blocks, the water side of the mercury U tube or ꟺ tube, etc. The room containing the apparatus is air-conditioned, and the temperature of the apparatus exposed to the atmosphere did not vary more than a few tenths of a degree during a run. The maximum

Downloaded from rsta.royalsocietypublishing.org

volume that is not specially thermostatically controlled should therefore not be more than a few cubic centimetres.

The pressure should be measured to better than 200 p.p.m.

4. Measurement of pressure

The pressure of the water was measured by two free-piston pressure balances of the kind described in part III, one of 0·516 in. diameter and one of 0·181 in. diameter. The temperature of the balances was measured by a mercury thermometer placed nearby; it did not vary by more than a few tenths of a degree during a run. The temperature coefficient of the effective area is about 22×10^{-6} degC^{-1}; hence the variation of the effective area due to this variation of temperature is negligible. The pressure balances were calibrated by Dr F. M. Kavcic to an accuracy of about 100 p.p.m. over their pressure range by means of the mercury column described in part III. Allowance was made for the different temperatures used for calibration and for normal use. The weights of 1 kg and above were calibrated by the Standards Division of the Department of Trade and Commerce, and those below 1 kg by ourselves.

For the compression measurements the balancing pressure was measured by a 3 kb Heise Bourdon gauge with a 12 in. face graduated at 5 b intervals. The gauge was calibrated to 1000 b to an accuracy of 1 or 2 b with the pressure balance. In an attempt to eliminate some of the hysteresis in the measurements described in §§10 and 14, the balancing pressure was connected to one leg of the ɯ tube for the thermal expansion measurements, and was thus within a few millibars of the experimental pressure.

The barometric pressure was measured by a Casella Fortin-type barometer calibrated in accordance with British Standard 2520 (1954).

5. Control and measurement of temperature

The thermostat in which the pressure vessel was suspended was a well-insulated stainless-steel tank filled with light transformer oil and fitted with a cover. The bath liquid was stirred vigorously, and was heated electrically by a steady and an intermittent heater. The intermittent heater usually delivered 15 to 25 W, and it was controlled by a 25 Ω metal-clad platinum resistance thermometer connected to a Rubicon 1551 Mueller bridge whose galvanometer operated a photorelay. At the lower temperatures cooling was required, and cooling water was pumped, through a copper coil in the main bath, from an auxiliary thermostat maintained about 2½ degC below the required temperature.

The temperature of the main bath was measured by a 25 Ω quartz-clad platinum resistance thermometer using a Leeds and Northrup 8069 G-2 Mueller bridge. The thermometer was calibrated at the triple point of water, and at the tin and zinc points in terms of the International Practical Temperature scale (1948) by the Division of Applied Physics, and was checked frequently at the triple point of water. The temperature of the bath as measured by this thermometer oscillated by ±0·002 degC or less about the mean temperature with a period of 30 to 90 s and the mean temperature remained constant within 0·001 degC over the 1 to 2 h required to measure one point. The mean temperature of the bath at the place of measurement was therefore known to 0·001 degC. The variation in

Downloaded from rsta.royalsocietypublishing.org

the mean temperature throughout the bath except near the intermittent heater was less than 0·002 degC.

The temperature of the volumometer was controlled by circulating water from a thermostat, through a copper coil wound around it, and by encasing it in a plastic box, This thermostat was maintained at 24 °C to ±0·005 degC by a mercury-in-glass contact thermometer. The temperature of the bath was measured by a Beckman thermometer which was checked monthly against a platinum resistance thermometer. The temperature of the volumometer was taken to be the temperature of the circulating water measured as it flowed away from the volumometer. It varied slowly within a range of 0·01 degC.

6. Pressure vessel

The pressure vessel is shown to scale in figure 2. It comprised an inner vessel made of 304 stainless steel having a volume of about 250 cm^3, and an outer vessel of Atlas steel SPS 245 heat-treated to a hardness of about 36 Rockwell C. To reduce contamination of the inner vessel as much as possible, it was carefully cleaned before the head was screwed on, and the head was welded to it without flux. To prevent the outer weld from cracking when the vessel was pressurized, a support ring of heat-treated A.I.S.I. 4340 steel was shrunk onto the welded end of the vessel as shown in figure 2.

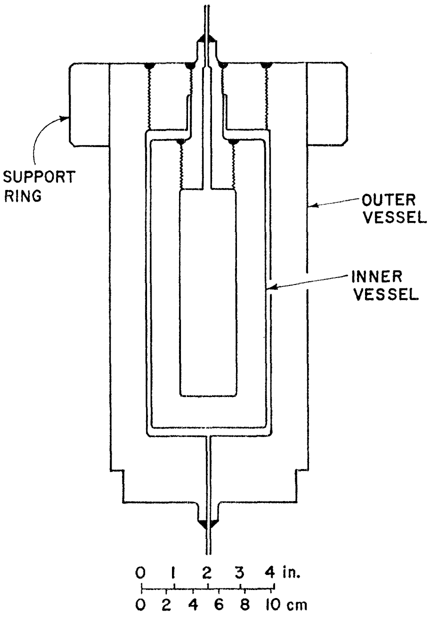

Figure 2. Pressure vessel.

7. Volumometer

The volumometer, which is illustrated in figure 3, is the crucial part of the apparatus, and consequently it is described in some detail. It is essentially a calibrated piston advanced into a cylinder by means of a screw thread. The piston is $\frac{5}{8}$ in. in diameter, made of heat-treated 440 C stainless steel, chromium plated to a depth of 0·001 in., lapped to a diameter constant to 0·0002 in., and polished to a mirror finish. It was pressed

Downloaded from rsta.royalsocietypublishing.org

and pinned accurately into the end of a rod, $\frac{3}{4}$ in. diameter and 16 in. long, of the same material, on which was cut a micrometer screw thread of 40 threads per inch. A micrometer thimble was bolted to the end of the micrometer screw. The thread was engaged with the corresponding thread on the fixed brass sleeve illustrated in figure 3. This thread was 5 in. long, and the two threads were carefully made and lapped together so as to be as uniform as practicable. The position of the piston could be read from a scale on the fixed brass sleeve and graduations on the thimble. The thimble was graduated in hundredths of a revolution and tenths of this could be estimated, so that the scale could be read to about ± 25 μin. or 0·6 μm which was equivalent to a volume of about 0·1 mm^3.

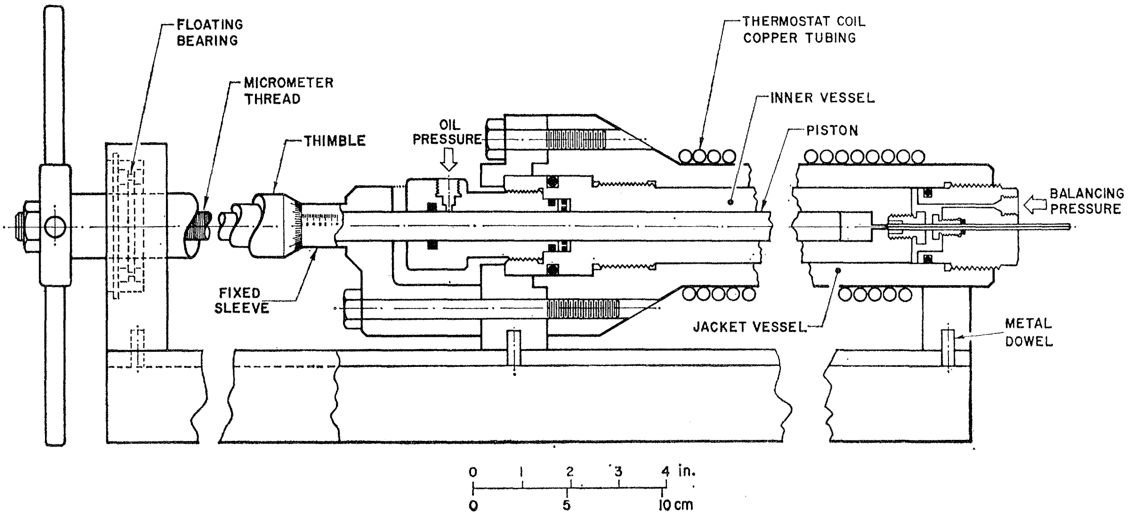

Figure 3. Volumometer.

The cylinder was made of heat-treated 431 stainless steel. The force exerted by the pressure within it was balanced in three ways. First, the cylinder was jacketed by a second vessel which was pressurized at the experimental pressure to avoid permanent deformation of the cylinder. The delivery tube of the volumometer passed through an O-ring seal in the head of the jacket in the manner shown on the right-hand side of figure 3. Secondly, the end thrust on the piston was balanced by the thrust of an exactly similar collinear piston subjected to the balancing pressure. The purpose of this was to minimize the stress in the micrometer screw threads and in the fixed sleeve (see figure 3), and to reduce the wear of the screw threads. The fact that the piston could be turned by a torque of about 15 ft. lbf. at a pressure of 1000 b shows that this was quite successful. During one preliminary experiment the balancer failed when the system was at 760 b. The volumometer shaft took the whole thrust for about half an hour while the balancer seal was repaired, and during this time the system was strained permanently by enough to cause the volumometer scale reading for the same pressure before and after the strain to change by 6×10^{-4} in. About half of this strain subsequently recovered. This result indicates the great increase in stability produced by the balancing system. And finally, the piston seal, which was an O-ring, was balanced by oil pressure generated by the pressure balance. The purpose of this was to reduce wear of the O-ring and to eliminate changes of volume due to extrusion of the O-ring.

Downloaded from rsta.royalsocietypublishing.org

The seal was originally designed to be a Teflon ring, but this was unsuccessful as there was too much friction and the Teflon extruded too much. The Teflon seal was therefore replaced by a metal ring containing two O-rings, as there was too much space for one standard-sized O-ring. This seal was successful except that the O-ring deteriorated too quickly by wear on the piston. The wear could not be reduced enough by changing the material of the O-ring or by polishing the shaft; it was eventually reduced to an insignificant amount by applying oil pressure from the pressure balances to one side of the O-rings as shown in figure 3, and in more detail in figure 4. This pressure is of course within a few millibars of the pressure of the water on the other side of the O-rings. Evidently the oil lubricates the seal, but in spite of careful tests, there is no evidence that measurable (> 0·5 mg per isotherm) quantities of oil enter or of water leave the cylinder of the volumometer. The O-rings had the diametral cross-sectional squeeze recommended by the manufacturers, and a slight longitudinal squeeze so that the O-rings were accurately positioned and defined a volume sharply. Deep scratches on the surface adjacent to the O-ring of the spacer in figure 4 permitted the water to press uniformly on the O-rings from the water side, and weep holes in the O-ring holder permitted the pressure to act uniformly on the oil side. One set of O-rings, installed in July 1962, was used for all the measurements reported in this paper. These O-rings were inspected in September 1963 and showed only the slightest trace of wear; they could probably be safely used for several years.

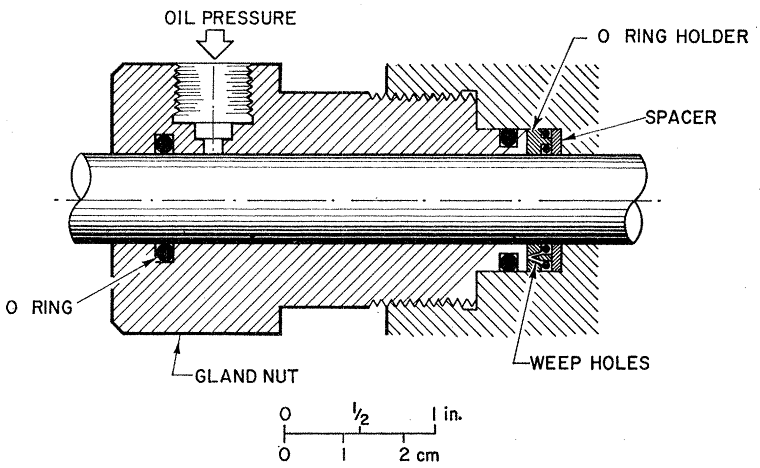

FIGURE 4. Detail of the seal of the piston of the volumometer.

The volumometer and the balancer were mounted on 6 in. × 2 in. channel iron, and both pieces of channel iron were mounted on a length of 12 × 5 I-beam to aline the two shafts.

8. U OR Ш TUBE, VALVES, TUBING, AND FITTINGS

Both the U tube and the Ш tube were made of 303 stainless steel. The contact pins were made of 304 stainless steel with welded platinum tips, and Nylon washers formed pressure and electrical seals. The lengths of the pins were measured by a cathetometer. Contact between the mercury and pins was detected by simple oscilloscopes, which gave an indication of the quality of contact as well as of the fact of contact. In the Ш tube, the clearance

Downloaded from rsta.royalsocietypublishing.org

MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES
THE ROYAL SOCIETY A
PHILOSOPHICAL TRANSACTIONS OF

between the pin and the side of the tube was so small that the pin had to be insulated, except for the tip, with a varnish of polymethylmethacrylate dissolved in methylene chloride. The U-tube was $\frac{3}{16}$ in. in diameter where contact was made. When the contact was made and broken on the water side by varying the position of the volumometer piston, keeping at the same time a constant pressure by means of the pressure balance, the difference in volume between make and break of the contact was usually about 3 mm³, and occasionally reached 5 mm³ or about 20 p.p.m. of the volume of the pressure vessel. When the Ш tube was used this was reduced to about 0·2 mm³, or about 1 p.p.m. of the volume of the pressure vessel, because the diameter of the tube where the contact was made had been reduced to $\frac{1}{16}$ in.

The amount of mercury in the tubes was controlled by means of a screw injector that could be connected to any or all of the tubes. To reduce the chance of mercury entering the connecting tubing due to too big a pressure difference across the Ш tube, a small mercury reservoir was provided above the position of contact by widening the tube to $\frac{1}{8}$ in. i.d. for $\frac{1}{2}$ in. The mercury was purified by shaking with dilute nitric acid and distilling three times in a current of air at a pressure of about 25 mb in a Pyrex still. The tubes were passivated by treating with concentrated nitric acid to reduce contamination of the mercury. The platinum tips of the contacts and the mercury surfaces gave good contacts indefinitely.

There were three valves in contact with the experimental water, labelled A, B and C in figure 1. Valve A was made of 304 stainless steel, had Teflon packing, and was thermostated by circulating water from the 24 °C bath (§5) through the cooling channel. Valves B and C were small commercial pressure valves; C was Teflon packed, and B was O-ring packed since the packing was not in contact with the experimental water except while the apparatus was being filled.

The capillary connecting tubing was 304 stainless steel, $\frac{1}{8}$ in. o.d. and 0·020 in. i.d. For the work with liquid water the amount of water in the tubing between the surface of the thermostat liquid and valve A was about 20 p.p.m. of the total water in the system. Its temperature was taken with sufficient accuracy as the mean temperature of the thermostat and the laboratory. The unthermostated connecting tubing between the various parts of the system was made as short as possible; the total length was 72 in., and its volume was about 0·3 cm³. The total volume not thermostatically controlled in the valves, U tube, and connecting tubing was about 0·7 cm³.

9. EXPERIMENTAL PROCEDURE

Great care was taken that all parts of the system were clean before the apparatus was assembled. They were washed with trichloroethylene, warm soapy water and a stiff brush, and reagent grade acetone, and were dried in a stream of nitrogen. The volumometer, pressure vessel, connecting tubing, etc., were evacuated through the valves A and B, usually over a week-end. The pressure reached in the pressure vessel is not known accurately as it cannot be measured. It can hardly be greater than 1 mb, mostly of water vapour, and so the amount of air in the system is negligible. The evacuated system was filled with water, which was prepared as described in §12, from an evacuated flask; because of the length of capillary tubing between valve B and the pressure vessel, the water

Downloaded from rsta.royalsocietypublishing.org

was pumped into the vessel by means of the volumometer. The amount of water put into the system was not usually accurately measured, as it was not required. The usual experimental procedure has been to fix the pressure as that given by an integral number of 10 kg weights on one of the pressure balances, and to adjust the volumometer shaft until electrical contact was made in the experimental-water leg of the U or Ш tube. This is easier than fixing the volumometer reading and adjusting the pressure balance. To avoid the effect of the hysteresis between make and break of electrical contact, readings were always taken as the contact was just made. Great care was taken that no unwanted interchange of materials occurred in the U or Ш tube. A careful watch was kept for entry of mercury into or loss of water from the vessel, but none that affected the reported measurements significantly was found.

Because of inevitable variations, the measurements were not all made at exactly the same pressures and temperatures. The pressure generated by the pressure balances with fixed weights varied with atmospheric pressure by a maximum of about 0·05 b. For convenience in computation the data were adjusted to the standard pressures tabulated in table 5. The temperature of the thermostat containing the vessel varied by up to 0·005 degC during the course of an isotherm, and that of the volumometer by up to 0·02 degC. Rather than make an adjustment of the temperature followed by a wait for the attainment of thermal equilibrium, the data were adjusted arithmetically to isothermal conditions. The maximum adjustment for temperature and pressure was 1 mg, or 4 p.p.m. of the mass of water in the system, and caused no significant error. The coefficients required for the adjustments were obtained from a preliminary analysis of the measurements on one sample of water.

10. Calibration of the volumometer

The fundamental measurement made in this work is the difference of the mass of water in the pressure vessel for two conditions of pressure and temperature. This is determined by the difference between two scale readings of the volumometer.

We first determine the general form of the equation relating the mass of water to the scale reading and the pressure. The total volume of the volumometer and connecting tubing when the connexion from the pressure vessel to valve A of figure 1 is plugged, including the water side of the U tube or the Ш tube, is V. If v_1 is the volume jacketed by the balancing pressure and is at temperature T_1, v_2 the volume not jacketed, i.e. the volume of the connecting tubing, valves, U or Ш tube, etc., up to the O-ring seal at M in the schematic diagram in figure 5 and is at temperature T_2, and v_3 the volume of the piston within the volumometer cylinder, i.e. to the left of the seal O in figure 5, then the mass m of water in the volumometer is

$$m = (v_1 - v_3)\,\rho_1 + v_2\,\rho_2, \tag{1}$$

where ρ_1 and ρ_2 are the densities of water at temperatures T_1 and T_2 and the pressure of the experiment. The values of v_1 and v_2 at pressure p are given, in terms of the values v_1^0 and v_2^0 at zero pressure, by

$$v_1 = v_1^0(1-\alpha_1 p), \tag{2}$$

and

$$v_2 = v_2^0(1-\alpha_2 p), \tag{3}$$

Downloaded from rsta.royalsocietypublishing.org

where α_1 and α_2 depend on the elastic constants. The volume v_3 is

$$v_3 = a_3 l_3, \tag{4}$$

where a_3 is the area of the piston enclosed within the volumometer cylinder, i.e. to the left of seal O, and l_3 is its length. Now

$$a_3 = a_3^0(1-\alpha_3 p), \tag{5}$$

where a_3^0 is the area of the piston at zero pressure and α_3 is two-thirds of the compressibility of the piston. The value of l_3 changes with pressure both because it is compressed and because part of the piston leaves the cylinder owing to the contraction of the rest of the piston when the pressure is increased. Hence

$$l_3 = l_3^0(1-\alpha_4 p) - L\alpha_5 p, \tag{6}$$

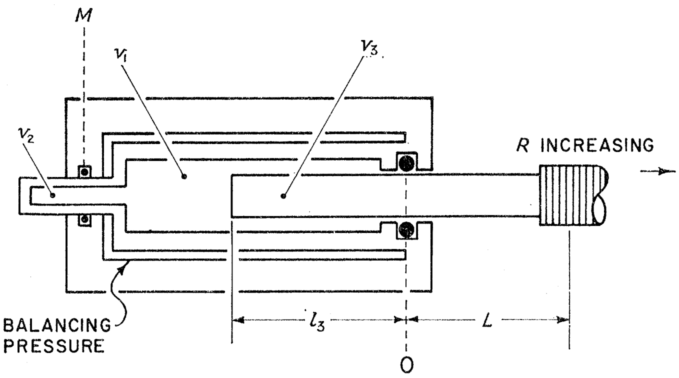

FIGURE 5. Schematic diagram of the volumometer.

where α_4 is the linear compressibility of the piston, L is the distance between seal O and the effective position of the female thread and is constant, and α_5 depends on the Young's moduli and dimensions of the parts of the piston not in the cylinder and on the distortions of the screw thread. The value of l_3^0 is related to the scale reading R of the volumometer, corrected for the non-linearity of the scale (see later in this section), by the relation

$$l_3^0 = N - R, \tag{7}$$

where N is a constant that allows for the different zeros of l_3^0 and R. By combining equations (1) to (7) and collecting terms, the mass of water in the volumometer and connecting tubing is given by an equation of the form

$$m = A(p) + RB(p) + C, \tag{8}$$

where A and B are functions of p but not of R, and C is a constant. $A(p)$ is by definition zero at 1 atm pressure, and so C is the mass of water in the volumometer at 1 atm when the scale reads zero. A, B and C could in principle be calculated from the dimensions and elastic constants of the volumometer parts and the equation of state of water, but it is much more accurate to determine them by calibration. The value of C is not required because only differences of mass are required.

