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Precise Measurements of the Density of Mercury at 20 degrees C. I. Absolute Displacement Method

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PRECISE MEASUREMENTS OF THE DENSITY OF MERCURY AT 20° C

I. ABSOLUTE DISPLACEMENT METHOD

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[Plates 2 and 3]

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This paper gives an account of the absolute measurement of the density of mercury at 20° C in units of length and mass, the result of which is probably correct to one part in a million. The densities of four samples of mercury have been measured by finding the mass of mercury displaced by an accurately formed cube of known volume that just sinks in mercury.

The cube is of tungsten carbide sintered with cobalt, its sides are 8·9 cm long, it weighs 9·7 kg in air and 217 g in mercury at 20° C. It was lapped with diamond dust to such an accurate form and good surface finish that the standard deviation of the volume of mercury displaced, as calculated from optical interference measurements of the dimensions of the cube, is 0·15 p.p.m. (part per million). The determined mass of the cube has a standard deviation of 0·1 p.p.m. and the measured weight of the cube in any one sample of mercury at 20° C has a standard deviation of 0·28 p.p.m.

The uncertainty in the density of any one sample of mercury is however greater, for two reasons, than the value of 0·3 p.p.m. that these figures indicate. First, all measurements of the temperature of the mercury are subject to a constant error which may reach 0·001° C, equivalent to 0·2 p.p.m. of the density of mercury. Secondly, and more important, the effective volume of the cube may be greater than the measured volume through layers of grease adhering to it despite very careful cleaning and the corresponding error probably varied from one group of weighings to another; it is difficult to estimate but is thought to be between 0·2 and 1 p.p.m.

The mean density at 20° C and 1 atm pressure of four samples of mercury from different sources is

$$13{\cdot}545\,892\ \mathrm{g/cm^3},$$

the range of the four values being 1·1 p.p.m.

The corresponding value at 0° C, calculated from the thermal expansion formula of Beattie, Blaisdell, Kaye, Gerry & Johnson (1941) is

$$13{\cdot}595\,086\ \mathrm{g/cm^3}.$$

The chemical and isotopic compositions of the samples cannot be specified with an accuracy corresponding to that of the measurements, but evidence is given indicating that our results should represent the density of pure mercury of average isotopic constitution to between 1 and 2 p.p.m.

Complementary measurements are now being prepared in which the mass of mercury that fills a box of fused silica is to be found.

1. Introduction

(*a*) *Reasons for the measurements*

Since the triple point of water (0·0100° C) can now be realized with an accuracy of the order of 0·0001° C and the resistance of a platinum resistance thermometer can be measured with corresponding accuracy or better, the International Temperature Scale could be reproduced to 0·0001° C between 0 and 100° C (an aim which is for more than one reason desirable) provided that the 100° C point, namely that temperature at which water boils under a pressure of one standard atmosphere, could be also realized to 0·0001° C. A change of 0·0001° C in the boiling point at atmospheric pressure corresponds to a change of 3·5 μb (microbar) in the pressure, and it is therefore desirable to measure the pressure to about 1 μb or one part in a million. The most accurate instrument for measuring a pressure of about 1 atm is the mercury barometer, and while there exist barometers in which the height of the mercury column can be measured to 2 p.p.m. (parts per million) or better, the uncertainty in comparing the results of different barometers (and therefore in comparing the reproduction of the International Temperature Scale at different places) is much greater, principally because of uncertainty in the density of mercury; the scatter of the existing measurements of the density of mercury is 10 p.p.m. so that it has hitherto been considered possible that the densities of any two samples of mercury might differ by this order. It was therefore decided to undertake a new determination of the density of mercury.

The existing values of the density of mercury were all derived from comparisons with the density of water and there are four reasons why the new measurements should be absolute. First, the 100° C point is defined to be the temperature at which water boils under a pressure specified in the absolute unit of dynes per square centimetre, and it should be possible to measure pressures in this unit independently of an insufficiently precise value of the density of water. Secondly, it is no doubt possible to correlate the indications of different barometers through intercomparisons by relative methods of the densities of the samples of mercury in them, but so far, these methods are not precise enough and should in any case be checked by absolute measurements of the highest precision. Thirdly, it is only by absolute measurements that one can be sure that pressure measurements made at long intervals of time are comparable. Lastly, as has become evident in the course of the present determinations, an absolute determination of the density of mercury may be capable of higher accuracy than a determination by comparison with the density of water, apart altogether from whatever uncertainty there may be in the value of the density of water at 4° C (at present 1 or 2 p.p.m.) The density of mercury is also required in absolute units when comparing the pressure exerted by a mercury column with that exerted by a free piston pressure balance (see Bett, Hayes & Newitt 1954), although at present the uncertainty of the density of mercury is not the limiting factor in these comparisons. Accordingly, it was decided that in the new measurements of the density of mercury the volume should be found directly from length measurements and not by comparison with water.

In the determination described in this paper a cube, slightly denser than mercury, was weighed in air and mercury and its volume was calculated from interferometric measurements of the distances between opposite faces. A second determination is being prepared in which the mass of mercury filling a transparent hollow cube will be found, the volume of this cube also being calculated from interferometric measurements of its dimensions.

(*b*) *Review of previous measurements*

The density of mercury has been found both by weighing a quantity of mercury in air and in water and by weighing a pycnometer filled first with water and then with mercury. Marek (1883), who measured the density of five samples of mercury, used both methods. His figures for the density at 0° C, corrected for the difference between the value for the specific volume of water at 0° C that he used (1·0001172) and the values at present accepted (1·0001324) (Scheel & Blankenstein 1925; Tilton & Taylor 1937) are the following:

method	hydrostatic weighing	pycnometer
sample A	13·595424 g/ml.	—
B	426	—
C	251	—
C′	723	—
D	318	13·595472 g/ml.
E	—	441

Marek was concerned to measure the relative density of the mercury in his barometers and did not set out to measure that of pure mercury. The various samples were therefore prepared in different ways, and it is possible that the effects of impurities amounted to several parts in a million (see § 5). Sample C was presumably contaminated since it

[redacted]

Results obtained by Thiesen & Scheel (1898), 13·595 45 g/ml., and Guye & Batuecas (1923), 13·595 47 g/ml., have been rejected by Henning & Jaeger (1926) because the experiments were not completed.

Batuecas & Casado (1945) have stated that there is an error in the result of Guye & Batuecas, due to the neglect of the difference between the volumes of the menisci of water and mercury in the capillary tube of the pycnometer, and they have corrected the value to 13·595 52 g/ml.; the range of four determinations was about 10 p.p.m.

Scheel & Blankenstein (1925) used the method of hydrostatic weighing to determine the densities of two samples of mercury, E and III, at the Physikalisch-Technische Reichsanstalt. The results differed by 13 p.p.m., but subsequent relative measurements by Jaeger & Steinwehr (1926) showed that the densities agreed to within about 3 or 4 p.p.m. The mean of Scheel & Blankenstein's values is 13·595 49 g/ml. The weighings in water were carried out at about 22 and 30° C and the results reduced to 0° C using expansion formulae for mercury and water that differ appreciably from the present accepted formulae. If the formulae of Tilton & Taylor (1937) is used for water and that of Beattie, Blaisdell, Kaye, Gerry & Johnson (1941) for mercury, Scheel & Blankenstein's results become:

for E	13·595 27 g/ml.
for III	13·595 44
mean	13·595 36 g/ml., 10 p.p.m. less than the published value.

However, this recomputation may not be justified: there is some indication that the expansion formulae used by Scheel & Blankenstein differ from the later formulae because of a difference in the temperature scales. If Scheel & Blankenstein measured their temperatures on the same scale as those on which the expansion formulae they used were determined, then their values of density at 0° C should not be altered.