The calibration was made as follows. First, the masses of water delivered by the volumometer at atmospheric pressure between the uncorrected scale readings R' and zero

Downloaded from rsta.royalsocietypublishing.org

were determined by ejecting successive amounts of about 0·1 cm^3 and weighing them. To avoid losses of water by evaporation, the water was not weighed directly, but was used to displace mercury from a reservoir in a thermostat controlled to ±0·005 degC. The mercury was delivered to a weighing bottle by a stainless steel tube 0·010 in. inside diameter, and was weighed to ±0·1 mg, which corresponds to 0·01 mg of water. The mass of water delivered was nearly linear in R' and was given by

$$m-C = \gamma R' + \delta, \tag{9}$$

where γ is the mean mass delivered per unit length of scale for the full travel of the piston, and δ is the small deviation from linearity. When the volumometer was at 24·00 °C the value of γ was 5·0121 g/in. The quantity $\gamma R' + \delta$ was put equal to γR, where R is the scale reading now adjusted so that the mass delivered at atmospheric pressure is exactly linear in R. That is

$$R = R' + \delta/\gamma. \tag{10}$$

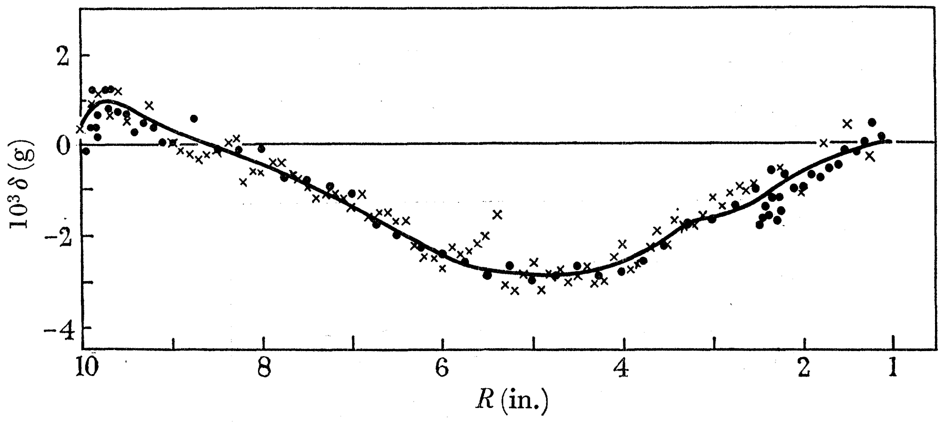

FIGURE 6. The departure from constancy of the delivery of the volumometer at atmospheric pressure. The deviations δ are defined by equation (9). × and ● represent independent calibrations.

Four calibration runs were made, two before and two after the measurements reported in this paper. Because of lack of experience in the early days, the first two were less accurate than the compression measurements and were not used. They agreed to within their accuracy with the last two calibrations. To indicate the reproducibility, δ is plotted as a function of R for the two final calibrations in figure 6. The maximum value of δ is 3 mg, which is 10 p.p.m. of the water in the system when the pressure vessel is filled with water, and the standard deviation of the points from the curve drawn in figure 6 was 0·5 mg.

The next step in the calibration was to determine the scale reading R as a function of pressure for each of the standard pressures in turn, with a fixed mass of water in the volumometer. The adiabatic compression of water warms it by 0·002 degC/b. To make thermal equilibration as rapid as possible, the water was compressed twice the required pressure interval for one half-life, which was about 8 min, and the pressure then reduced to the required value. Thermal equilibrium, as determined by the condition that the volumometer reading did not change by more than 0·5 mg in 10 min took a further 30 min.

Readings were taken at a series of increasing pressures, and again at the same pressures in descending order. There were systematic differences between the two sets of readings,

Downloaded from rsta.royalsocietypublishing.org

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

the differences being of two kinds. The first, which is not illustrated, was an apparent permanent decrease in the mass in the vessel of about 4 mg. This occurred only during the first run after the system has been filled with a fresh sample of water, and it could be eliminated by pressurizing a new sample in the system to 500 b. Runs affected by this error were not used. The cause of this apparent decrease in mass is not certain; it may be due to a difficulty of penetration of water into the corners between the O-rings and the metal and into the various grooves on the metal, perhaps because of surface tension or because there are traces of air in the corners which dissolve only under pressure.

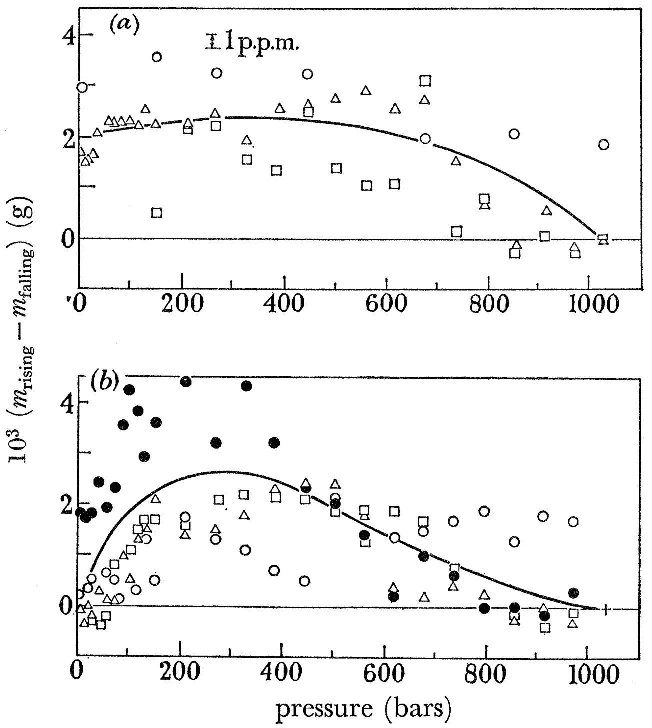

FIGURE 7. Hysteresis during the calibration of the volumometer. (*a*) U tube. There is an unexplained lack of closure in this early work. (*b*) ɯ tube. The loop closes almost perfectly here, as in all work subsequent to that in (*a*). Normally one reading at 1026 b is common to both rising and falling runs and the hysteresis is identically zero there. The three symbols in (*a*) and the four in (*b*) denote independent determinations of the hysteresis.

The second systematic difference between duplicate runs with rising and falling pressures is illustrated in figure 7. It is a hysteresis, the loop of which had a maximum width of about 3 mg. In the first calibration, which is shown in figure 7 (*a*), the loop did not close, indicating permanent deformation of about 5 mm^3 per pressurization. The reason for the failure to close in this first calibration is not known. The smoothed curve of figure 7 (*a*) was used in the calibration of the volumometer that was used in the measurements of the compression of water that are reported in § 14. In those measurements the loop closed to within about 0·3 mg. Figure 7 (*b*) shows the hysteresis for the calibration with the ɯ tube; the loop closed to within 0·3 mg. This calibration was used in the measurement of the compressibility of the pressure vessel. The hysteresis was only slightly larger when the pressure vessel was attached than when the volumometer was used alone, and it

Downloaded from rsta.royalsocietypublishing.org

decreased only slightly when the U tube was replaced by the W tube. The cause is likely to be mainly in the volumometer and associated equipment, but the exact cause is unknown. The calibration that was used was the mean of the values obtained with rising and with falling pressures. As the hysteresis is much the same during the calibration and the experimental isotherm, the results of the compressions would not be changed significantly if only rising pressures or only falling pressures were used both for measurement of the compression and for calibration. A prohibitive amount of work would have been required to measure each compression isotherm at both rising and falling pressures, and so only a few compression runs were made in this way. The hysteresis was plotted, and the freehand curve through the points was used to reduce the other isotherms which were made with the pressure varying in one direction only.

This calibration was repeated with four different masses of water in the volumometer. For a given mass, m, we have from equation (8)

$$m-C = A(p)+RB(p). \tag{11}$$

For a given pressure p_1 and several different masses therefore, $m-C$ is linear in R with intercept $A(p_1)$ and slope $B(p_1)$. The values of $A(p_1)$ and $B(p_1)$ were determined by least squares. The volumometer was calibrated for delivery at atmospheric pressure, whereas the scale readings R corresponding to a fixed mass of water in the volumometer were taken at the standard pressures, the lowest of which was 5·30 b. In order to obtain the mass of water in the volumometer it was, therefore, necessary to extrapolate these scale readings as a function of pressure to atmospheric pressure. A cubic equation in the pressure adequately represents the compression of water near room temperature (see § 18), so the volumometer readings were extrapolated to atmospheric pressure by fitting them to a cubic equation in ($p-1$ atm) by least squares. For all the calibration runs the deviations from this equation were apparently random, and the standard deviation was about 100 μin. The extrapolated value of R at 1 atm gave the value of m_A-C for the run, where m_A was the mass of water in the volumometer at atmospheric pressure. Since the extrapolation to 1 atm was based on 27 points between 5·3 and 1026 b, the standard error of the value of R at 1 atm was 40 μin., and so the standard error of m_A-C was 0·2 mg.

The values of $A(p)$ and $B(p)$ obtained directly at the standard pressures by the above procedure were used for determining the mass of water in the volumometer during the compression measurements. However, to determine the internal consistency of the values of $A(p)$ and $B(p)$ as a function of pressure they were fitted to equations by the method of least squares. If the compression of water is adequately represented by a cubic equation, then $A(p)$ and $B(p)$ are represented by the relations

$$A(p) = a_1(p-1\ \text{atm})+a_2(p-1\ \text{atm})^2+a_3(p-1\ \text{atm})^3, \tag{12}$$

$$B(p) = b_A+b_1(p-1\ \text{atm})+b_2(p-1\ \text{atm})^2+b_3(p-1\ \text{atm})^3, \tag{13}$$

where b_A is γ of equation (10). The standard deviation of $A(p)$ was 0·1 mg. The deviations from these equations, which indicate the smoothness of the data, are shown in figure 8. The values of $A(p)$ for the U tube are independent of those for the W tube, and figure 8 (*a*) shows the deviation of each set from equation (12) fitted with the appropriate parameters. The values of $B(p)$ ought to be the same for both the U tube and W tube. Figure 8 (*b*)

Downloaded from rsta.royalsocietypublishing.org

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

shows the deviations of both sets of data from equation (13) fitted to the ɯ tube data. Each curve is smooth to about 10 p.p.m. of the mass of water in the pressure vessel, but the values for the U tube tend downward relative to those for the ɯ tube by an amount that is approximately proportional to the pressure and that reaches 100 p.p.m. in $B(p)$ at 1000 b. If this quantity can be taken as indicative of the lack of reproducibility of the calibration of the volumometer under pressure, an error in the specific volume of liquid water of 4 p.p.m. at 1000 b is produced.

The standard error of $m-C$, obtained by combining the standard errors of the various measurements involved in the calibration, was 0·7 mg at the lower pressures, and about 1·2 mg at 1000 b.

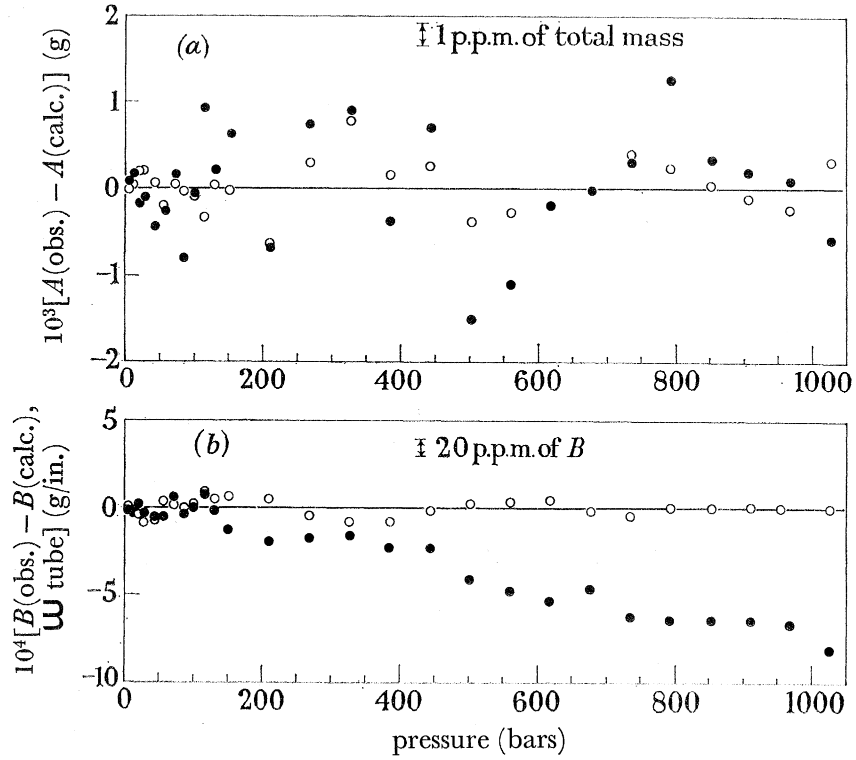

FIGURE 8. Deviations of (a) $A(p)$ and (b) $B(p)$ from equations (12) and (13) respectively. Values of A(calc.) for the U tube and the ɯ tube were calculated with different values of the parameters a_1, a_2, and a_3 in equation (12). Values of B(calc.) for both U tube and ɯ tube were obtained from the fit to the values for the ɯ tube.

11. VOLUME OF THE PRESSURE VESSEL

The volume of the pressure vessel was determined by filling it with water which was distilled out and weighed. The vessel was evacuated at 40 °C, filled with distilled and degassed water, and pressurized to 500 b to ensure that it was completely filled (see §10). The pressure was reduced to 5·30 b and the temperature adjusted to 40·000 °C. The thermal equilibration of the water was followed by means of the volumometer. When thermal equilibrium was reached, as determined by there being no significant change ($\leqslant$ 0·5 mg) in the volumometer reading in 10 min, valve A (figure 1) was disconnected from the vessel. Two half-lives (about 16 min) were again allowed for thermal equilibrium after the

Downloaded from rsta.royalsocietypublishing.org

decompression from 5·30 to 1 b, and water was removed from the tip of the capillary tube leading from the vessel until the meniscus was just level with the end. The capillary tube was then connected to the vacuum system by another valve, and the water was distilled out and condensed in four traps in series immersed in liquid nitrogen. There was no visible condensation in the fourth trap, so verifying that no water (i.e. $<$ *ca.* 1 mg) passed through the first three. The vessel was heated to 90 °C to accelerate the distillation, which took about 12 h. The pressure of water vapour left in the vessel is not known but it must be less than about 1 mb, which corresponds to about 0·2 mg, and does not contribute appreciably to the total error of the volume of the vessel. Three determinations were made, with the following results: 246·108, 246·124, 246·092 g. The mean volume is $248{\cdot}038 \pm 0{\cdot}012\,\mathrm{cm}^3$, where the uncertainty given is the standard error estimated from the variation of the results. Most of the uncertainty is probably introduced during the condensation of the water and the weighing of the freezing traps. The density of water at 40 °C was that given by Tilton & Taylor (1937).

12. Water samples

The water used for the compression measurements was distilled water which was further purified and degassed by two distillations *in vacuo*. All glassware that came in contact with the water was boiled for several hours to remove soluble material, and the part of the vacuum system that contained the water was free from grease, the valves being of metal with O-ring packings.

The water used in the thermal expansion measurements was equilibrium conductivity water, degassed by boiling vigorously at atmospheric pressure until 20% of the volume had boiled off. As soon as boiling was stopped the hot flask was connected to a vacuum system and was pumped briefly to remove traces of air. Two samples were used in the measurements. One was prepared as described, and the other was further distilled in vacuum into a flask cooled in liquid nitrogen. The thermal expansions (see § 16) of both samples agreed to within the experimental error. Some isotopic fractionation will occur when 20% by volume is boiled off. This may affect the density by several parts per million (Christiansen, Crabtree & Laby 1935) but will not affect the thermal expansivity by a detectable amount (Steckel & Szapiro 1963).

The difference between the two methods of preparing the water is not significant for the measurements.

PART II. COMPRESSION AND THERMAL EXPANSION OF WATER

13. Compression of the pressure vessel

The 304 stainless steel used for the inner vessel of the pressure vessel is neither homogeneous nor isotropic, and so the elastic moduli (see, for example, Garofalo, Malenock, & Smith 1952) are not suitable for determining accurate compressibilities. The compressions of the vessel have therefore been measured relative to mercury.

The mercury was purified as described in § 8. It was transferred to a flask, which was then evacuated and weighed to 1 mg. The pressure vessel was evacuated, the mercury flask was connected to it by valve *A* of figure 1, and the mercury allowed to run into the

Downloaded from rsta.royalsocietypublishing.org

vessel. The flask was weighed again. The weight of mercury in the vessel was 3229·756 g, which left 5 to 10 cm^3 of the pressure vessel, depending on the temperature, to be filled with water. This was done, and compressions measured at 10, 50, 100 and 150 °C at the standard pressures. At 50 and 150 °C measurements were made at both ascending and descending pressures.