Two very careful pycnometer determinations have been made by Batuecas & Casado (1936) and Batuecas & Fernandez Alonso (1948). These are superior to previous results in that the mercury was carefully purified and that the pycnometer was filled under vacuum at 0° C. The only auxiliary constant required to obtain the density in grams per millilitre is therefore the density of water at 0° C, and this appears to be well determined (Tilton & Taylor 1937).

The original values of Batuecas & Casado (1936) are affected by the meniscus error mentioned before and have been corrected by Batuecas & Casado (1945); the corrected values, and those of Batuecas & Alonso are the following:

mercury sample	Batuecas & Casado (1936, 1945)	Batuecas & Alonso (1948)
5	13·595 60 g/ml.	13·595 62 g/ml.
6	56	50
8	53	55

The differences between samples are within the scatter of the observations.

The greatest uncertainty of these measurements appears to be that of the volume of the pycnometer as found from the weight of water contained in it; for instance, the range of seven determinations of this weight by Batuecas & Alonso is 30 p.p.m., whereas the range of six determinations of the weight of mercury of sample 8 is 9 p.p.m.

The results of all the above measurements are collected in table 1.

To summarize, it seems that the results of Batuecas & Casado and Batuecas & Alonso are less liable to systematic errors than those of other observers, but that they are equally subject to relatively large random errors and it is not necessary to suppose, as has sometimes been suggested, that the variability of the published values might be due to variable isotopic constitution, for the whole range could be accounted for by chemical impurities (Marek) or by possible systematic errors such as the uncertainty of Scheel & Blankenstein's reduction from 22 and 30 to 0° C, as well as by the internal scatter of the various determinations. The results of Batuecas and his collaborators show no difference between different fractions distilled from the same source and although Brönsted & Hevesy (1920) effected some separation of isotopes by distillation, the difference of density was only a few parts in a million and was attained only after prolonged fractional distillation at very low pressure. Brönsted & Hevesy (1922) have also shown that the densities of samples from different sources do not differ by more than a few parts in a million.

TABLE 1. MEASUREMENTS OF THE DENSITY OF MERCURY AT 0° C

author	corrected density		uncertainty
	(g/ml.)	($\mathrm{g/cm^3}$)	(p.p.m.)
Marek	13.59546	13·59508	>10
Thiesen & Scheel	13·59545	13·59507	—
Guye & Batuecas	13·59552	13·59514	~10
Scheel & Blankenstein (*a*)	13·59549	13·59511	>10
(*b*)	13·59536	13·59498	>10
Batuecas & Casado	13·59556	13·59518	< 5
Batuecas & Alonso	13·59556	13·59518	< 5
mean	13·59549	13·59511	

(*c*) *Outline of the displacement method*

This paper describes the measurement of the density of mercury by weighing in it a body of known mass and volume. The method has been used in the most accurate measurements of the density of water (Chappuis 1910; de Lépinay, Buisson & Benoît 1910), but has not previously been applied to mercury, probably because a suitable material for the heavy body has not been available. The main potential source of error is the surface tension force on the wire which supports the body from the balance; because the surface tension of mercury is large and the angle of contact variable, it is essential that the wire should be very fine so that the force and its possible variations may correspond to no more than small errors in the density. The heavy body should, therefore, be only slightly more dense than mercury so that its weight in mercury is small. Tungsten carbide sintered with cobalt is a most suitable material because the proportion of cobalt can be chosen to bring the density close to that of mercury, and although the body used in these experiments has a mass of 9723 g, it weighs only about 217 g in mercury and could be supported in mercury by a tungsten wire 0·05 mm in diameter on which the maximum possible range of surface tension forces is from +7 to −7 dyn or about 1·5 p.p.m. of the upthrust of the mercury. The material can be ground and lapped to give flat smooth faces intersecting in sharp edges with few imperfections, and the body was therefore made in the form of the cube, the sides of which are 8·9 cm long. An important advantage of a cube is that its dimensions can be measured accurately by optical interference methods. The volume was measured in three stages: the average roughness of the surface was measured, the forms of the faces, which are slightly concave, were found by interferometric comparison with the plane surface of a liquid, and the lengths of the edges were measured by an adaptation of a standard optical interference method of measuring end-gauges. In addition, the angles between face normals were measured.

The determination of the mass of mercury displaced by the cube involves weighing the cube in air to find its mass (which is straightforward) and weighing it in mercury. An ordinary knife-edge balance was used for the weighings in mercury, but the sensitivity had to be reduced so that the balance was not overdamped when the cube was immersed in mercury. The cube had to be cleaned very carefully to remove all grease and the mercury was poured round it at a pressure of about 2 μb lest bubbles of air should adhere to it. The cube was either suspended in a cage denser than mercury to which a suspension wire was attached, or else the optical flat face of a small chromium plated disk of heavy tungsten alloy was brought into wringing contact with the upper face of the cube, a suspension wire being attached to a small hook let into the top of the disk.

The change in the angle of contact of the mercury against the tungsten suspension wire as the wire moved up and down with the oscillations of the balance, was measured in a separate experiment. The control and measurement of the temperature of the mercury is important because the coefficient of cubic expansion of mercury is $1{\cdot}8\times10^{-4}/^\circ$ C, and the experiment was therefore done in a room with the temperature controlled to about $\pm0{\cdot}1^\circ$ C and the mercury vessel was heavily lagged. Thermocouples were used to compare the mercury temperature with that of two platinum resistance thermometers calibrated on the International Temperature Scale (1948).

Since a few parts in ten million by weight of some impurities can alter the density of mercury by more than 1 p.p.m., the mercury samples had to be purified very carefully and all equipment which came in contact with mercury was kept scrupulously clean. Samples of the mercury were submitted to chemical and isotopic analysis and although unfortunately, the sensitivity of methods available for most elements does not correspond to 1 p.p.m. of the density, Dr F. M. Reynolds of the Chemical Research Laboratory has shown, subsequently, that the methods of purification we employed were very efficient.

It may be helpful for the reader to bear in mind the errors to which the various parts of the operation are subject, and the following figures are therefore taken from the subsequent sections of the paper.

Standard deviation of the measurements entailed in measuring the density of mercury, expressed as fractions of the density

(1) *Volume of the cube of tungsten carbide*

surface finish	3×10^{-8}
form of faces	$1{\cdot}0\times10^{-7}$
lengths of edges	$1{\cdot}1\times10^{-7}$
corrections for material missing from edges and corners, scratches and other imperfections less than	1×10^{-8}
overall standard deviation of volume	$1{\cdot}6\times10^{-7}$

(2) *Upthrust of the mercury*

mass of cube	1×10^{-7}
weight of cube in mercury at 20° C (includes random errors of temperature)	$1\cdot5 \times 10^{-7}$
surface tension force on wire	1×10^{-7}
systematic error in temperature up to	2×10^{-7}
overall standard deviation of density of a given sample of mercury	$2\cdot8 \times 10^{-7}$

Uncertainty due to possible impurities in a sample may be of the order of 1 p.p.m.

Finally, it should be stated that the density is found in grams per cubic centimetre at 20° C on the International Temperature Scale (1948); that the standard of length is the wavelength of the green line of the mercury-198 spectrum referred to the present spectroscopic reference standard, the wavelength 0·643 846 96 μ of the red line of cadmium in standard air; that the standard of mass is the International Prototype Kilogram through the British copy; and that the equivalent density at 0° C is calculated using the expansion formula of Beattie *et al.* (1941).