The volumometer readings were extrapolated to 1 atm by fitting them to a cubic equation in the pressure by least squares, to give m_A the mass of water in the volumometer at 1 atm. The volume of the vessel at pressure p is given by

$$V = M_{\mathrm{Hg}} \bar{V}_{\mathrm{Hg}} + (M_{\mathrm{H_2O}} - m_p + m_A)\, \bar{V}_{\mathrm{H_2O}}, \tag{14}$$

where m_p is the mass of water in the volumometer at pressure p, M_{Hg} is the mass of mercury in the vessel, $M_{\mathrm{H_2O}}$ is the mass of water in the vessel at 1 atm, and $\bar{V}_{\mathrm{Hg}}$ and $\bar{V}_{\mathrm{H_2O}}$ are the specific volumes of mercury and water at pressure p and the temperature of the vessel. The values of $M_{\mathrm{H_2O}}$ were obtained from the known volume of the vessel at 40 °C (§ 11) and the thermal expansion of the vessel (§ 15). The values of $\bar{V}_{\mathrm{H_2O}}$ were obtained from a preliminary analysis of the present results; their uncertainty did not contribute to the uncertainty of the change of volume. The compression of mercury is not known to the accuracy of the present measurements. The only useful measurements are the compressions relative to iron (Bridgman 1911) in the range 0 to 12 kb at 0 and 22 °C, sound velocities at 1 b in the range 0 to 70 °C (Hubbard & Loomis 1928) and at 50 and 150 °C (Kleppa 1949), and the compressions relative to glass in range 0 to 30 b, 10 to 55 °C (Diaz Peña & McGlashan 1959). All these data except the last mentioned have been critically examined by Bett, Weale & Newitt (1954), but apparently without correcting Bridgman's (1911) values for the more recent compression of iron (Bridgman 1940). They proposed a particular equation of state based on these data and on the thermal expansions of Beattie, Blaisdell, Kaye, Gerry & Johnson (1941). The compressibilities obtained by Diaz Peña & McGlashan (1959) agree well with the proposed equation of state. The base density of mercury was that given by Cook & Stone (1957) and Cook (1961). The specific volumes at atmospheric pressure are probably known to 1 p.p.m., but it is impossible to make any reasonably objective estimate of the uncertainties of the specific volumes under pressure in the whole range because large extrapolations have to be made. The isothermal compressibilities at low pressures in the range 0 to 70 °C are determined mainly by Hubbard & Loomis's (1928) sound velocities. The sound velocities in water determined by the same authors agree within 1 in 1000 with the recent careful measurements of Greenspan & Tschiegg (1957), and it is likely that the sound velocities in mercury, which are of a similar magnitude to those in water, are of comparable accuracy. The isothermal compressibilities at low pressure are therefore probably accurate to about $0{\cdot}01 \times 10^{-6}\ \mathrm{b}^{-1}$, which corresponds to an uncertainty in the specific volume of 10 p.p.m. at 1000 b. The uncertainty in the specific volume at 150 °C and 1000 b is probably ten or twenty times this figure because the variation of the compressibility with pressure is determined entirely by Bridgman's (1911) measurements at 0 and 22 °C as smoothed, interpolated, and extrapolated to 150 °C. There are, however, considerations, which are discussed below, based on our own measurements that suggest that the specific volumes from the correlating equation are more accurate than this.

Downloaded from rsta.royalsocietypublishing.org

MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES
THE ROYAL SOCIETY A
PHILOSOPHICAL TRANSACTIONS OF

The densities of mercury at 10, 50, 100 and 150 °C and the standard pressures used in this work were calculated from the equation of state of Bett *et al.* (1954), and the values used and the volumes of water in the vessel, are given in table 2. The compressibility of the vessel can be recalculated when new values of the density of mercury under pressure become available. If $\Delta\rho_{\mathrm{Hg}}$ is the (small) increase of the density of mercury from that tabulated in table 2, the volume of the vessel is increased $\Delta V = -M_{\mathrm{Hg}}/\Delta\rho_{\mathrm{Hg}}$. The increase $\Delta\kappa_v$ in the compressibility of the vessel is then obtained by fitting the ΔVs to the equation

$$\Delta V = V_0(1-\Delta\kappa_v p).$$

TABLE 2. THE VALUES OF THE DENSITY OF MERCURY ρ_{Hg} USED IN THE DETERMINATION OF THE COMPRESSIBILITY OF THE PRESSURE VESSEL, AND OF THE VOLUME OF WATER $V_{\mathrm{H_2O}}$ IN THE PRESSURE VESSEL DURING THE DETERMINATION OF THE COMPRESSIBILITY OF THE VESSEL

These numbers, plus the mass of mercury, 3229·756 g, will permit modification of the present results when more accurate values of the density of mercury under pressure become available.

	10 °C		50 °C		100 °C		150 °C	
p(bar)	ρ_{Hg}(g cm^{-3})	$V_{\mathrm{H_2O}}$(cm^3)	ρ_{Hg}(g cm^{-3})	$V_{\mathrm{H_2O}}$(cm^3)	ρ_{Hg}(g cm^{-3})	$V_{\mathrm{H_2O}}$(cm^3)	ρ_{Hg}(g cm^{-3})	$V_{\mathrm{H_2O}}$(cm^3)
5·30	13·57068	9·6709	13·47280	8·4257	13·35174	6·8864	13·23171	5·3594
12·60	13·57108	9·6769	13·47321	8·4318	13·35217	6·8930	13·23217	5·3665
20·00	13·57147	9·6828	13·47363	8·4377	13·35261	6·8990	13·23262	5·3728
27·40	13·57187	9·6889	13·47404	8·4426	13·35304	6·9055	13·23308	5·3800
42·11	13·57266	9·6994	13·47486	8·4559	13·35390	6·9200	13·23399	5·3942
56·81	13·57345	9·7113	13·47569	8·4681	13·35477	6·9325	13·23490	5·4076
71·51	13·57424	9·7220	13·47651	8·4787	13·35564	6·9453	13·23581	5·4218
86·31	13·57503	9·7334	13·47733	8·4912	13·35650	6·9579	13·23672	5·4360
101·01	13·57582	9·7440	13·47815	8·5039	13·35736	6·9719	13·23763	5·4495
115·71	13·57661	9·7559	13·47897	8·5163	13·35823	6·9846	13·23853	5·4633
130·52	13·57740	9·7672	13·47979	8·5280	13·35909	6·9975	13·23944	5·4779
151·89	13·57855	9·7835	13·48099	8·5453	13·36034	7·0154	13·24076	5·4987
210·28	13·58167	9·8287	13·48424	8·5934	13·36376	7·0706	13·24435	5·5551
268·57	13·58479	9·8721	13·48748	8·6405	13·36717	7·1216	13·24793	5·6093
326·95	13·58789	9·9159	13·49071	8·6874	13·37056	7·1720	13·25150	5·6643
385·22	13·59100	9·9607	13·49394	8·7357	13·37396	7·2238	13·25507	5·7198
443·49	13·59410	10·0047	13·49717	8·7820	13·37735	7·2747	13·25863	5·7737
501·85	13·59720	10·0490	13·50039	8·8294	13·38073	7·3257	13·26218	5·8284
560·11	13·60028	10·0925	13·50360	8·8762	13·38410	7·3757	13·26572	5·8821
618·47	13·60337	10·1357	13·50681	8·9225	13·38747	7·4262	13·26926	5·9364
676·71	13·60644	10·1803	13·51001	8·9697	13·39083	7·4767	13·27279	5·9907
735·06	13·60951	10·2237	13·51320	9·0161	13·39418	7·5259	13·27631	6·0445
793·29	13·61258	10·2667	13·51639	9·0616	13·39753	7·5766	13·27982	6·0978
851·63	13·61565	10·3098	13·51958	9·1077	13·40088	7·6271	13·28333	6·1516
909·85	13·61870	10·3528	13·52275	9·1533	13·40421	7·6764	13·28683	6·2044
968·08	13·62175	10·3960	13·52592	9·1992	13·40754	7·7263	13·29032	6·2577
1026·39	13·62480	10·4372	13·52909	9·2446	13·41086	7·7750	13·29381	6·3106

Then, to terms of first order, the specific volumes listed in tables 4 and 11 are to be multiplied by the quantity $\{1-\Delta\kappa_v(p-p_A)\}$, and the compressibilities in table 14 are to be increased by the amount $\Delta\kappa_v$.

There was, as usual in this work, a hysteresis between measurements made at ascending and at descending pressures, and these differences are shown in figure 9 (*b*). The hysteresis obtained here scarcely differs from that obtained during the calibration of the volumometer and ꟺ tube, when the pressure vessel was not connected. Any permanent

MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES
THE ROYAL SOCIETY A
PHILOSOPHICAL TRANSACTIONS OF

Downloaded from rsta.royalsocietypublishing.org

deformation did not appear to exceed 4 p.p.m. of the total volume at any temperature. The deviation of the points from the free-hand line drawn in figure 9 (*b*) is about 2 p.p.m. of the total volume, and the maximum hysteresis is 2·7 mm^3 or about 10 p.p.m. of the total volume. For measurements made with both ascending and descending pressures the means were taken; measurements made in one direction only were adjusted according to the line drawn in figure 9 (*b*).

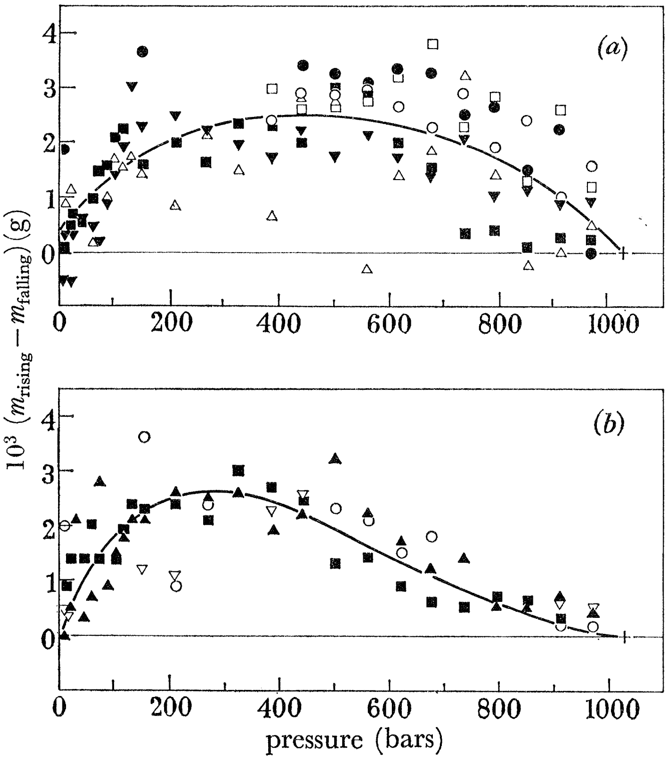

Figure 9. Hysteresis of the apparent mass in the system from the volumometer readings: (*a*) during the compression measurements, and (*b*) during the measurement of the compressibility of the pressure vessel.

Table 3. The compressibility of the pressure vessel at various temperatures

temp. (°C)	$10^6\kappa_v$(b^{-1})	standard deviation of $10^6\kappa_v$(b^{-1})
10	0·7041	0·0010
50	0·7006	0·0013
100	0·6967	0·0020
150	0·7391	0·0011

At each temperature the volume was linear in the pressure and could be represented within experimental error by the equation

$$V_p = V_0(1-\kappa_v p), \tag{15}$$

where κ_v is the isothermal compressibility of the vessel. This equation was fitted by least squares and the values κ_v and standard errors are given in table 3. The measurements were apparently scattered randomly about the line, and the standard deviation of the volume was 2 p.p.m. The statistical standard error of the compressibility is much smaller than the

Downloaded from rsta.royalsocietypublishing.org

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

uncertainty of the compressibility of the reference substance, mercury (Bett *et al.* 1954). There is however, internal evidence from our measurements that the compression of mercury at the higher temperatures is not far wrong. The specific volume of iron and other hard metals (Bridgman 1958) is linear in the pressure in the range 0–1000 b to within about 2 p.p.m. at 30 and 75 °C, and it seems justifiable to assume that it is linear to a few parts per million up to 150 °C. Consequently, the fact that the compression of our pressure vessel, determined from the compression relative to mercury and equation of state of Bett *et al.* (1954) for mercury, is linear in the pressure to the precision of the measurements, indicates that the curvature of the $V-p$ isotherm of Bett *et al.* for mercury is correct to a few parts per million of the volume. The compressibility of the vessel is constant

$$0{\cdot}700\times10^{-6}\,\mathrm{b}^{-1}\quad\text{within}\quad 0{\cdot}004\times10^{-6}\,\mathrm{b}^{-1}$$

at 0, 50, and 100 °C, and the value of $0{\cdot}739\times10^{-6}\,\mathrm{b}^{-1}$ at 150 °C is almost certainly correct within $0{\cdot}04\times10^{-6}\,\mathrm{b}^{-1}$. This latter uncertainty introduces an uncertainty of 40 p.p.m. in the relative volume of the vessel at 150 °C and 1000 b.

In the computations, the compressibilities of the vessel in table 3 were interpolated by means of the quadratic equation

$$10^6\kappa_v = 0{\cdot}7124-6{\cdot}29\times10^{-2}t+5{\cdot}30\times10^{-4}t^2\,\mathrm{b}^{-1}, \tag{16}$$

where t is the Celsius temperature. The standard deviation was $0{\cdot}009\times10^{-6}\,\mathrm{b}^{-1}$. It must be emphasized however, that there is no real evidence that the compressibility of the vessel is a function of temperature in this range.

14. Compression of water

Three samples of water were used in the measurements, and the runs for which they were used are summarized in table 4. The experimental points in some isotherms were measured in order of ascending pressure only, in others in order of descending pressure. The values reported for 0 °C are the means of two runs, one made in order of ascending pressures, and one in order of descending pressures. They were averaged to take account of hysteresis as there was no independent hysteresis curve for the system and ⋃ tube under these conditions. The hysteresis curve for these measurements is shown in figure 9 (*a*); it is of much the same shape as that (figure 7) obtained during the calibration of the U tube, and closed to within 1 p.p.m. of the total volume.

Compressions were measured in this work but are not directly reported, as specific volumes are more useful. From 0 to 40 °C the densities ρ_A of water at various temperatures and 1 atm required to do this were based on the data of Chappuis (1907) as formulated by Tilton & Taylor (1937). From 50 to 70 °C the values of Owen, White & Smith (1956) were used. Above 80 °C the densities given in §16 were used. The specific volume of water at the pressure p of the experiment was then calculated from the relation

$$\bar{V} = \frac{1-\kappa_v(p-p_A)}{\rho_A+(m_A-m_p)/V_A},$$

where m_p and m_A are the masses of water in the volumometer at the pressure of the experiment and at 1 atm respectively, and V_A is the volume of the vessel at the temperature of the

Downloaded from rsta.royalsocietypublishing.org

TABLE 4. EXPERIMENTAL SPECIFIC VOLUMES OF WATER (cm^3/g)

R indicates a run made for a series of rising pressures, and *F* indicates one made for falling pressures.

	T(°C)						
p (bar)	0·000	10·002	19·997	24·998	24·998	25·005	30·112
5·30	0·999882	1·000091	1·001596	1·002759	1·002760	1·002765	1·004206
12·60	0·999512	0·999745	1·001264	1·002437	1·002436	1·002436	1·003880
20·00	0·999138	0·999389	1·000923	1·002095	1·002098	1·002100	1·003551
27·40	0·998762	0·999040	1·000588	1·001770	1·001769	1·001770	1·003222
42·11	0·998025	0·998346	0·999917	1·001106	1·001104	1·001106	1·002565
56·81	0·997282	0·997649	0·999250	1·000445	1·000445	1·000447	1·001906
71·51	0·996550	0·996962	0·998592	0·999801	0·999802	0·999800	1·001267
86·31	0·995813	0·996268	0·997921	0·999138	0·999137	0·999142	1·000608
101·01	0·995088	0·995587	0·997266	0·998490	0·998487	0·998491	0·999961
115·71	0·994362	0·994906	0·996612	0·997846	0·997842	0·997847	0·999325
130·52	0·993637	0·994223	0·995955	0·997199	0·997190	0·997196	0·998681
151·89	0·992594	0·993239	0·995008	0·996262	0·996257	0·996262	0·997752
210·28	0·989782	0·990577	0·992451	0·993736	0·993732	0·993735	0·995259
268·57	0·987033	0·987991	0·989962	0·991276	0·991274	0·991280	0·992816
326·95	0·984329	0·985432	0·987487	0·988841	0·988840	0·988838	0·990401
385·22	0·981681	0·982923	0·985069	0·986443	0·986443	0·986442	0·988031
443·49	0·979074	0·980462	0·982702	0·984099	0·984097	0·984100	0·985708
501·85	0·976526	0·978023	0·980344	0·981765	0·981765	0·981770	0·983400
560·11	0·974014	0·975641	0·978040	0·979493	0·979491	0·979497	0·981141
618·47	0·971560	0·973290	0·975770	0·977248	0·977248	0·977248	0·978915
676·71	0·969142	0·970991	0·973544	0·975049	0·975050	0·975048	0·976737
735·06	0·966770	0·968730	0·971352	0·972882	0·972879	0·972880	0·974580
793·29	0·964442	0·966509	0·969197	0·970750	0·970750	0·970745	0·972466
851·63	0·962150	0·964314	0·967069	0·968642	0·968640	0·968642	0·970377
909·85	0·959904	0·962161	0·964976	0·966572	0·966569	0·966569	0·968318
968·08	0·957699	0·960045	0·962916	0·964535	0·964530	0·964531	0·966296
1026·39	0·955529	0·957958	0·960887	0·962524	0·962521	0·962522	0·964300
sample	3	2	1	1	1	2	1
R or *F*	both	*F*	*F*	*R*	*F*	*F*	*F*

	T(°C)						
p (bar)	39·999	50·007	60·001	70·003	80·003	90·007	100·005
5·30	1·007652	1·011917	1·016894	1·022545	1·028817	1·035728	1·043232
12·60	1·007327	1·011600	1·016568	1·022213	1·028479	1·035366	1·042867
20·00	1·006990	1·011260	1·016231	1·021873	1·028125	1·035000	1·042486
27·40	1·006664	1·010936	1·015904	1·021533	1·027779	1·034644	1·042117
42·11	1·006019	1·010283	1·015242	1·020855	1·027085	1·033926	1·041373
56·81	1·005362	1·009636	1·014582	1·020185	1·026395	1·033217	1·040628
71·51	1·004729	1·009004	1·013940	1·019529	1·025721	1·032518	1·039905
86·31	1·004078	1·008348	1·013281	1·018857	1·025034	1·031807	1·039167
101·01	1·003439	1·007708	1·012636	1·018199	1·024353	1·031110	1·038438
115·71	1·002808	1·007078	1·011992	1·017548	1·023685	1·030417	1·037721
130·52	1·002165	1·006436	1·011342	1·016889	1·023004	1·029720	1·036990
151·89	1·001247	1·005517	1·010408	1·015944	1·022033	1·028713	1·035948
210·28	0·998774	1·003033	1·007902	1·013386	1·019414	1·026011	1·033152
268·57	0·996353	1·000618	1·005456	1·010903	1·016860	1·023388	1·030429
326·95	0·993953	0·998224	1·003034	1·008443	1·014342	1·020789	1·027738
385·22	0·991605	0·995869	1·000665	1·006030	1·011875	1·018242	1·025115
443·49	0·989306	0·993563	0·998340	1·003664	1·009457	1·015763	1·022547
501·85	0·987016	0·991268	0·996030	1·001317	1·007059	1·013298	1·020002
560·11	0·984778	0·989029	0·993770	0·999027	1·004719	1·010896	1·017523
618·47	0·982575	0·986824	0·991547	0·996771	1·002416	1·008529	1·015081
676·71	0·980415	0·984660	0·989369	0·994560	1·000159	1·006215	1·012699
735·06	0·978276	0·982524	0·987218	0·992378	0·997930	1·003934	1·010347
793·29	0·976180	0·980426	0·985103	0·990232	0·995747	1·001698	1·008048
851·63	0·974107	0·978349	0·983010	0·988117	0·993586	0·999488	1·005768
909·85	0·972064	0·976314	0·980956	0·986038	0·991470	0·997323	1·003540
968·08	0·970057	0·974302	0·978938	0·983989	0·989379	0·995191	1·001348
1026·39	0·968073	0·972322	0·976940	0·981966	0·987322	0·993087	0·999189
sample	1	2	1	1	1	2	1
R or *F*	*R*	*F*	*R*	*F*	*R*	*R*	*F*

Downloaded from rsta.royalsocietypublishing.org

MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES
PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A

Table 4 (*cont.*)