2. Description of the cube of tungsten carbide

The cube is made of tungsten carbide mixed with 15 % by weight of cobalt and was formed by sintering in a carbon mould. The tungsten carbide particles are mostly between 0 and 5 μ in size with a few up to 10 μ.† As supplied to the National Physical Laboratory by the makers (Messrs Protolite Ltd.) it was ground all over and the faces were flat and square or parallel to each other to well within 0·03 mm. The cube was lapped to its final form in the Metrology Division workshop. Two cast-iron lapping plates were used, each chequered by shallow vee grooves at right angles with a spacing of 2·5 mm. Two grades of diamond dust were used, the slightly coarser, of 0·5 to 3 μ size at first and the finer of 0 to 2 μ size to finish with. The dust was distributed in paraffin oil. Lapping was continued until all grinding marks had been removed and the faces were of good figure and square or parallel to each other. The figure was tested by comparison with a glass optical flat and mechanical tests were used for parallelism and squareness.

Only a limited study of the surface of the cube itself was possible, largely because the size and weight of the cube precluded its being placed in the necessary apparatus, and accordingly small specimens of similar material were prepared with surfaces lapped to a similar finish, and these surfaces were examined in detail. The results obtained were of great use in interpreting the restricted examination of the cube.

The surface of one of the small specimens was photographed by Dr J. W. Menter (at that time at the Department of Physical Chemistry, Cambridge University) in his reflexion electron microscope with oblique illumination and viewing (Menter 1952). Features of three types were distinguished in the photographs, namely, a few isolated holes, numerous shallow scratches and a general undulation of the surface. The dimensions of the holes as measured in the plane of the surface are of the same order as those of the tungsten carbide particles, that is, up to 8 μ. The width of the shallow scratches, which are probably

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† Information supplied by the makers.

lapping marks, is less than 1 μ and the depth, estimated from the shadow geometry, appears to be of the order of 40 nm.† The general undulation has a period of about 2 μ; the depth is more difficult to estimate but seems to be about the same as that of the shallow scratches.

Surfaces of the small specimens have also been examined in the Metallurgy Division of the National Physical Laboratory. A lapped surface on which a layer of silver about 0·3 μ thick had been evaporated, when examined both with a phase-contrast microscope and with a Linnik-type interference microscope (Kinder 1937), showed variations of the phase of the reflected light of the same order as an unsilvered lapped surface, indicating that the phase variations over the unsilvered surface were almost entirely due to the geometry of the surface and very little to differences between the phases of reflexion from possible different components of the surface. When the lapped surface was lightly etched electrolytically the discrete particles of tungsten carbide were revealed and the phase variations shown by phase contrast and interference examination appeared greater on an unsilvered than on a silvered surface. Since tungsten carbide is a semi-conductor it might be expected that the phase change on reflexion from it would be very different from that on reflexion from the metal cobalt. No such difference seems to have been detected on the unetched lapped surface and, since it is known that cobalt flows readily when lapped or polished, it seems possible that the lapped surface of tungsten carbide is covered with a thin layer of cobalt.

This examination also showed that the surfaces have negligible porosity and that the surface irregularities were less than 0·1 μ.

The cube itself could be examined only with the interference microscope. The photographs obtained (see, for example, figure 3, plate 2) show shallow scratches and general irregularities which seem to be very similar to those revealed by Dr Menter's photographs.

The photographs of the cube in figures 1 and 2, plate 2, show very striking differences of appearance between different areas of the same face. Under the interference microscope no difference can be discovered between these areas and the surface roughness measured as described in § 3 (*b*) shows no difference. The most prominent feature, the triangular patch shown in figure 2 can, however, be detected in the interference photographs taken for the measurement of the concavity of the faces (§ 3 (*c*)) and it appears that there is a slight phase shift, either optical or geometrical, of this area relative to the rest of the face. It was of course undesirable to etch the surface for a more detailed examination and the reason for the non-uniform surface texture remains unknown.