	T(°C)						
p (bar)	110·005	110·003	120·007	130·010	140·009	150·016	150·016
5·30	1·051365	1·051369	1·060124	1·069547	1·079632	1·090462	1·090462
12·60	1·050983	1·050982	1·059719	1·069114	1·079179	1·089968	1·089970
20·00	1·050586	1·050584	1·059300	1·068671	1·078710	1·089467	1·089468
27·40	1·050197	1·050193	1·058890	1·068236	1·078248	1·088977	1·088976
42·11	1·049414	1·049416	1·058076	1·067378	1·077328	1·087995	1·087994
56·81	1·048637	1·048641	1·057259	1·066515	1·076413	1·087019	1·087018
71·51	1·047885	1·047881	1·056463	1·065668	1·075522	1·086065	1·086062
86·31	1·047112	1·047111	1·055652	1·064812	1·074609	1·085095	1·085095
101·01	1·046353	1·046349	1·054851	1·063972	1·073718	1·084144	1·084144
115·71	1·045602	1·045601	1·054063	1·063137	1·072835	1·083205	1·083205
130·52	1·044843	1·044842	1·053269	1·062302	1·071943	1·082256	1·082261
151·89	1·043759	1·043759	1·052129	1·061101	1·060670	1·080907	1·080906
210·28	1·040833	1·040840	1·049058	1·057873	1·067261	1·077281	1·077284
268·57	1·037999	1·038000	1·046092	1·054756	1·063965	1·073781	1·073781
326·95	1·035198	1·035204	1·043172	1·051687	1·060745	1·070362	1·070364
385·22	1·032469	1·032479	1·040323	1·048693	1·057588	1·067025	1·067029
443·49	1·029807	1·029808	1·037545	1·045778	1·054522	1·063802	1·063802
501·85	1·027160	1·027161	1·034789	1·042904	1·051501	1·060618	1·060618
560·11	1·024588	1·024604	1·032120	1·040107	1·048569	1·057529	1·057533
618·47	1·022059	1·022068	1·029491	1·037364	1·045692	1·054504	1·054514
676·71	1·019592	1·019598	1·026931	1·034688	1·042883	1·051558	1·051572
735·06	1·017171	1·017164	1·024408	1·032062	1·040137	1·048680	1·048685
793·29	1·014790	1·014788	1·021931	1·029490	1·037447	1·045860	1·045869
851·63	1·012437	1·012443	1·019498	1·026960	1·034810	1·043097	1·043107
909·85	1·010139	1·010143	1·017115	1·024491	1·032227	1·040400	1·040407
968·08	1·007881	1·007880	1·014772	1·022056	1·029696	1·037756	1·037759
1026·39	1·005650	1·005649	1·012481	1·019665	1·027206	1·035158	1·035160
sample	1	1	1	2	1	2	2
R or *F*	*F*	*F*	*F*	*F*	*R*	*R*	*F*

experiment and 1 atm. For a given isotherm the values of m_p were measured at pressures of 5·30 b and higher; the value of m_A was determined by fitting the values of m_p to a cubic equation in the pressure, or to a quartic above 120 °C, by the method of least squares. The values of m_p were apparently randomly distributed about the fitted line and the standard deviation was in the range 0·8 to 1·5 mg, which was 3 to 6 p.p.m. of the mass of water in the system. Since m_A was obtained by a small extrapolation to 1 atm from the range 1026·4 to 5·30 b, its standard error is about half the standard deviation of m_p, and it is known more accurately than the individual values of m_p. For this reason it is better to use the extrapolated value at 1 atm as the reference pressure rather than one of the experimental values.

The observed specific volumes of water are given in table 4 for each isotherm. Three runs were done at 25 °C, two with one sample of water and one with a second sample. There is no evidence of systematic differences greater than 5 p.p.m. of the specific volume between the runs.

The various errors of measurement have been discussed in detail or can be derived from data given in this paper. They can be conveniently divided into two kinds. The first are those that contribute to the error of the compression of water relative to mercury; their estimated values are summarized in the top part of table 5. Some of these errors depend upon the temperature, and so a mean value over the range 0 to 50 °C and a value

Downloaded from rsta.royalsocietypublishing.org

at 150 °C are given. Some errors are approximately independent of the pressure and some are approximately proportional to the pressure. For those proportional to the pressure the values at 1000 b are given; the values at lower pressures can be obtained by proportion. The second kind of error is in addition to the preceding. It enters into the conversion of the compressions of water relative to mercury to specific volumes, and contributes to the error of the specific volumes; the estimated values are given in the lower part of table 5. The most important is undoubtedly that due to the uncertainty in the compression of mercury. There is no doubt that compressions of mercury are badly needed to the highest accuracy of present-day techniques.

Table 5. Estimate of the errors of the data in table 4

The standard errors are shown in parts per million of the specific volume. Errors of less than ½ p.p.m. have been rounded to zero. A blank indicates that no error arises in our method of analysis. The errors shown for low pressures also hold for high pressures, and in addition there are errors that are approximately proportional to the pressure. The values of these are shown at 1000 b. The total errors are the square roots of the sum of squares of the separate errors.

	0 to 50 °C		150 °C	
	low pressure	1000 b	low pressure	1000 b
Quantities affecting the accuracy of the compression of water relative to mercury				
temperature	0		1	
pressure	0		0	
calibration of volumometer (see part I)				
for delivery	2		2	
under pressure	2	4	2	4
reading of volumometer $(m-m_A)$	2		2	
hysteresis	2		2	
compressibility of pressure vessel	0	4†	0	4†
calculated standard error affecting internal consistency	4	7	4	7
observed standard deviation of isotherm‡	3–5		4–5	
Additional quantities affecting the absolute error of the specific volume				
temperature	1		1	
pressure		4		4
volume of pressure vessel (1 atm)		2		2
compressibility of mercury		~40		~40
thermal expansion of pressure vessel	0		0	
conversion ml. to cm^3	4		4	
reference densities	1		20	
calculated total standard error	6	~40	21	~40

† This arises from the uncertainty of the compressibility of the vessel as a function of temperature.
‡ A cubic equation of state was used at 0 to 110 °C and a quartic equation of state at 120 to 150 °C.

15. Thermal expansion of the pressure vessel

The thermal expansion of the pressure vessel was obtained from two independent sets of measurements, both made at 5·30 b. In the first set, the expansions relative to water were measured at nine temperatures from 10 to 85 °C. The densities of water at temperatures up to 40 °C were taken from Tilton & Taylor's (1937) formula. These are generally accepted to be accurate to 1 to 2 p.p.m. and so are quite adequate for our purposes. Up to 75 °C the values of Owen *et al.* (1956) were used; their values at 80 and 85 °C were not used for reasons discussed later in this section. In the second set of measurements, the

Downloaded from rsta.royalsocietypublishing.org

vessel was nearly filled with mercury and the rest of the space, about 5 % by volume, was filled with water, as described in § 13. The thermal expansions of the vessel relative to the contents were measured at six temperatures from 10 to 150 °C. The data were treated by an obvious modification of the method summarized in § 16 below. The approximate values of the thermal expansion of water above 75 °C that were required to allow for the small amount of water present were obtained with sufficient accuracy from the thermal expansions of water relative to the vessel, which are reported in § 16, and prior information on the thermal expansion of the 304 stainless steel. The relative specific volumes of mercury reported by Beattie *et al.* (1941) were used, as recommended by Cook (1956), and were adjusted to a pressure of 5·30 b using the isothermal compressibilities recommended in Bett *et al.* (1954). The accuracy of the specific volumes of mercury appears to be about 1 p.p.m. (Cook 1956). The volume of the vessel had been measured at 40 °C (§ 11), and the ratio of the volume V_t at temperature t to the volume V_{40} at 40 °C was calculated. The reproducibility of the measurements is illustrated graphically in figure 10 in which deviations of the values of V_t/V_{40} from a fitted equation (equation (19) below) are plotted. The standard deviation is 6 p.p.m.

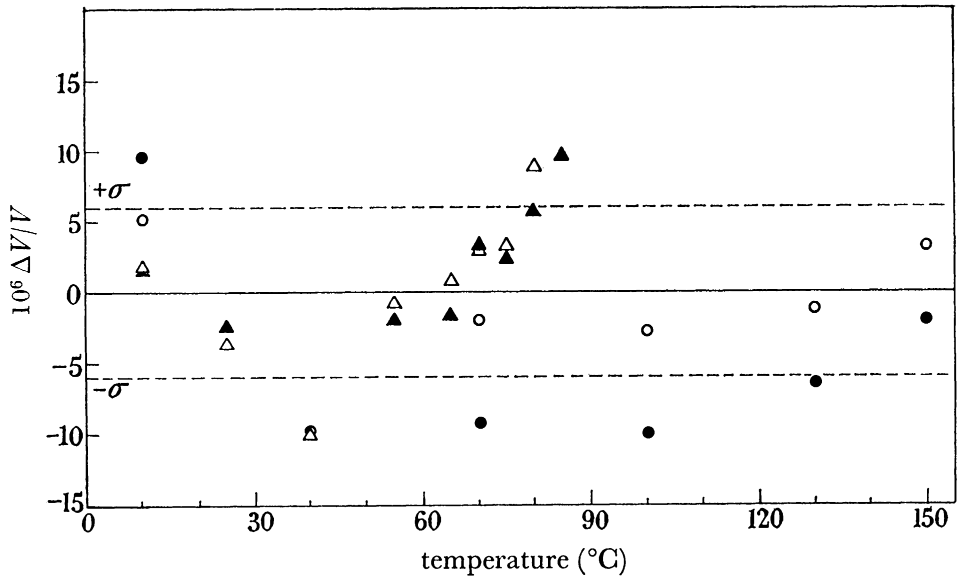

FIGURE 10. Deviations of the volume of the pressure vessel from equation (19). By definition all four points coincide at 40 °C. The standard deviation of the volumes from equation (19) is shown by σ. ○, ●, Expansion measured relative to mercury; △, ▲ relative to water.

As can be seen from figure 10, the values at 80 and 85 °C obtained from the densities of water reported by Owen *et al.* (1956) do not fit on a smooth line through the other points; they do not deviate much more than the values at lower temperatures, but have a trend that does not seem correct. They were therefore omitted from further consideration, and were not used in fitting equation (19) below.

The values of V_t/V_{40} were fitted to quadratic equations in the Celsius temperature t. The seven measurements relative to water in the range 10 to 75 °C give

$$V_t/V_{40} = 0·998075 + 46·819 \times 10^{-6}t + 32·94 \times 10^{-9}t^2, \qquad (17)$$

Downloaded from rsta.royalsocietypublishing.org

with deviations that are apparently random, and with a standard deviation of 2 p.p.m. The six measurements relative to mercury in the range 10 to 150 °C give

$$V_t/V_{40} = 0{\cdot}998074+47{\cdot}055\times10^{-6}t+27{\cdot}22\times10^{-9}t^2, \tag{18}$$

with deviations that are apparently random, and with a standard deviation of 4 p.p.m. In the range 10 to 70 °C equations (17) and (18) agree, as do the original measurements, to a few parts per million, and so the expansion of the vessel is known accurately in this region. Equation (17), when extrapolated beyond the region 10 to 75 °C in which it was fitted, deviates considerably from the measurements relative to mercury as summarized in equation (18), and the difference reaches 100 p.p.m. at 150 °C. This demonstrates that accurate extrapolation of a measured thermal expansion over a useful range is impossible, and emphasizes a danger inherent in the method used by Owen *et al.* (1956) in their determination of the thermal expansion of water in the range 45 to 85 °C. They measured the thermal expansions of their pycnometers relative to water in the range 5 to 35 °C (not to 45 °C as they claimed because Tilton & Taylor's formula is valid only to 42 °C), and extrapolated the expansion to 85 °C. Clearly, it is not surprising that the extrapolation appears to fail noticeably at the higher temperatures. The agreement between our measurements relative to mercury and relative to water tends to confirm the consistency of the densities of mercury and water in the range 10 to 70 °C, and since the density of mercury as determined by Beattie *et al.* (1941) and the density of water is determined by Chappuis (1907) and Owen *et al.* (1956) are independent, this agreement confirms their accuracy in this range.

The equation that was used in subsequent work to represent the thermal expansion of the vessel was obtained by fitting all the data, both those derived from the expansion relative to water in the range 10 to 75 °C and those from the expansion relative to mercury, to a quadratic equation in the temperature, by least squares. The resulting equation is

$$V_t/V_{40} = 0{\cdot}998062+47{\cdot}448\times10^{-6}t+24{\cdot}94\times10^{-9}t^2. \tag{19}$$

The deviations of the observed values of V_t/V_{40} from this equation and the standard deviation σ of the observed values from the fitted lines are shown in figure 10. The standard deviation is 6 p.p.m.

16. THERMAL EXPANSION OF WATER IN THE RANGE 80 TO 150 °C

The thermal expansion was measured at 5·30 b. Four series of measurements were made on two samples of water, each sample being measured with both rising and falling temperatures. The differences between readings at the same temperature for rising and falling temperatures and the same sample of water were never more than 1·5 mg, or 7 p.p.m. of the volume, and were normally about half that amount. The change of the scale reading of the volumometer caused by a change of temperature of the vessel yields directly the change of mass of water in the vesssel. The calculations are straightforward. The results, taking the expansion of the vessel from equation (19), are given in table 6. Runs 1 and 2 were with the same sample of water, and runs 3 and 4 were with another sample. Runs 1 and 3 were with rising temperatures and runs 2 and 4 were with falling temperatures. The mean specific volume, all runs having the same weight, is also given in table 6. The scatter of the values at any one temperature corresponds to a standard deviation

Downloaded from rsta.royalsocietypublishing.org

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

of 4 p.p.m., which is about twice the standard deviation of a volumometer reading. The standard deviation of the thermal expansion of the vessel is 6 p.p.m. according to the fit of equation (19). The specific volume of water at 40 °C, which was used to determine the volume of water in the system, is known to about 4 p.p.m. (Tilton & Taylor 1937). The standard error of the mean densities listed in table 6 is therefore about 8 p.p.m. A more subjective, but probably more accurate, estimate of the error is that the mean values given in table 6 are unlikely to have a standard error of more than 5 p.p.m. at 80°, 10 p.p.m. at 100°, and 20 p.p.m. at 150 °C.

TABLE 6. SPECIFIC VOLUME $\bar{V}/\mathrm{cm^3\,g^{-1}}$ OF LIQUID WATER AT 5·30 b

°C	run 1	run 2	run 3	run 4	mean
80	1·028818	1·028821	1·028824	1·028822	1·028821
85	1·032188	1·032193	1·032196	1·032189	1·032192
90	1·035712	1·035717	1·035723	1·035718	1·035718
100	1·043231	1·043230	1·043236	1·043227	1·043231
110	1·051361	1·051367	1·051365	1·051363	1·051364
120	1·060121	1·060119	—	1·060126	1·060122
130	1·069533	1·069537	—	—	1·069535
140	1·079627	1·079628	—	—	1·079628
150	1·090443	1·090444	—	—	1·090444

TABLE 7. THE SPECIFIC VOLUME, DENSITY, AND THERMAL EXPANSIVITY OF LIQUID WATER AT A PRESSURE OF 1 atm AND AT SATURATION

	1 atm			saturation			
°C	$\bar{V}$ (cm³ g⁻¹)	ρ (g ml.⁻¹)	$10^6\alpha_p$ (degC⁻¹)	$\bar{V}$ (cm³ g⁻¹)	ρ_s (g ml.⁻¹)	$10^6\alpha_s$ (degC⁻¹)	p^s (b)†
80	1·029024	0·971822	640·9	1·029050	0·971797	639·7	0·47
85	1·032398	0·968646	668·6	1·032419	0·968626	667·4	0·58
90	1·035928	0·965345	695·9	1·035943	0·965331	694·6	0·70
100	1·043450	0·958386	750·4	1·043450	0·958386	748·7	1·01
110	1·051593	0·950965	804·0	1·051571	0·950985	801·2	1·43
120	1·060363	0·943100	857·6	1·060308	0·943149	854·1	1·99
130	1·069790	0·934789	912·8	1·069690	0·934876	907·7	2·70
140	1·079900	0·926038	969·1	1·079736	0·926178	962·2	3·61
150	1·090734	0·916839	1027·6	1·090481	0·917052	1018·6	4·76

† p_s is the saturation pressure.

The specific volume $\bar{V}$ at a pressure of 1 atm is given in table 7, together with the density in units of g/ml. since most previous workers have expressed their results in units of g/ml. They were calculated from the values in table 6 and the compressions given in §14. The volumes above 100 °C are those for the metastable superheated liquid, and for reasons of computational convenience these values, rather than values in the stable region, were used in the preparation of the tables given in §14. The relation between the cubic centimetre and the millilitre was taken to be (Pérard 1950)

$$1\ \mathrm{ml.} = 1{\cdot}000028\ \mathrm{cm}^3,$$

with a standard error of 4 p.p.m. (Cohen, Crowe & Dumond 1957). Table 7 also gives the isobaric thermal expansivities α_p

$$\alpha_p = \frac{1}{\bar{V}}\left(\frac{\partial \bar{V}}{\partial T}\right)_p = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p.$$

Downloaded from rsta.royalsocietypublishing.org

The derivatives were calculated by writing the observed density as the sum of that calculated from the formulation of Tilton & Taylor (1937) extrapolated beyond its valid range plus a residual δ

$$\rho\,(\text{g/ml.}) = 1 - \frac{(t-3{\cdot}9863)^2\,(t+288{\cdot}9414)}{508929{\cdot}2(t+68{\cdot}12963)} + \delta, \tag{20}$$

where t °C is the temperature. The Tilton & Taylor expression was differentiated algebraically, and the residual δ was differentiated graphically with an uncertainty of about $0{\cdot}1 \times 10^{-6}$ degC^{-1}. The total uncertainty of the expansivities based on the consistency of the table is about $0{\cdot}5 \times 10^{-6}$ degC^{-1}. Table 7 also gives the specific volumes, densities, and thermal expansivities α_s along the saturation curve. Here

$$\alpha_s = \frac{1}{\overline{V}_s}\left(\frac{\partial \overline{V}}{\partial T}\right)_s,$$

where $\overline{V}_s$ is the specific volume at saturation and the partial derivative is taken along the saturation curve. The calculations were similar to those for the isobaric expansivity except that different values of δ in equation (20) were used. The saturation pressures are from Osborne, Stimson & Ginnings (1939).

For completeness, the values of δ of equation (20) and its derivative have been interpolated graphically at 10 degC intervals from 95 to 145 °C, and the same quantities as given in table 7 have been calculated at these temperatures. To distinguish clearly between interpolated and directly measured values, the interpolated values are given in table 8.

TABLE 8. THE SPECIFIC VOLUMES, DENSITIES, AND THERMAL EXPANSIVITIES OF LIQUID WATER AT A PRESSURE OF ONE ATMOSPHERE AND AT SATURATION PRESSURE, OBTAINED BY INTERPOLATION FROM THE VALUES IN TABLE 2

	1 atm			saturation			
°C	$\overline{V}$ (cm^3 g^{-1})	ρ (g ml.$^{-1}$)	$10^6\,\alpha_p$ (degC^{-1})	$\overline{V}_s$ (cm^3 g^{-1})	ρ_s (g ml.$^{-1}$)	$10^6\,\alpha_s$ (degC^{-1})	p_s (b)†
95	1·039614	0·961922	722·2	1·039625	0·961912	720·5	0·85
105	1·047444	0·954732	777·2	1·047438	0·954737	774·8	1·21
115	1·055900	0·947086	830·8	1·055865	0·947117	827·7	1·69
125	1·064998	0·938995	885·0	1·064921	0·939063	880·6	2·32
135	1·074760	0·930466	940·7	1·074633	0·930576	934·8	3·13
145	1·085226	0·921493	998·1	1·085016	0·921671	989·8	4·16

† p_s is the saturation pressure.

17. THERMAL EXPANSION OF WATER NEAR 50 °C

Antonoff & Conan (1949) have reported that the density of water as a function of temperature is kinked near 50·5 °C, and n-propanol (Antonoff 1944) is reported to show similar behaviour. Kretschmer (1951) examined the thermal expansion of water and n-propanol and found no evidence of kinks; the volume of water was smooth in the temperature to 3 p.p.m. at 10 points between 41 and 59 °C, but he was unable to calibrate his apparatus to yield a thermal expansion.

The apparatus used in the present work should be capable of testing Antonoff's conclusions to a greater precision. Observations were made, therefore, in the manner described in §16 at intervals of approximately 0·25 degC over the range 47·5 to 52·0 °C

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Downloaded from rsta.royalsocietypublishing.org

in order of rising temperatures, and then the last observation was made at 50·0 °C, which is below the reported kink. The measurements were made immediately before the 50 °C isotherm of § 14 was run, and the same sample of water was used. All the measurements were made by one operator to obtain maximum reproducibility. The thermal expansion of the vessel was taken to be that given by equation (19). The measurements were made at a pressure of 5·30 b. The value of the density at 50 °C and atmospheric pressure given by Owen *et al.* (1956), which is equivalent to a specific volume of 1·0121075 cm^3/g, was assumed and was converted to the specific volume at 5·30 b by using the measured compressibility. This specific volume is recorded in the last row of the third column of table 9. Experiment gives deviations from this value. Table 9 summarizes the results. The first column gives the temperatures, and the second the mass $m-C$ of water in the volumometer in excess of the mass at zero scale reading and atmospheric pressure. The values of $m-C$ were fitted by a quadratic equation in the temperature, and the interpolated value at 50·000 °C is given in the last line of the table. The third column gives the specific volumes $\bar{V}_{5\cdot30}$ at 5·30 b calculated from the specific volume at 5·30 b and 50·000 °C, the thermal expansion of the vessel, and the values of $m-C$. The specific volumes at atmospheric pressure $\bar{V}_A$ were calculated using the equation for the compressibility of water given in § 18, and are listed in the fourth column of table 9. These values were fitted by least squares to the equation

Table 9. Specific volume of water near 50 °C

The quantity $(m-C)$ gives the mass of water in the volumometer, $\bar{V}_{5\cdot30\text{ b}}$, the observed specified volume at 5·30 b, $\bar{V}_A$ the corresponding specific volume at atmospheric pressure, and $\bar{V}_A$ (smoothed) the values obtained by smoothing $\bar{V}_A$ using a quadratic function. The last line at 50 °C gives quantities used in the calculations.

t (°C)	$(m-C)$ (g)	$\bar{V}_{5\cdot30\text{ b}}$ (cm^3 g^{-1})	$\bar{V}_A$ (cm^3 g^{-1})	$\bar{V}_A$ (smoothed) (cm^3 g^{-1})	10^6 ($\bar{V}_A-\bar{V}_A$(smoothed)) (cm^3 g^{-1})
47·500	24·8236	1·010777	1·0109681	1·0109675	0·6
47·783	24·8508	1·010903	1·0110945	1·0110943	0·2
48·064	24·8780	1·011029	1·0112208	1·0112212	−0·4
48·349	24·9063	1·011160	1·0113515	1·0113501	1·4
48·628	24·9329	1·011284	1·0114753	1·0114765	−1·2
48·937	24·9629	1·011423	1·0116148	1·0116178	−3·0
49·192	24·9891	1·011544	1·0117354	1·0117345	1·9
49·475	25·0169	1·011673	1·0118645	1·0118645	0·0
49·757	25·0452	1·011804	1·0119956	1·0119947	0·9
50·039	25·0735	1·011935	1·0121264	1·0121258	0·6
50·321	25·1020	1·012067	1·0122584	1·0122570	1·4
50·606	25·1301	1·012197	1·0123890	1·0123903	−1·3
50·887	25·1589	1·012330	1·0125218	1·0125220	−0·2
51·170	25·1877	1·012463	1·0126553	1·0126554	−0·1
51·453	25·2167	1·012598	1·0127895	1·0127892	0·3
51·737	25·2459	1·012733	1·0129248	1·0129242	0·6
52·018	25·2746	1·012865	1·0130573	1·0130581	−0·8
49·988	25·0682	1·011910	1·0121020	1·0121018	0·2
50·000	25·0694	1·0119158		1·0121075	

$$\bar{V} = a+b(t-50)+c(t-50)^2,$$

where t is the Celsius temperature. The smoothed specific volumes obtained are given in the fifth column of table 9, and the deviations of the smoothed from the measured values

Downloaded from rsta.royalsocietypublishing.org

are given in the sixth column. The deviations are apparently random and the standard deviation is $1{\cdot}1\times10^{-6}$ cm³ g⁻¹. The values of the parameters obtained were:

$$a = 1{\cdot}0121075\ \mathrm{cm^3\,g^{-1}},\quad b = 464{\cdot}37\times10^{-6}\ \mathrm{cm^3\,g^{-1}\,degC^{-1}},$$

and

$$c = 3{\cdot}34\times10^{-6}\ \mathrm{cm^3\,g^{-1}\,degC^{-2}}.$$

At 50 °C the smoothed specific volume a agrees, as it should, with the starting value. At 50 °C the thermal expansivity α is b/a and is $458{\cdot}8\pm0{\cdot}2\times10^{-6}$ degC⁻¹, and $\partial\alpha/\partial t$ is $(2ac-b^2)/a^2$ which is $6{\cdot}5\pm0{\cdot}4\times10^{-6}$ degC⁻². For comparison the values of Owen *et al.* (1956) are $457{\cdot}98\times10^{-6}$ degC⁻¹ and $6{\cdot}86\times10^{-6}$ degC⁻². The thermal expansivities differ by $1{\cdot}2\times10^{-6}$ degC⁻¹ which is several times the combined estimated errors. This might be due to unrecognized errors in either or both of the measurements. It might also be due to Owen *et al.* using too few points and an inadequate interpolation formula; they measured specific volumes at 10 degC intervals and interpolated them by Tilton & Taylor's formula. The thermal expansivity of water changes by about 1·5 %/degC, and so their procedure may be inadequate for precise measurements. If the thermal expansion of the pressure vessel (see §15) had been based entirely on the data of Owen *et al.* it would have been $0{\cdot}30\times10^{-6}$ degC⁻¹ larger, according to the data in figure 10. The use of this expansion would have made our thermal expansivity of water greater by $0{\cdot}3\times10^{-6}$ degC⁻¹, and made the difference from the value of Owen *et al.* even larger, $1{\cdot}5\times10^{-6}$ degC⁻¹.

This work indicates that any kink in the density of water cannot exceed about 1 p.p.m., and hence that Antonoff's kink, which was claimed to be much bigger than that, does not exist. It seems pointless to speculate as to what experimental error produced Antonoff's results.

18. Analysis of specific volumes

The specific volumes in table 4 need to be analysed numerically to allow interpolation and differentiation, and also to allow comparison with previous work. The data were measured at points that form a rectangular array in the $p-T$ plane, and because of this if they are fitted to an equation of the kind

$$\overline{V}(T_i, p_j)/\overline{V}(T_i, 1\ \mathrm{atm}) = \sum_k \sum_l \alpha_{kl}\theta_k(T_i)\ \phi_l(p_j), \tag{21}$$

where $\theta(T)$ is a function of temperature only and $\phi(p)$ is a function of pressure only, and α_{kl} are numerical coefficients, it is necessary only to fit each isotherm by least squares and to fit the parameters obtained as a function of temperature by least squares to obtain a least squares fit of all the data to equation (21).

The proof of this is as follows; it is probably not new, but the theorem does not seem to be generally known and the proof is worth giving.† Let z be measured as a function of x and y at a set of values x_i, y_j, $i = 1, 2, \ldots, s$, $j = 1, 2, \ldots, t$, and let the values of z have equal weights. Let the supposed mathematical relations between z and x and y be

$$z(x, y) = \sum_{k=1}^{m}\sum_{l=1}^{n} \alpha_{kl}\theta_k(x)\ \phi_l(y), \tag{22}$$

---

† We are indebted to Mr R. W. Bain, of the National Engineering Laboratory, East Kilbride, for a hint that led us to this conclusion.

Downloaded from rsta.royalsocietypublishing.org

where $\theta_k(x)$ are functions of x only and $\phi_l(y)$ are functions of y only, and α_{kl} are numerical coefficients. Then the calculated value z_{ij} (calc.) for the particular values x_i, y_j is

$$z_{ij}(\text{calc.}) = \sum_k \sum_l \alpha_{kl}\,\theta_k(x_i)\,\phi_l(y_j). \tag{23}$$

For a given value of j we can also write

$$z_{ij}(\text{calc.}) = \sum_k a_{kj}\,\theta_k(x_i), \tag{24}$$

where

$$a_{kj} = \sum_l \alpha_{kl}\phi_l(y_j). \tag{25}$$

It is required that a least squares determination of the α_{kl} by fitting all the data to equation (22) directly yields the same results as first fitting the values of z_{ij} for fixed j to equation (24) to determine the a_{kj}, and then fitting the a_{kj} for fixed k to equation (25). The sum of squares S of deviations for all x_i, y_j from equation (22) is

$$S = \sum_i \sum_j \{z_{ij}(\text{obs.}) - \sum_k \sum_l a_{kl}\,\theta_k(x_i)\,\phi_l(y_j)\}^2. \tag{26}$$

The condition for a minimum value of S is

$$\partial S/\partial \alpha_{kl} = 0 \quad (\text{all } k, l), \tag{27}$$

from which we find the mn equations

$$\sum_i \sum_j \theta_k(x_i)\,\phi_l(y_j)\,\{z_{ij}(\text{obs.}) - \sum_k \sum_l \alpha_{kl}\,\theta_k(x_i)\,\phi_l(y_j)\} = 0 \quad (\text{all } k, l). \tag{28}$$

The least squares conditions for determining the a_{kj} for a given value of j according to equation (24) are the m equations

$$\sum_i \theta_k(x_i)\,\{z_{ij}(\text{obs.}) - \sum_k a_{kj}\,\theta_k(x_i)\} = 0 \quad (\text{all } k), \tag{29}$$

and there are t sets of these equations, one for each value of j. The least squares conditions for determining the α_{kl} by fitting the a_{kj} determined by equation (29) to equation (25) are the n equations

$$\sum_j \phi_l(y_j)\,\{a_{kj} - \sum_l \alpha_{kl}\phi_l(y_j)\} = 0 \quad (\text{all } l), \tag{30}$$

and there are m sets of these equations, one for each value of k. By multiplying equation (29) by $\phi_l(y_j)$ and summing over all j we have the equation

$$\sum_i \sum_j \theta_k(x_i)\,\phi_l(y_j)\,\{z_{ij}\,(\text{obs.}) - \sum_k a_{kj}\,\theta_k(x_i)\} = 0 \quad (\text{all } k, l). \tag{31}$$

By multiplying equation (30) by $\theta_k(x_i)$ and summing over all k, multiplying again by $\theta_k(x_i)$ and summing over all i, and using the resulting equation to eliminate a_{kj} from equation (31) we have

$$\sum_i \sum_j \theta_k(x_i)\,\phi_l(y_j)\,\{z_{ij}(\text{obs.}) - \sum_k \sum_l \alpha_{kl}\,\theta_k(x_i)\,\phi_l(y_j)\} = 0. \tag{32}$$

This equation is identical with equation (28), which proves the theorem.

If $z(x, y)$ cannot be put in the form of equation (22), it will usually be possible to choose approximate values of the parameters and, by expanding the sum of squares of the deviations in a Taylor series, to reduce the problem to the form described.

The isotherms were fitted to the equation

$$\overline{V}/\overline{V}_A = 1 + c_1(p - p_A) + c_2(p - p_A)^2 + c_3(p - p_A)^3 + c_4(p - p_A)^4 \tag{33}$$

by the method of least squares. The data for replicate isotherms were analysed separately.

Downloaded from rsta.royalsocietypublishing.org

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

The quartic term was not needed at temperatures from 0 to 110 °C and was not used. The coefficients c_1, c_2, c_3 and c_4, obtained by analysing each isotherm separately, may be taken as constant over narrow ranges of temperature. They were averaged where two or more runs were available at a temperature, and were used as the basis for interpolating specific volumes. The values of these coefficients are listed in table 10 along with the standard deviations, or mean standard deviations, for the isotherm. The specific volumes calculated using these coefficients are given in table 11 for rounded values of the pressure in bars.

Table 10. Coefficients c_i used with equation (33) in the calculation of table 11

t (°C)	$-10^6 c_1$ (b^{-1})	$10^9 c_2$ (b^{-2})	$-10^{13} c_3$ (b^{-3})	$10^{17} c_4$ (b^{-4}†)	standard deviation of isotherm (p.p.m.)
0	50·9930	8·2845	9·215	—	2·4
10	47·8435	7·1053	6·847	—	4·3
20	45·8944	6·6197	6·819	—	4·0
25	45·2294	6·4147	6·216	—	4·7
30	44·8010	6·4692	7·320	—	3·8
40	44·3043	6·5113	8·109	—	4·0
50	44·1017	6·3413	7·021	—	5·1
60	44·5136	6·7819	8·939	—	5·8
70	45·0950	7·0099	9·267	—	4·1
80	46·1298	7·5745	11·035	—	3·5
90	47·3467	8·0229	11·546	—	4·3
100	48·9121	8·7572	13·701	—	4·7
110	50·7766	9·5488	15·440	—	5·1
120	53·1418	11·2463	27·970	46·575	5·4
130	55·6670	12·2801	28·826	37·503	4·1
140	58·7217	14·3295	43·242	91·288	5·6
150	62·1439	16·1802	49·224	95·071	4·3

† The value of c_4 was set equal to zero in the range 0 to 110 °C.

For the purpose of fitting a function of the form given in equation (21), with the general term $\alpha_{kl}\theta_k(T)\,\phi_l(p)$ in the specific form $\alpha_{kl}t^k(p-p_A)^l$, the isotherms above 120 °C were analysed with equation (33) putting c_4 equal to zero. This did not provide the best fit to the data in the range 120 to 150 °C, but as the compressibility of mercury is in doubt in this temperature range, the cubic approximation to these isotherms introduces no further error for the present purposes. The coefficients c_1, c_2 and c_3 of all the isotherms were then fitted as a quintic function of temperature by the equations

$$c_l = \sum_{k=0}^{5} \alpha_{kl} t^k, \tag{34}$$

where t is the Celsius temperature. The coefficients of the 0° isotherm were given a weight twice that of the others because this isotherm is the average of a rising and a falling run and so is equivalent to two runs. The coefficients α_{kl} are listed in table 12; they are of course the coefficients of the equation of state

$$\bar{V}(t,p)/\bar{V}(t,1\text{ atm}) = 1 + \sum_{k=0}^{5}\sum_{l=1}^{3} \alpha_{kl} t^k (p-p_A)^l. \tag{35}$$

Downloaded from rsta.royalsocietypublishing.org

TABLE 11. SPECIFIC VOLUMES OF WATER (cm^3/g) INTERPOLATED USING EQUATION (33) WITH THE COEFFICIENTS OF TABLE 10.

	T(°C)								
p(bar)	0·0	10·0	20·0	25·0	30·0	40·0	50·0	60·0	70·0
0·0	1·000212	1·000349	1·001844	1·003008	1·004415	1·007887	1·012153	1·017133	1·022789
1·0	1·000161	1·000301	1·001798	1·002962	1·004370	1·007843	1·012108	1·017093	1·022743
5·0	0·999957	1·000109	1·001614	1·002781	1·004190	1·007664	1·011930	1·016912	1·022559
10·0	0·999703	0·999871	1·001385	1·002555	1·003965	1·007441	1·011707	1·016686	1·022329
25·0	0·998942	0·999156	1·000698	1·001877	1·003293	1·006775	1·011041	1·016010	1·021641
50·0	0·997682	0·997973	0·999561	1·000755	1·002180	1·005670	1·009937	1·014891	1·020501
75·0	0·996432	0·996798	0·998432	0·999640	1·001075	1·004574	1·008840	1·013780	1·019369
100·0	0·995192	0·995632	0·997310	0·998534	0·999978	1·003486	1·007752	1·012677	1·018247
125·0	0·993963	0·994474	0·996197	0·997435	0·998888	1·002405	1·006671	1·011583	1·017695
150·0	0·992743	0·993325	0·995092	0·996344	0·997807	1·001332	1·005598	1·010497	1·016027
175·0	0·991533	0·992185	0·993995	0·995261	0·996733	1·000268	1·004532	1·009419	1·014930
200·0	0·990333	0·991053	0·992906	0·994185	0·995667	0·999210	1·003474	1·008349	1·013842
225·0	0·989142	0·989929	0·991824	0·993117	0·994608	0·998161	1·002424	1·007287	1·012761
250·0	0·987961	0·988814	0·990750	0·992056	0·993557	0·997119	1·001381	1·006233	1·011689
275·0	0·986790	0·987707	0·989684	0·991003	0·992513	0·996084	1·000345	1·005187	1·010625
300·0	0·985628	0·986608	0·988625	0·989957	0·991477	0·995057	0·999317	1·004148	1·009569
350·0	0·983332	0·984435	0·986531	0·987888	0·989426	0·993024	0·997282	1·002094	1·007480
400·0	0·981072	0·982293	0·984465	0·985847	0·987404	0·991019	0·995275	1·000069	1·005422
450·0	0·978848	0·980183	0·982429	0·983835	0·985409	0·989043	0·993297	0·998073	1·003395
500·0	0·976660	0·978104	0·980422	0·981850	0·983443	0·987094	0·991345	0·996105	1·001396
550·0	0·974506	0·976055	0·978442	0·979894	0·981503	0·985171	0·989420	0·994166	0·999427
600·0	0·972386	0·974037	0·976490	0·977964	0·979590	0·983275	0·987522	0·992253	0·997486
650·0	0·970299	0·972047	0·974565	0·976061	0·977702	0·981404	0·985649	0·990366	0·995572
700·0	0·968245	0·970087	0·972667	0·974184	0·975840	0·979558	0·983801	0·988506	0·993684
750·0	0·966222	0·968155	0·970794	0·972332	0·974003	0·977736	0·981978	0·986670	0·991823
800·0	0·964231	0·966250	0·968947	0·970506	0·972190	0·975938	0·980179	0·984858	0·989986
850·0	0·962269	0·964373	0·967125	0·968705	0·970401	0·974163	0·978404	0·983070	0·988174
900·0	0·960338	0·962523	0·965328	0·966927	0·968634	0·972410	0·976652	0·981305	0·986386
950·0	0·958435	0·960699	0·963554	0·965174	0·966891	0·970680	0·974922	0·979562	0·984621
1000·0	0·956561	0·958901	0·961804	0·963443	0·965169	0·968970	0·973214	0·977841	0·982879

	T(°C)							
p(bar)	80·0	90·0	100·0	110·0	120·0	130·0	140·0	150·0
0·0	1·029072	1·035978	1·043502	1·051647	1·060420	1·069850	1·079964	1·090802
1·0	1·029024	1·035929	1·043451	1·051594	1·060364	1·069791	1·079900	1·090735
5·0	1·028834	1·035733	1·043247	1·051381	1·060139	1·069553	1·079647	1·090464
10·0	1·028598	1·035488	1·042992	1·051114	1·059858	1·069256	1·079331	1·090126
25·0	1·027889	1·034756	1·042231	1·050318	1·059018	1·068369	1·078387	1·089118
50·0	1·026717	1·033545	1·040972	1·049001	1·057631	1·066904	1·076830	1·087455
75·0	1·025554	1·032344	1·039724	1·047697	1·056258	1·065454	1·075291	1·085813
100·0	1·024400	1·031153	1·038486	1·046405	1·054899	1·064021	1·073770	1·084192
125·0	1·023256	1·029972	1·037260	1·045124	1·053554	1·062602	1·072266	1·082591
150·0	1·022121	1·028801	1·036045	1·043855	1·052223	1·061199	1·070780	1·081010
175·0	1·020995	1·027640	1·034840	1·042598	1·050905	1·059810	1·069311	1·079447
200·0	1·019878	1·026488	1·033645	1·041353	1·049600	1·058436	1·067859	1·077904
225·0	1·018770	1·025346	1·032461	1·040119	1·048308	1·057076	1·066422	1·076379
250·0	1·017670	1·024213	1·031287	1·038896	1·047028	1·055731	1·065002	1·074872
275·0	1·016580	1·023089	1·030123	1·037684	1·045761	1·054398	1·063596	1·073383
300·0	1·015498	1·021974	1·028969	1·036483	1·044506	1·053080	1·062206	1·071910
350·0	1·013359	1·019772	1·026691	1·034113	1·042032	1·050482	1·059470	1·069015
400·0	1·011253	1·017606	1·024451	1·031784	1·039603	1·047935	1·056790	1·066184
450·0	1·009179	1·015473	1·022248	1·029496	1·037219	1·045437	1·054165	1·063414
500·0	1·007137	1·013375	1·020081	1·027248	1·034877	1·042987	1·051591	1·060703
550·0	1·005125	1·011308	1·017949	1·025037	1·032576	1·040582	1·049067	1·058047
600·0	1·003143	1·009274	1·015851	1·022863	1·030315	1·038221	1·046591	1·055445
650·0	1·001190	1·007270	1·013786	1·020725	1·028093	1·035903	1·044161	1·052893
700 0	0·999264	1·005296	1·011752	1·018621	1·025907	1·033625	1·041775	1·050391
750·0	0·997366	1·003352	1·009749	1·016551	1·023757	1·031386	1·039433	1·047936
800·0	0·995493	1·001435	1·007776	1·014512	1·021642	1·029186	1·037132	1·045527
850·0	0·993646	0·999546	1·005832	1·012505	1·019560	1·027021	1·034871	1·043161
900·0	0·991824	0·997683	1·003915	1·010526	1·017511	1·024892	1·032649	1·040838
950·0	0·990025	0·995845	1·002024	1·008576	1·015494	1·022797	1·030466	1·038555
1000·0	0·988249	0·994032	1·000159	1·006653	1·013507	1·020734	1·028320	1·036313

Downloaded from rsta.royalsocietypublishing.org

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

The deviations of the observed values of $\overline{V}/\overline{V}_A$ from this equation for all the experimental points are given in table 13. The standard deviation is 3 p.p.m. at the lower pressures, and 10 p.p.m. at the higher pressures.

TABLE 12. COEFFICIENTS α_{kl} OF EQUATION (35)

Units: t, °C; p, bars; and p_A is 1 atm.

temp. term	pressure term 1	$10^{-6}\,(p-p_A)$	$10^{-9}(p-p_A)^2$	$10^{-13}(p-p_A)^3$
1	1	$-50{\cdot}9769$	$8{\cdot}2627$	$-9{\cdot}109$
$10^{-1}t$		$3{\cdot}71999$	$-1{\cdot}3794$	$2{\cdot}626$
$10^{-3}t^2$		$-7{\cdot}01760$	$3{\cdot}4032$	$-8{\cdot}913$
$10^{-5}t^3$		$6{\cdot}00227$	$-3{\cdot}6432$	$11{\cdot}467$
$10^{-7}t^4$		$-3{\cdot}09041$	$2{\cdot}0836$	$-7{\cdot}102$
$10^{-10}t^5$		$5{\cdot}93416$	$-4{\cdot}1744$	$14{\cdot}841$

The measurements reported here extend to sufficiently low pressures, and are sufficient in number at the lower pressures, to permit a reliable determination of the isothermal compressibility at atmospheric pressure. The compressibilities at 1 atm are $-c_1$ of equation (33). The values obtained by analysing each isotherm separately are listed in table 14. Isotherms above 120 °C were analysed by a quartic equation. The error in c_1 estimated from the least squares fit is $0{\cdot}02$–$0{\cdot}05 \times 10^{-6}\,\mathrm{b}^{-1}$, and the deviation of replicate runs from

TABLE 13. DEVIATIONS OF THE OBSERVED POINTS FROM EQUATION (35) AND THE COEFFICIENTS GIVEN IN TABLE 11.

The quantity shown is the observed minus the calculated value (p.p.m.)

	t(°C)										
p(bar)	0·000	10·002	19·997	24·998	24·998	25·005	30·112	39·999	50·007	60·001	70·003
5·30	−4	−3	−4	−7	−6	−4	−3	2	−2	−4	−1
12·60	−3	0	−1	2	0	−1	−2	1	6	0	4
20·00	−1	−4	−3	−6	−3	−3	0	−7	−5	−4	3
27·40	−2	0	0	2	1	1	1	−5	0	1	3
42·11	2	3	−1	−1	−3	−3	−2	−1	−2	−2	−3
56·81	−3	0	−1	−4	−4	−4	−8	−13	−2	−6	−4
71·51	−1	4	5	7	8	4	1	−2	12	5	5
86·31	−2	3	−1	1	0	3	−7	−8	3	0	1
101·01	1	8	3	3	0	1	−11	−9	2	2	3
115·71	−1	9	4	6	2	4	−6	−5	9	2	8
130·52	−1	9	5	7	−1	3	−7	−11	6	−2	8
151·89	−2	7	2	2	−3	0	−14	−13	3	−8	8
210·28	−6	−3	−4	−6	−11	−9	−13	−16	−4	−10	−1
268·57	−5	10	10	5	3	7	−8	−10	12	−1	17
326·95	−4	10	1	5	4	0	−10	−18	12	−5	17
385·22	−3	13	4	−2	−2	−5	−12	−18	8	−1	17
443·49	−10	19	18	6	4	5	−4	−8	13	9	23
501·85	−2	9	6	−10	−10	−7	−15	−21	−3	−3	11
560·11	−9	10	6	−6	−8	−4	−17	−22	−4	−6	12
618·47	−1	5	6	−6	−6	−9	−19	−20	−4	−6	13
676·71	−5	8	9	−2	−1	−6	−11	−14	0	1	18
735·06	−3	15	13	4	2	−1	−13	−16	1	3	20
793·29	−4	19	16	7	7	0	−11	−12	3	5	20
851·63	−6	16	15	4	2	1	−10	−14	−1	−1	21
909·85	−7	14	12	2	0	−3	−17	−19	1	−2	21
968·08	−6	14	8	2	−2	−4	−16	−20	−3	2	21
1026·39	−5	12	8	0	−2	−4	−18	−22	−1	1	20

Downloaded from rsta.royalsocietypublishing.org

MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES
PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A

Table 13 (*cont.*)

	t(°C)									
p(bar)	80·003	90·007	100·005	110·005	110·003	120·007	130·010	140·009	150·016	150·016
5·30	−6	5	−4	−4	2	−5	1	−6	−1	0
12·60	2	1	3	3	4	−1	1	1	−4	−1
20·00	−2	−5	−3	−2	−1	−7	−4	−4	−8	−7
27·40	0	−1	3	2	−1	−5	−4	−2	−4	−5
42·11	−3	−5	0	−6	−2	−4	0	−6	−10	−11
56·81	−7	−5	−8	−12	−6	−10	−7	−12	−16	−17
71·51	3	2	2	2	0	−1	−3	0	−7	−10
86·31	0	−1	−1	−3	−2	−5	−6	−9	−15	−15
101·01	−3	0	−4	−4	−6	−10	−6	−9	−17	−17
115·71	2	3	1	−1	−1	−7	−5	−6	−13	−13
130·52	−4	2	−7	−5	−4	−8	−5	−12	−19	−14
151·89	−5	−5	−10	−7	−4	−12	−7	−16	−19	−20
210·28	−10	−10	−10	−17	−8	−27	−16	−19	−28	−25
268·57	−3	6	2	−2	1	−11	4	−1	−15	−14
326·95	−2	1	−4	−10	−2	−9	4	16	−8	−5
385·22	0	−5	0	−7	5	−6	2	10	−14	−10
443·49	7	9	9	7	9	7	10	20	9	9
501·85	−5	−4	−5	−14	−11	−12	0	6	−7	−6
560·11	−5	−4	−5	−17	1	−6	0	7	−10	−6
618·47	−3	−6	−10	−21	−10	−10	−3	1	−18	−8
676·71	0	−2	−3	−17	−9	−2	0	−5	−22	−8
735·06	−2	0	−7	−7	−13	−2	3	−3	−19	−13
793·29	3	4	2	−7	−7	−8	2	−6	−25	−16
851·63	−2	1	−8	−16	−8	−12	0	−5	−27	−17
909·85	0	4	−8	−14	−9	−13	8	−4	−22	−15
968·08	−5	5	−8	−11	−10	−14	6	1	−15	−12
1026·39	−3	7	−5	−14	−12	2	12	9	−3	−2

TABLE 14. EXPERIMENTAL ISOTHERMAL COMPRESSIBILITIES AT ATMOSPHERIC PRESSURE

The order of the runs is the same as in table 4.

t(°C)	$10^6\kappa_A$(b^{-1})		t(°C)	$10^6\kappa_A$(b^{-1})	
0·000	50·993		80·003	46·130	
10·002	47·844		90·007	47·347	
19·997	45·894		100·005	48·912	
24·998	45·218	45·246	110·005	50·789	
25·005	45·225		110·003	50·764	
30·112	44·801		120·007	53·142	
39·999	44·304		130·010	55·667	
50·007	44·102		140·009	58·722	
60·001	44·514		150·016	62·146	62·142
70·003	45·095				

their mean is never more than $0{\cdot}02\times10^{-6}$ b^{-1}, or 1 part in 2000. The uncertainties of the compressibility of mercury are of this magnitude. The compressibilities at 1 atm were fitted to a power series in the temperature by least squares. A moderately good representation required a quintic equation,

$$\begin{aligned}10^6\kappa = {} & 50{\cdot}9804-0{\cdot}374957t+7{\cdot}21324\times10^{-3}t^2\\ & -64{\cdot}1785\times10^{-6}t^3+0{\cdot}343024\times10^{-6}t^4\\ & -0{\cdot}684212\times10^{-9}t^5\ \mathrm{b}^{-1}.\end{aligned} \tag{36}$$

The standard deviation of the compressibilities from this equation is $0{\cdot}04\times10^{-6}$ b^{-1}.

Downloaded from rsta.royalsocietypublishing.org

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

19. Comparison of specific volumes at low pressure with previous measurements

There are few density determinations in the range 80 to 150 °C that are of a precision comparable to the work reported here, and it seems worthwhile to make comparisons at 100 and 150 °C only. Several values of the specific volume at 100 °C are summarized in table 15. Chappuis (1907) made a single determination of the density of water at 100 °C which is of particular interest as it was obtained using one apparatus of the two he used to obtain his values between 0° and 42 °C. Our value is not entirely independent of that of Chappuis since his work is the basis of the measurements relative to water that enter into equation (19). However, the volume of the vessel as given by equation (19) at temperatures above 100 °C is primarily controlled by measurements relative to mercury, and is little affected by the measurements relative to water, and so there is only a moderate dependence on Chappuis's values. Chappuis's value is 6 p.p.m. less than our value, which is satisfactory agreement. The value in table 15 due to Thiessen (1904) is his observed value, and is 7 p.p.m. greater than our value, again in satisfactory agreement. The value he computed from his formula is 12 p.p.m. greater than our value. The value due to Smith & Keyes (1934) is that obtained by them directly from their 100 °C isotherm. It agrees with ours to 10 p.p.m., which is well within the accuracy of 100 p.p.m. claimed for their work. The value calculated from their formulation is 1·04338 cm^3/g, 150 p.p.m. greater than our value. A number of other workers, for example, Vukalovich, Zubarev, Aleksandrov & Kalinin (1959, 1961), have made measurements at wide intervals of pressure. Their data are given only to 100 p.p.m. and cannot be extrapolated to atmospheric pressure with a precision comparable to the other measurements in table 15; the extrapolated specific volume differs from ours by several hundred parts per million.

Table 15. Values obtained by different workers for the specific volume of water at 1 atm and 100 °C

	cm^3/g
this work	1·043450
Chappius (1907)	1·0434440
Thiessen (1904)	1·043457
Smith & Keyes (1934)	1·04344
Vukalovich *et al.* (1959, 1961)	1·0438

At 150 °C, values to compare with the present ones are even fewer, and their precision is only about 100 p.p.m. Holser & Kennedy (1958) measured the thermal expansions at 300 b. Their specific volume at 300 b and 150 °C is 1·0724 cm^3/g which is 500 p.p.m. greater than the value reported here for those conditions. An extrapolation of the data of Vukalovich *et al.* (1961) at 150 °C to 1 atm gives 1·0914 cm^3/g which is 700 p.p.m. greater than our value. The series III experiments of Smith & Keyes (1934) were extrapolated by us to give a specific volume of 1·09073 cm^3/g, in excellent agreement with our value of 1·090734 cm^3/g. Since the specific volumes derived by Smith & Keyes from the measurements of their series III agree within 50 p.p.m. with the value given by Tilton & Taylor (1937) at 30 °C, by Owen *et al.* (1956) at 50 and 75 °C, and by ourselves at 100 and

Downloaded from rsta.royalsocietypublishing.org

150 °C, the inadequacies of the Smith & Keyes formulation should not in our view obscure the fact that their experimental specific volumes, at low pressures in any event, seem to be correct to the precision they claim.

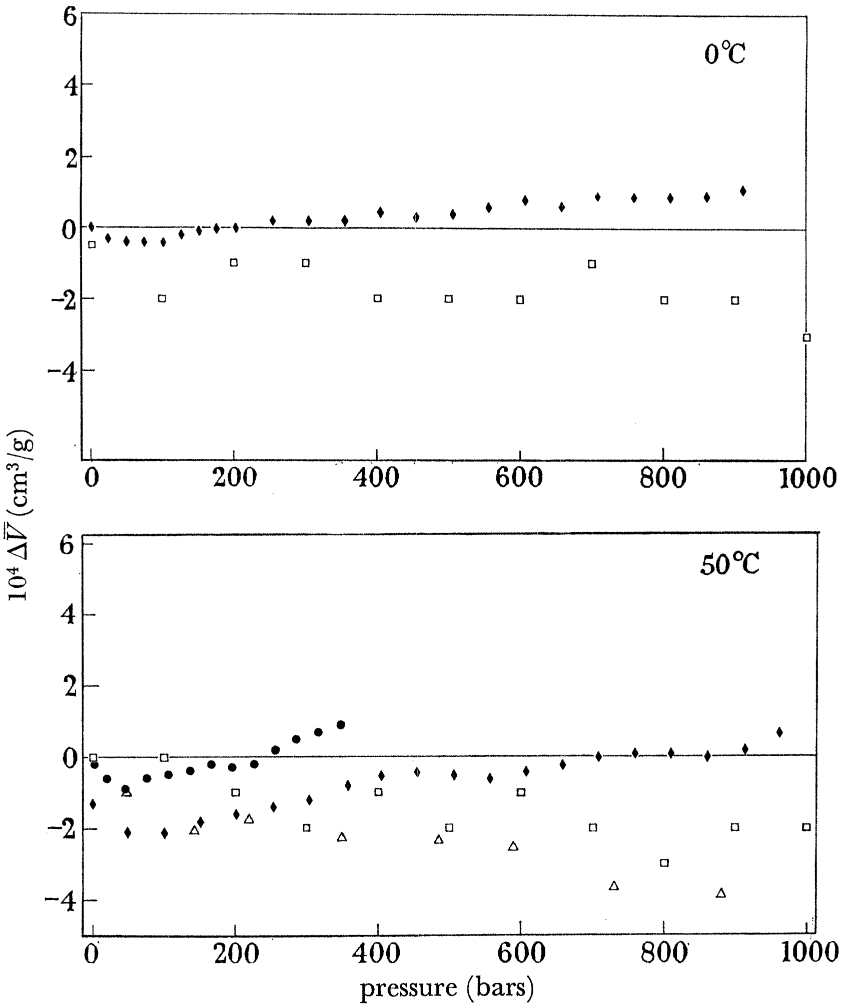

FIGURE 11. Comparison of specific volumes of water at 0 and 50 °C. $\Delta\overline{V}$ is the deviation from equation (33) fitted to the data of table 4. Symbols: ◆, Amagat (1893); ●, Smith & Keyes (1934), series III; □, Kennedy, Knight & Holser (1958); △, Vukalovich *et al.* (1959, 1961), series I.

20. COMPARISON OF SPECIFIC VOLUMES UNDER PRESSURE WITH PREVIOUS MEASUREMENTS

It would be a major task to compare every specific volume of water that has ever been measured in our experimental range with our values. Few measurements have been made under pressure to the reproducibility of those reported here, and a cursory comparison of values soon showed that measurements of other authors nearly always agreed within their claimed accuracy with our values. A detailed comparison has therefore been undertaken only at the temperatures 0, 50, 100, and 150 °C, which are the temperatures required for the International Skeleton Tables of the Properties of Steam. The comparison is made in figures 11 and 12 by plotting the deviation $\Delta\overline{V}$ of the specific volumes reported by various workers from the specific volumes calculated according to

Downloaded from rsta.royalsocietypublishing.org

equation (33) using the coefficients in table 10. The deviation of our measurements from these equations rarely reaches $0{\cdot}1 \times 10^{-4}$ cm^3/g, so the distribution of our results is not much wider than the central line in the diagram. Jůza, Kmoníček & Šifner's (1961) measurements which overlap ours in the range 80 to 150 °C and 500 to 1000 b claim an accuracy of 0·001 cm^3/g, and agree within this accuracy with ours. The values published by Amagat (1893) and Kennedy, Knight & Holser (1958) had already been smoothed graphically. The unsmoothed data of Smith & Keyes (1934) and Vukalovich *et al.* (1959, 1961) have been compared.

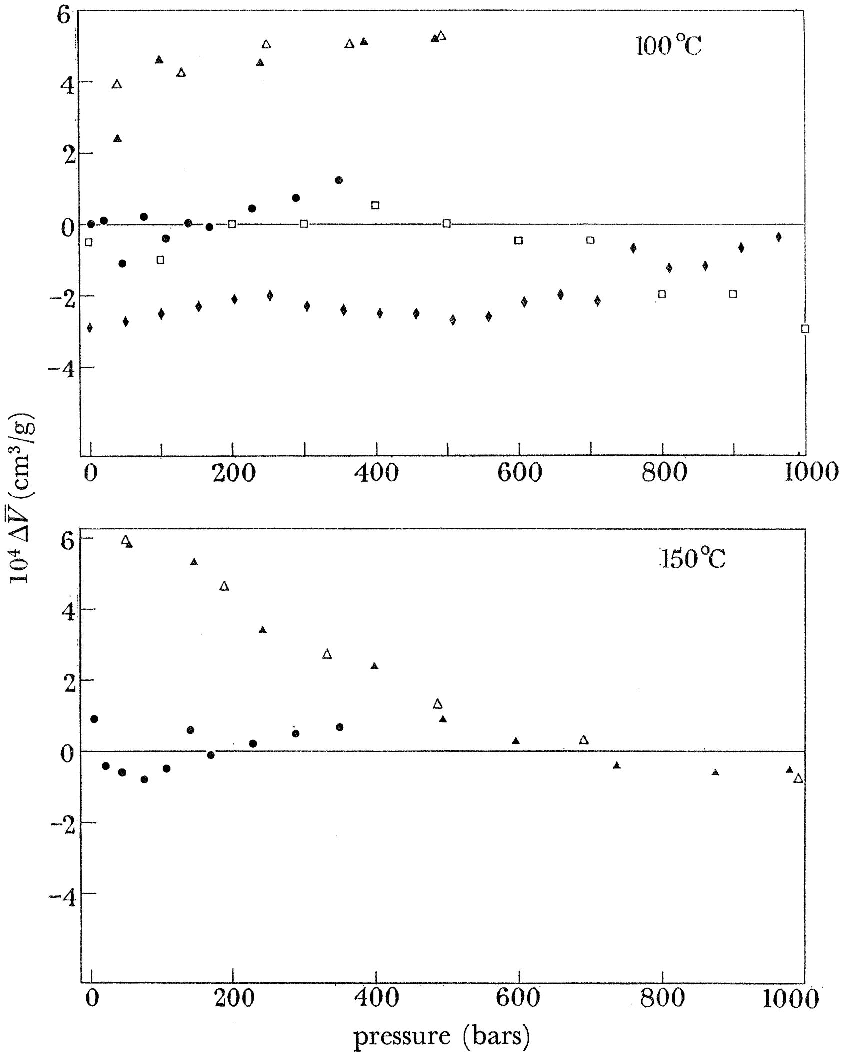

FIGURE 12. Comparison of the specific volumes of water at 100 and 150 °C. The symbols are as in figure 11, plus ▲ Vukalovich *et al.* (1959, 1961), series II.

The deviations of the various values of the compressibility, both ours and those of other workers, from equation (36) are plotted in figure 13. The values obtained by Smith & Keyes (1934) from their formulation of their measurements differ greatly from our values, and are no doubt in error. The original measurements of the compressions in series III of Smith & Keyes, which were taken up to about 350 b, have been fitted by least squares to a cubic equation in $(p-p_A)$, and the compressibilities obtained are also shown in figure 13.

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Downloaded from rsta.royalsocietypublishing.org

They agree satisfactorily with ours, and there is no doubt that Smith & Keyes's measurements are much better than their formulation. The other directly measured compressibilities (Diaz Peña & McGlashan 1959, Vukalovich *et al.* 1959, 1961) shown in figure 13 probably agree with ours within the accuracy of the various measurements.

The adiabatic compressibility κ_s can be obtained from the velocity of sound u in regions where there is no dispersion by means of the relation

$$\kappa_s = \overline{V}u^{-2}.$$

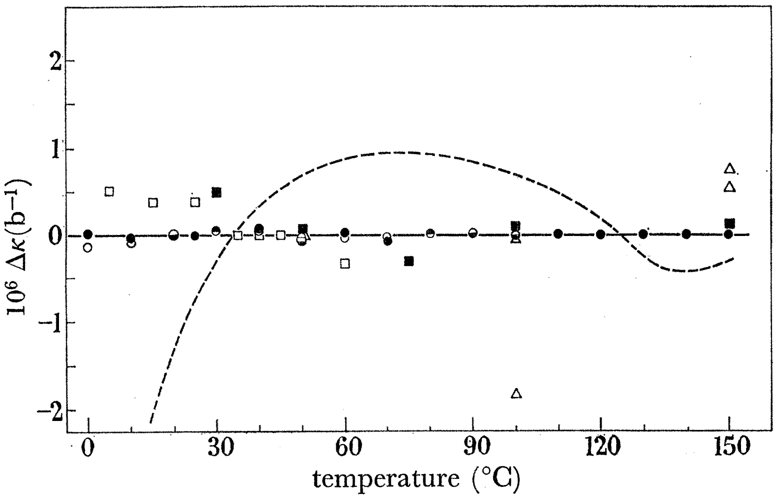

FIGURE 13. Comparison of values of the compressibility of water at 1 atm. $\Delta\kappa$ are the deviations from equation (36). ●, this work; ○, Greenspan & Tschiegg; □, Diaz Peña & McGlashan; ■, Smith & Keyes (series III); △, Vukalovich *et al.* (1959); – – –, Smith & Keyes (formulation).

TABLE 16. ISOTHERMAL COMPRESSIBILITIES AT ATMOSPHERIC PRESSURE, CALCULATED FROM VELOCITY OF SOUND MEASUREMENTS OF GREENSPAN & TSCHIEGG

t(°C)	$10^6\kappa(\mathrm{b}^{-1})$	t(°C)	$10^6\kappa(\mathrm{b}^{-1})$
0	50·86	60	44·48
10	47·81	70	45·15
20	45·91	80	46·12
30	44·80	90	47·41
40	44·28	100	49·01
50	44·16		

The isothermal compressibility κ can be obtained from the adiabatic compressibility by means of the relation

$$\kappa = \kappa_s + T(\partial\overline{V}/\partial T)_p^2/C_p\overline{V},$$

where C_p is the heat capacity at constant pressure. Sound velocities in water have been measured several times (see Diaz Peña & McGlashan (1959) for a review) and the isothermal compressibilities derived from them agree with one another and with other values to within 1%. The sound velocities reported by Greenspan & Tschiegg (1957) appear to have been carefully measured and agree with the results of Wilson (1961). They have been converted to isothermal compressibilities using the thermal expansivities calculated from the formulation of Tilton & Taylor (1937) for 0 to 40 °C, those reported by Owen *et al.* (1956) for 50 to 70 °C, and those reported in § 16 above 80 °C, and the heat capacities given by Stimson (1955). The isothermal compressibilities thus obtained are listed in table 16. The agreement with ours is excellent.

Downloaded from rsta.royalsocietypublishing.org

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

PART III. THE MERCURY COLUMN

21. General description

The column is located in the Applied Chemistry Building of the National Research Council, and extends the inside height of the building. A block diagram is shown in figure 14. A column of mercury in the shape of a U with one leg a few cm long and the other leg about 17·5 m long is enclosed in a steel tube. A pressure balance can be connected to the end of each leg of the U tube. Both balances are at the lower end for convenience and pressure is transmitted to the top by means of a tube that contains oil; each balance can be connected to the top or the bottom by manipulating valves. The bottom of the U consists of a double valve (shown diagrammatically as two single valves in figure 14) and a mercury injector, so arranged that the amount of mercury in each leg can be controlled independently. The mercury surfaces at the top and bottom are located by means of level blocks that carry adjustable insulated needles, the distance between which is measured by means of an invar tape. The temperatures of the mercury and oil are controlled by means of a water jacket.

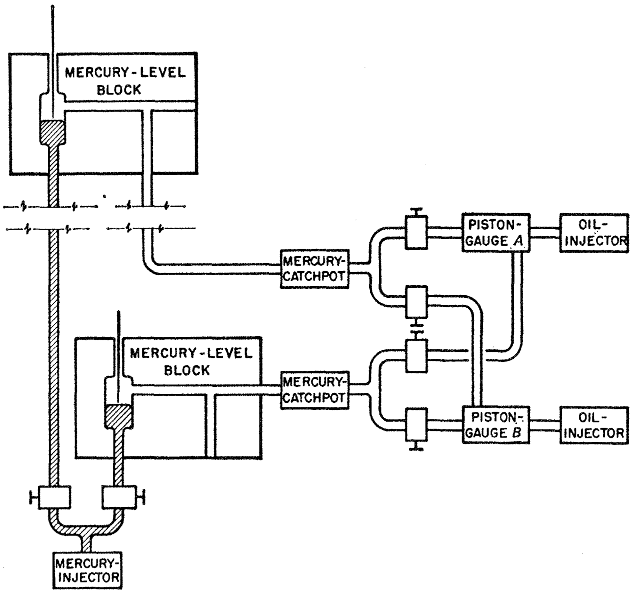

Figure 14. Block diagram of the mercury column.

There are two main methods of operating the column, the additive method and the differential method (see Bett *et al.* 1956 for details). In this work only the differential method has been used.

22. Tubing, fittings, and support of the column

The tubing used for transmitting oil pressure is $\frac{9}{16}$ in. outside diameter and $\frac{3}{16}$ in. inside diameter, and made of A.I.S.I. 4130 (low-alloy) steel. A fairly large size was chosen in order to reduce the time required for the pressures in the system to come to equilibrium and to make the smallest allowed rate of leak of oil conveniently high. The mercury-containing tubes are the same size but are composite, consisting of an outer tube of A.I.S.I.

Downloaded from rsta.royalsocietypublishing.org

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

4130 steel and an inner tube of type 304 stainless steel whose purpose was to resist embrittlement by mercury. Short lengths of the composite tube were tested to pressures of 8·5 kb without a burst occurring. The tubing was in lengths of about 18 ft. and joins were made by means of standard commercial cone-and-socket connectors made of type 304 stainless steel. The mercury-containing tube and connectors were passivated by treating with concentrated nitric acid to reduce contamination of the mercury.

The double valve in the mercury line was a standard commercial valve made of type 304 stainless steel. In order to avoid the change of volume that occurs when a valve whose stem advances through a packing is turned, and the disturbance of the equilibrium caused by this, all other valves were similar to those described by Whalley & Lavergne (1959) for pressures of 10 kb. The stem of the valve rotates in, but does not advance through, the packing, and the needle is advanced by means of a screw thread that is inside the high-pressure volume. The only change of volume when the valve is closed is due to the deformation of the seat and needle tip, and is small.

It is necessary that the vibration of the mercury surfaces be small. The water jacket was supported at its base on three legs that rested on a concrete block that was itself poured on bedrock. At intervals of about 12 ft. the jacket was fixed to one of the main supporting columns of the building by means of stout clamps. The pipe that was to contain the tape was very closely vertical, so that the tape would easily swing free of the walls. The three tubes that are contained in the water jacket were held loosely in spacers at about 17 ft. intervals. Each joint in the pressure tubing was carefully tested for leaks before it was covered by the water jacket.

23. The mercury-level blocks

The mercury-level blocks are made as shown in figures 15 and 16. The mercury meniscus is 2·5 cm in diameter to ensure that meniscus corrections are quite negligible. The mercury is in contact with only austenitic stainless steel in order to avoid the danger of mercury embrittlement. The blocks were made of low-alloy steel heat-treated to a hardness of 28 to 30 Rockwell C, and a stainless steel liner that was to contain the mercury was screwed into the bottom of the block. A good line-contact seal with the block was made initially and the plastic flow of the insert that occurred when pressure was applied did not cause a leak. In the upper block, outlet B carried the oil and A was plugged. In the lower block, outlet A carried the oil and B was plugged.

In order to avoid the tedium of adjusting, by altering weights on the balances, the mercury levels at both the top and the bottom to touch fixed needles, and the waiting for equilibration of pressures after every small alteration of weight, the needles should be made adjustable. They should, however, be adjustable without changing the volume of the system, otherwise it would be necessary to wait for equilibrium after each adjustment. This is accomplished as shown in figure 16. The needle 1 is carried by the hollow shaft 2 and insulated from it by the glass ring 3; the pressure seals between the needle, glass, and carrier, are formed by lapped surfaces in contact. The needle is in two parts which are screwed together near the glass ring; the surfaces between the two parts of the needle are ground so that the length of the needle was accurately reproducible after disassembling. The upper part of the needle is made of drill rod; it is insulated from the carrier by

Downloaded from rsta.royalsocietypublishing.org

a coating of lacquer. The lower part of the needle is made of an alloy containing 30% iridium and 70% platinum in order to avoid contamination of the mercury and to be strong enough to withstand the stresses at pressures of 3 kb. In order to ensure that the glass seal is always tight even when there is no internal pressure, a chuck 6 similar to a drill chuck is attached to the needle by friction. A spring bears upon the chuck and the needle carrier, and is insulated from the carrier by a Bakelite and a steel washer, and so keeps the glass seal under compression. The needle carrier has an acme thread on the outside, carefully made and smooth in order to reduce friction as much as possible, and it screws into the gland nut. The thread is kept tight by means of a heavy spring that bears on the top of the gland nut and on a small nut that is screwed onto the needle carrier; the small nut is kept in position by pins.

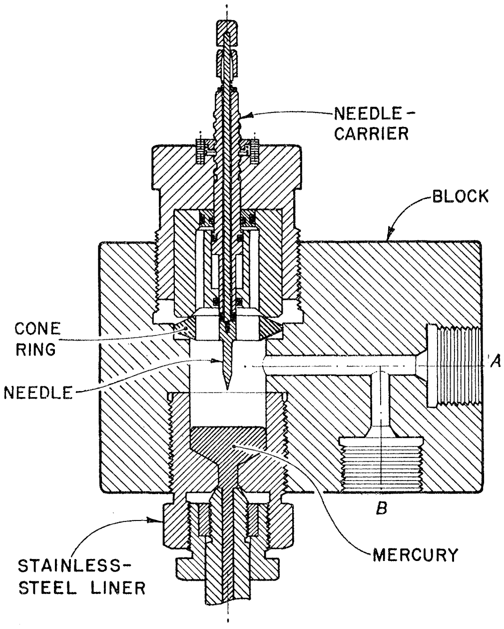

FIGURE 15. The mercury-level blocks.

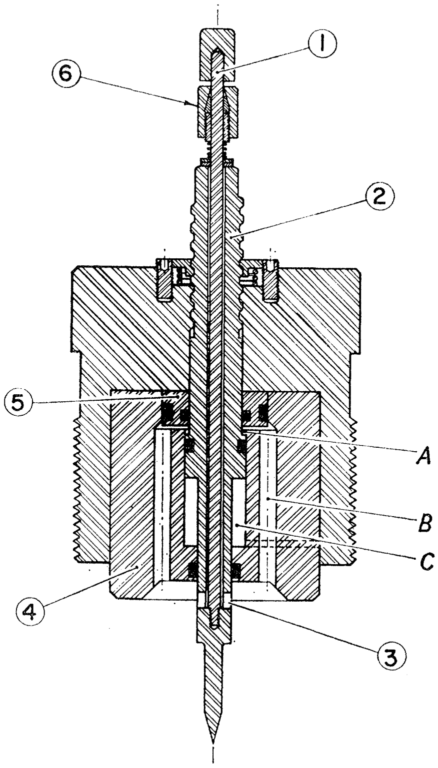

FIGURE 16. Detail of needle carrier.

The needle carrier slides inside the central hole of part 4. Two O-rings, one on the carrier and one on part 4, provide pressure seals. The space between these seals, labelled *C*, is connected by way of a radial hole in part 4 shown, rotated 45°, in dotted lines, and the screw threads, to the atmosphere. Another seal between part 4 and the needle carrier is provided by the collar 5 and its two O-rings. Part 4 contains four holes *B* drilled parallel to the axis whose function is to connect the oil in the block to the space *A*. When the needle carrier is screwed in, oil is displaced at the lower end. But at the same time the volume of space *A* increases by an amount that is made to be, by choosing properly the various diameters, exactly equal to the volume that is displaced by the lower end of the needle. Consequently, when the position of the needle is altered, oil neither enters nor leaves the block, and the system rapidly comes to equilibrium.

Downloaded from rsta.royalsocietypublishing.org

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

The components of the block were made so that when the block was assembled the needles were as close as practicable to being perpendicular to the top face of the block. The needles can be as much as 0·5° off vertical without causing appreciable error, and it was verified that when the upper surfaces of the blocks were made horizontal then the needles were vertical well within this limit.

24. Temperature control and measurement

The temperature was controlled by jacketing the column throughout its length by a 5 in. diameter pipe lagged with fibreglass. The arrangement at the top of the column was as shown in figure 17. The upper mercury-level block was almost completely submerged in the water, so its temperature was well controlled. Water was pumped from a 90-gallon tank controlled to ±0·005 degC through the jacket at the rate of about 16 gallons/min. The overflow from the top was returned to the tank by a pipe that was isolated from the column to avoid vibration. In order to avoid transmitting the vibration of the water-pump to the mercury a 30-gallon tank was interposed between the pump and the column and it was kept partly full of air.

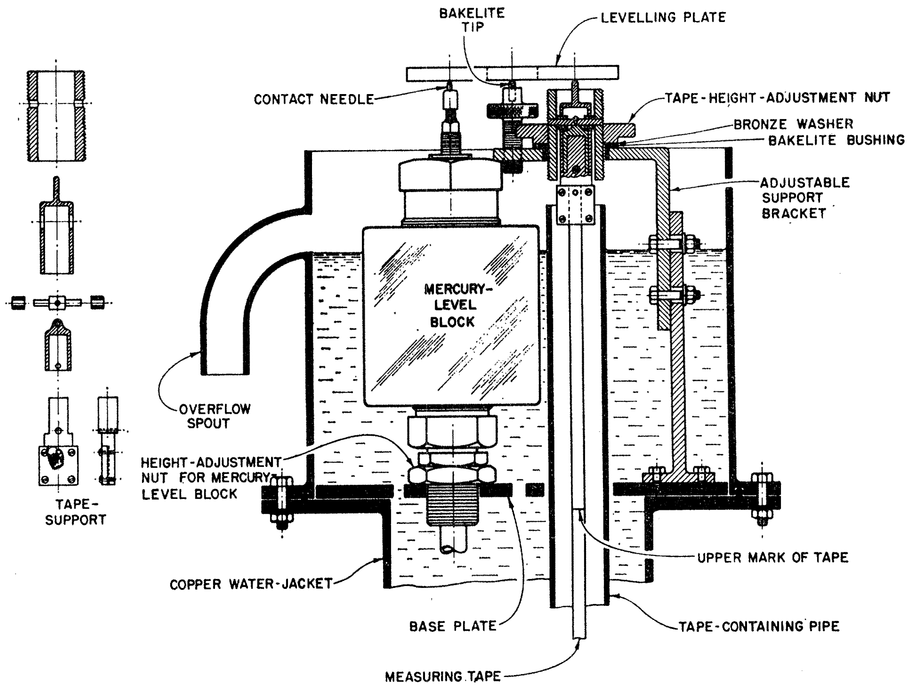

Figure 17. Details of the arrangement at the top of the column, including the tape suspension.

The temperature of the column was measured by two 25 Ω platinum resistance thermometers, one at the lower end in a well in the copper pipe, and one at the upper end. The temperatures at the top and bottom of the column are usually slightly different because the water expands approximately adiabatically from about 3 to 1 b and so cools, and because there is a small heat leak. The cooling due to adiabatic expansion is about 0·003 degC per column length. The total difference between top and bottom was rarely

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Downloaded from rsta.royalsocietypublishing.org

more than about 0·007 degC, and the mean was taken as the mean temperature of the column.

At the lower end of the column, part of the mercury, of length about 30 cm, is below the water jacket, and so also is the lower mercury-level block. The various injectors, catchpots, pressure balances, tubing, valves, etc., are also not thermostated by the column jacket. They were enclosed in a Lucite box controlled to ±0·1 degC, which was provided with appropriate doors and optically flat windows.

25. Measurement of the length of the column

The length of the column was measured by means of an invar tape, 0·25 in. wide × 0·020 in. thick. Two graduation marks were engraved on the tape about 55·2 ft. apart. Beyond the lower mark the tape was subdivided to 0·01 in. for a length of 2 in. The tape was suspended at the upper end of the column by means of a universal joint in the manner shown in figure 17. The tape support is shown in a partly exploded view which is largely self-explanatory. The tape and its suspension could be raised and lowered by turning the knurled adjustment nut. The support bracket was insulated electrically from the column by a Bakelite bushing so that contact between the tape and its pipe could be tested.

The tops of the tape suspension and the contact needle were made the same height using a levelling plate, an auxiliary adjustable point, and two levels.

The tape was stretched taut by means of a 10 kg weight whose motion was damped by vanes immersed in oil. To ensure that the tape and needle were as close as possible the weight was located beneath the lower mercury-level block by means of a universal joint and a stainless steel yoke. In order to compare the lower needle, which can be rotated, with the tape, a cylindrical cap with a fiducial mark was fitted over the end of the needle; and the fiducial mark and the tape were compared with a cathetometer.

26. Calculation of the pressure generated by the column

This can be conveniently divided into two parts, the head of mercury and the head of oil.

The length of the mercury column is obtained from the comparison of the tape and the needles, and the difference between the reference marks of the needles and the needle tips. The measurement of all of these is straightforward. Under pressure, the part of the needle that is immersed in the pressure-transmitting fluid changes in length because of its compression and because of distortion near the seal; it is easily shown that this is quite negligible. The mercury was purified as described in §8. The acceleration due to gravity was measured near both the bottom and the top of the column by Bancroft (1955) of the Dominion Observatory, Ottawa, relative to the value of the Reference Pier at the Dominion Observatory, which is 980·62200 cm/s^2 on the Potsdam System. The results are

near the bottom end 980·63175 cm/s^2,

near the top end 0·00385 ± 0·00002 cm/s^2 lower.

In order to calculate the pressure generated by the mercury the mean value 980·633 is used. The Potsdam System appears (Preston-Thomas, Turnbull, Green, Dauphinee

Downloaded from rsta.royalsocietypublishing.org

& Kalra 1960; see also Cook 1952) to be about 0·014 cm/s^2 too high, and so the most probable value of g near the bottom is 980·619 ± *ca.* 0·002 cm/s^2. The error of g is then a few parts per million and is an appreciable part of the error of the column when used as a single column. The density of mercury was taken to be that obtained by Cook & Stone (1957) and Cook (1961), who purified their mercury in a manner very similar to ourselves. Their value is 13·54589 g/cm^3 at 20 °C and 1 atm, with a claimed error of 1 or 2 p.p.m. The thermal expansion measured by Beattie *et al.* (1941) was used to convert this to the temperature of the experiment.

The compression of mercury was calculated as described in §13.

When the column is being used as a single column, and the top is open to the atmosphere, the difference in atmospheric pressure between the bottom and top of the column must be known. If the air is in equilibrium, this can be obtained from the formula

$$\frac{\delta p_{\text{air}}}{\delta p_{\text{Hg}}} = \frac{\rho_{\text{air}}}{\rho_{\text{Hg}}},$$

where p_{air} and p_{Hg} are the pressures in the air and mercury, δ indicates the difference between the top and bottom of the column, and ρ_{air} and ρ_{Hg} are the densities of air and mercury. At 25 °C this is 88 p.p.m. Consequently, since the reproducibility of the column when it is used as an open column is 5 or 10 p.p.m., δp_{air} should be known if possible to to 2 or 3%. For much of the year this is not easy because there is frequently in the winter a temperature difference of 40 °C between the outside and the inside of the building, and this causes quite strong draughts in the building. In order to eliminate the effects of these draughts, the upper mercury surface is connected to the atmosphere at the lower end of the column by means of the oil pipe. The difference in pressure is then easily calculated accurately. In order to avoid fouling of the mercury surface, the oil pipe is filled with carbon dioxide which is allowed to flow continually through the tube from the top. When the column is being used in a differential manner, the head of air does not of course affect the measurements.

When the column is used as a single column, the only oil head is that between the lower mercury surface and the base of the piston, and it is quite small. When the column is being used differentially there is also an oil head between the upper mercury surface and the base of the piston, and this is quite large.

The pressure-transmitting liquid was liquid paraffin with 0·5% of Kontol 77 added to inhibit corrosion of the steel. Its density was measured, and the compressions reported by Bett *et al.* (1954) were assumed to apply to our sample. No error significant for the present purposes, which is to calibrate the pressure balances more accurately than the accuracy of the compression measurements, i.e. to 100 p.p.m., should be introduced by this procedure.

The weights and weight support were calibrated by the Standards Division of the Department of Trade and Commerce, and the weight *in vacuo* was determined with an accuracy of about 1 p.p.m. The buoyancy of the air was allowed for with an error less than 1 p.p.m. by assuming a constant relative humidity of 50%, and measuring the pressure and temperature of the air. The buoyancy of the oil on the piston, and the surface tension of the oil were allowed for.

Downloaded from rsta.royalsocietypublishing.org

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

27. The pressure balances

Pressure balances may be divided into two main types according to whether the piston and cylinder is simple or differential. Both have been used in precision instruments and there appears to be no choice between them on the grounds of accuracy. The main advantage of the differential balance appears to be that it is possible to reach high pressures with a very robust piston that has only a small differential area, whereas a simple balance requires either very heavy weights or a small and relatively fragile piston. On the other hand, the differential balance is much more difficult to make because the larger diameter necessitates a smaller clearance between the piston and cylinder to avoid an excessive leak of oil, and because it is very difficult to make the pistons and cylinders coaxial. Furthermore, differential pistons and cylinders apparently (Michels 1923) must be rotated at more than about 30 to 40 rev/min in order to prevent contact between the piston and cylinder. For a well cleaned simple piston and cylinder, less than 1 rev/min is needed to prevent contact. Consequently, we have preferred the simple piston and cylinder.

There have been discussions from time to time about whether a piston should be rotated or oscillated in order to prevent it from sticking to the cylinder. Both oscillating and rotating gauges appear to have been made equally precise, at least up to pressures of a few hundred bars, and there is no experimental evidence that either is more accurate than the other. Because oscillating pistons touch the cylinder at the end of every stroke (Keyes & Dewey 1927), an observation which we have confirmed, and because the force required to oscillate the piston is much greater than that required to rotate it at about 1 or 2 rev/min., and will disturb it more, we have used simple pistons and cylinders.

Relative motion of piston and cylinder can be obtained by rotating both piston and weights, as is most commonly done, by rotating the piston only (Johnson & Newhall 1953), or by rotating the cylinder only. We have preferred to rotate both weights and piston in order to disturb the piston as little as possible. The balance is of the overhanging pattern.

The weight carrier is driven by means of a piece of light horizontal thread looped around it and around a wheel driven by a motor and a speed reducer. The motor was carefully balanced on a ball-bearing support so that it swung freely without a preferred position. Tension was applied to the driving thread by means of a 2 g weight attached to the motor by a light thread which was looped over a pulley wheel. The driving thread was supported close to the weight carrier in order to reduce the weight of thread on the carrier; it contributes 0·04 g to the weight on the balance. The effect of the tension in the thread is to slightly increase the precession of the piston in the cylinder, but tests with the mercury column have shown no effect of the tension on the effective area to well within the required accuracy.

The pistons and cylinders were made from Jessop's Superior oil-hardening tool-steel heat treated to 60 to 64 Rockwell C, and stabilized.

It is important that the pistons and cylinders be well polished to remove spiral grooves. Any roughness on the surface will tend to make the gauge constant and its pressure coefficients depend on the viscosity (see §28), and scratches can collect grinding and lapping grit which may become dislodged during use, and scratch the piston and cylinder

Downloaded from rsta.royalsocietypublishing.org

MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES
PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A

and may cause them to gall. The usual lapping and polishing operations for cylindrical surfaces are not satisfactory because the work is turned always in the same direction. Pieces of grit may then dig into the surface and cause long scratches because they are always pushed in the same general direction. Mr A. Lavergne has devised a method of polishing cylindrical surfaces in which the polishing tool moves over the work in a 'figure-of-eight' motion similar to that used in polishing flat surfaces. The work is rotated alternately one way and the other, while the polishing tool is oscillated over the surface at a frequency that is not simply related to the frequency of rotation. In this way a mirror finish similar to that required for the metallurgical examination of flat specimens is easily obtained. The final polishing was usually done with 1 μm sapphire polishing paste. When the pistons and cylinders are polished in this way there is no difficulty in rotating the pistons at 1 rev/min without electrical contact with the cylinder.

It is most important that the cylinder be held in its block so that it does not distort significantly under the applied pressure. The most promising way to do this appears to be to use an O-ring seal, and to hold the cylinder by means of an integral collar well removed from the working part of the cylinder, as illustrated in figure 18.

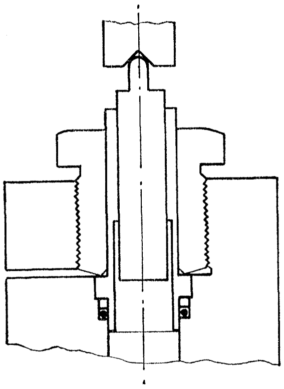

FIGURE 18. Method of holding the cylinder in the pressure balance.

The pistons and cylinders were made in the Mechanical Engineering Workshops of the National Research Council. They were specified to be circular and parallel to 10 μin. and to have a surface finish of 2 μin. (r.m.s.). The uniformity of the bore of the cylinder was routinely tested during manufacture by means of an air-gauge developed by Mr E. Green of the Division of Applied Physics. A final check was performed by measurement of the diameter at various positions along the bore to an accuracy of about 10 μin. These measurements were kindly performed by Mr Green and his associates. For routinely checking the clearance between the piston and cylinder when the piston was made, the speed of rotation of the piston under a given torque generated by means of weights, thread, and pulleys, was measured, and also the rate of fall under a given load. Since the rate of fall is inversely proportional to $\overline{c^{-3}}$, where c is the clearance between the piston and cylinder, and the rate of rotation under a given torque is inversely proportional to $\overline{c^{-1}}$, agreement between $(\overline{c^{-3}})^{-\frac{1}{3}}$ and $(\overline{c^{-1}})^{-1}$ is a check on the constancy of c.

Oil that leaks from the piston and cylinder tends to collect on the top of the cylinder and so form a metastable meniscus. This is undesirable because the oil exerts a buoyancy

Downloaded from rsta.royalsocietypublishing.org

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

on the piston, and for the most accurate work the depth of immersion of the piston should be known to 0·02 cm. In order to enable the oil to flow quickly from the top of the cylinder a leaf spring was arranged to touch the outer edge of the cylinder obliquely; this effectively removed the trouble.

28. THEORY OF PRESSURE BALANCES

The pressure coefficient of the effective area of some pressure balances has been reported (Dadson 1958) to depend on the pressure-transmitting fluid. It would be preferable if the balances could be designed so that the effective area is independent of the fluid. In this section the theory of pressure balances is reexamined mainly to determine the conditions required for this independence.

One way in which the fluid can determine the gauge constant is by the heating effect of the energy dissipated in the fluid during the rotation. The higher this is, the hotter the piston and cylinder relative to the ambient temperature. The temperature coefficient of the area of a balance is about 22×10^{-6} degC^{-1}, so a relatively small heating could influence the gauge constant; and because the viscosity of the fluid normally increases with increasing pressure, the heating effect will normally increase with increasing pressure. There is no experimental evidence as to the importance of this effect. However, we have preferred to minimize it by rotating the pistons as slowly as practicable, and rates of 1 or 2 rev/min have usually been used. Two other ways in which the pressure coefficient of the gauge constant can be a function of the medium can be seen by examining the theory of the pressure balance. We shall assume that the piston and cylinder are concentric. In fact, they usually are not concentric because the concentric position is metastable (Michels 1923), and the piston precesses in the cylinder. We shall assume that the effect of this is of higher order than the effects we are considering The piston and cylinder are cylindrically symmetrical. Let a be the radius of the piston, b be that of the cylinder, and c be the width of the annulus, so that

$$c = b-a,$$

all at distance x from the bottom of the cylinder. Let u be the velocity of the fluid in the annulus at radius r distance x from the bottom of the cylinder. It is assumed that the variation of c with x is small enough that the velocity of the fluid at any point can be put equal to what it would be if the fluid were flowing between a long piston and cylinder that have a uniform annulus c. Furthermore, c is assumed to be small enough that the velocity in the annulus is the same as it would be if the radius b were very large. For any well-constructed balance c is usually less than about $10^{-3}a$, and the variation of c with x is very small, so these approximations are probably satisfactory. The usual hydrodynamic theory then yields for the effective area A_e

$$A_e = \pi a_1^2+\frac{\pi}{p_1-p_a}\int_{p_a}^{p_1} ac\,\mathrm{d}p+\frac{2\pi}{p_1}\int_{x=0}^{x=l} ap\,\mathrm{d}a, \tag{37}$$

where a_1 is the area of the piston at the lower end, and the surface tension force has been omitted for present purposes. If a and c are uniform at zero pressure gradient, and both are changed by pressure in proportion to the total pressure in the annulus, thus

$$a = a_0(1-\beta p+\gamma p_1),$$
$$c = c_0+a_0(\delta p-\epsilon p_1),$$

Downloaded from rsta.royalsocietypublishing.org

where a_0 and c_0 are the constant zero-pressure values of a and c, then equation (37) becomes

$$A_e = \pi(a_0^2+a_0c_0)+\pi a_0^2p_1(2\gamma-\beta+\tfrac{1}{2}\delta-\epsilon), \tag{38}$$

which is independent of the viscosity of the fluid.

Hence, the gauge constant will be independent of the fluid if the usual hydrodynamic assumptions are valid and if both the pistons and cylinders are uniform in diameter at low pressures and smooth enough that the usual boundary conditions hold. Departures from these conditions will introduce a fluid-dependent term into the equation for the effective area. An attempt was made to ensure that these conditions were fulfilled as far as practicable (see §27).

We are greatly indebted to Mr A. Lavergne for invaluable help in setting up and maintaining the high-pressure equipment and the mercury column, to Dr F. M. Kavcic for calibrating the pressure balances, and to Mr G. E. McLaurin for help with the measurements of the thermal expansion and the calculations.

REFERENCES

Amagat, E.-H. 1893 *Ann. Chim.* **29**, 543.
Antonoff, G. 1944 *J. Phys. Chem.* **48**, 80.
Antonoff, G. & Conan, R. J. 1949 *Science*, **109**, 255.
Bancroft, A. M. 1955 Private communication dated 21 September.
Beattie, J. A., Blaisdell, B. E., Kaye, J., Gerry, H. T. & Johnson, C. A. 1941 *Proc. Amer. Acad. Arts Sci.* **74**, 371.
Beattie, J. A. & Edel, W. L. 1931 *Ann. Phys., Lpz.*, **11**, 41.
Bett, K. E., Hayes, P. F. & Newitt, D. M. 1956 *Phil. Trans.* A, **247**, 59.
Bett, K. E. & Newitt, D. M. 1963 *The physics and chemistry of high pressures*, p. 99. London: Society of Chemical Industry.
Bett, K. E., Weale, K. E. & Newitt, D. M. 1954 *Brit. J. Appl. Phys.* **5**, 243.
Bridgeman, O. C. 1927 *J. Amer. Chem. Soc.* **49**, 1174.
Bridgman, P. W. 1911 *Proc. Amer. Acad. Arts Sci.* **47**, 347.
Bridgman, P. W. 1940 *Proc. Amer. Acad. Arts Sci.* **74**, 11.
Bridgman, P. W. 1958 *The physics of high pressure.* London: G. Bell and Sons, Ltd.
Chappuis, P. 1907 *Trav. Bur. int. Poids Més.* **13**, D1.
Christiansen, W. N., Crabtree, R. W. & Laby, T. H. 1935 *Nature, Lond.*, **125**, 870.
Cohen, E. R., Crowe, K. M. & Dumond, J. W. M. 1957 *Fundamental constants of physics.* New York: Interscience Publishers, Inc.
Cook, A. H. 1952 *Proc. Roy. Soc.* A, **213**, 408.
Cook, A. H. 1956 *Brit. J. Appl. Phys.* **7**, 285.
Cook, A. H. 1961 *Phil. Trans.* A, **254**, 125.
Cook, A. H. & Stone, N. W. B. 1957 *Phil. Trans.* A, **250**, 35.
Dadson, R. S. 1958 *Proceedings of conference on thermodynamic and transport properties of fluids*, p. 37. London: Inst. of Mech. Engineers.
Diaz Peña, M. & McGlashan, M. L. 1959 *Trans. Faraday Soc.* **55**, 2018.
Garofalo, F., Malenock, P. R. & Smith, G. V. 1952 *Tech. Publ. Amer. Soc. Test. Mater.* no. 129, p. 10.
Greenspan, M. & Tschiegg, C. E. 1957 *Bur. Stand. J. Res., Wash.* **59**, 249.
Holborn, L. & Schultze, H. 1915 *Ann. Phys., Lpz.*, **47**, 1089.
Holser, W. T. & Kennedy, G. C. 1958 *Amer. J. Sci.* **256**, 744.

Downloaded from rsta.royalsocietypublishing.org

Hubbard, J. C. & Loomis, A. L. 1928 *Phil. Mag.* **5**, 1177.

Johnson, D. P., Cross, J. L., Hill, J. D. & Bowman, H. A. 1957 *Ind. Eng. Chem.* **49**, 2046.

Johnson, D. P. & Newhall, D. M. 1953 *High pressure measurement*, p. 4. New York: Amer. Soc. Mech. Eng.

Jůza, J., Kmoníček, V. & Šifner, O. 1961 *Acta Tech.* (*Czech.*), **6**, 553.

Kennedy, G. C., Knight, W. L. & Holser, W. T. 1958 *Amer. J. Sci.* **256**, 590.

Keyes, F. G. & Dewey, J. 1927 *J. Opt. Soc. Amer.* **14**, 491.

Keyes, F. G. 1933 *Proc. Amer. Acad. Arts Sci.* **68**, 505.

Keyes, F. G. & Keenan, J. H. 1955 *Mech. Eng.* **77**, 127.

Keyes, F. G., Smith, L. B. & Gerry, H. T. 1935 *Proc. Amer. Acad. Arts Sci.* **70**, 319.

Kleppa, O. J. 1949 *J. Chem. Phys.* **17**, 668.

Kretschmer, C. B. 1951 *J. Phys. Colloid Chem.* **55**, 1351.

Meyers, C. H. & Jessup, R. S. 1931 *Bur. Stand. J. Res., Wash.*, **6**, 1061.

Michels, A. 1923 *Ann. Phys. Lpz.*, **72**, 285.

Michels, A., Wassenaar, T., Zweitering, Th. & Smits, P. 1950 *Physica*, **16**, 501.

Osborne, N. S., Stimson, H. F. & Ginnings, D. C. 1939 *Bur. Stand. J. Res., Wash.*, **23**, 261.

Owen, B. B., White, J. R. & Smith, J. S. 1956 *J. Amer. Chem. Soc.* **78**, 3561.

Pérard, A. 1950 *P.-v. Bur. int. Poids Més.* **22**, 94.

Preston-Thomas, H., Turnbull, L. G., Green, E., Dauphinee, T. M. & Kalra, S. N. 1960 *Canad. J. Phys.* **38**, 824.

Roebuck, J. R. & Cramm, W. 1947 *Rev. Sci. Instrum.* **18**, 215.

Smith, L. B. & Keyes, F. G. 1934 *Proc. Amer. Acad. Arts Sci.* **69**, 285.

Steckel, F. & Szapiro, S. 1963 *Trans. Faraday Soc.* **59**, 331.

Stimson, H. F. 1955 *Amer. J. Phys.* **23**, 614.

Thiessen, M. 1904 *Wiss. Abh. phys.-tech. Reichsanst.* **4**, 1.

Tilton, L. W. & Taylor, J. K. 1937 *Bur. Stand. J. Res., Wash.*, **18**, 205.

Vukalovich, M. P., Zubarev, V. N., Aleksandrov, A. A. & Kalinin, Yu. Ya. 1959 *Teploenergetika*, **6**, no. 10, 74.

Vukalovich, M. P., Zubarev, V. N., Kalinin, Yu. Ya. & Aleksandrov, A. A. 1961 *Teploenergetika*, **8**, no. 4, 76. (In this the data of Vukalovich *et al.* (1959) have been adjusted for small departures from the nominal temperature.)

Whalley, E. & Lavergne, A. 1959 *J. Sci. Instrum.* **36**, 46.

Wilson, W. D. 1961 *J. Acoust. Soc. Amer.* **33**, 314.