The entire length of the edges of the cube was examined by the interference microscope as well as with an ordinary microscope. The radius of curvature of the edge is less than 1 μ and as shown by the typical photograph reproduced in figure 3, the surface is flat to within a micron or so of the edge. Most corners have a radius of about 20 μ. The edges are slightly chipped in a few places and a roughly tetrahedral chip the volume of which is about 10^{-9} of the cube volume is missing from one corner. The total volume missing due to all edge and corner defects is estimated to be less than 10^{-8} of the cube volume.

The cube is protected with Vaseline when not in use. There are one or two small corrosion marks on it and the triangular area shown in figure 2 has become more obvious in the course of 3 years, possibly a corrosion effect. Again, however, these imperfections make a negligible contribution to the volume of the cube.

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† 1 nm (nanometre) $= 10^{-9}$ m $= 10$ Å.

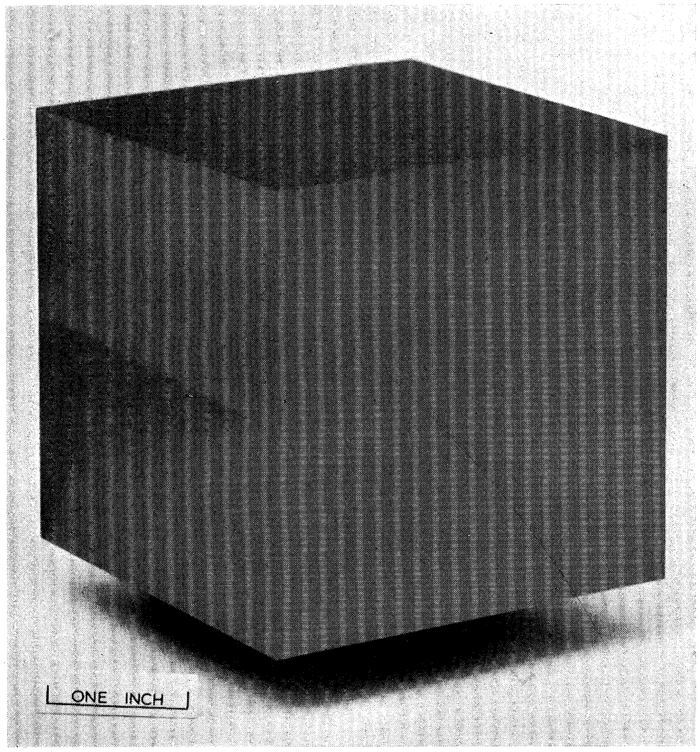

FIGURE 1. General view of cube of tungsten carbide and cobalt.

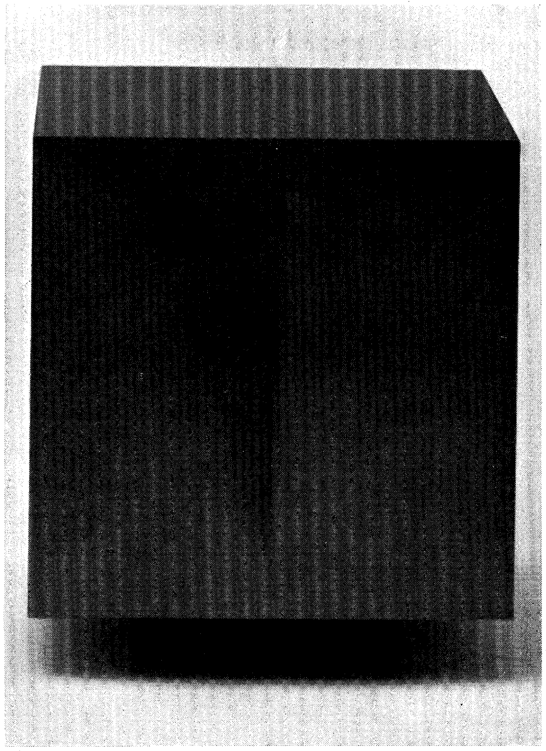

FIGURE 2. Face 1 of cube showing areas of different superficial appearance.

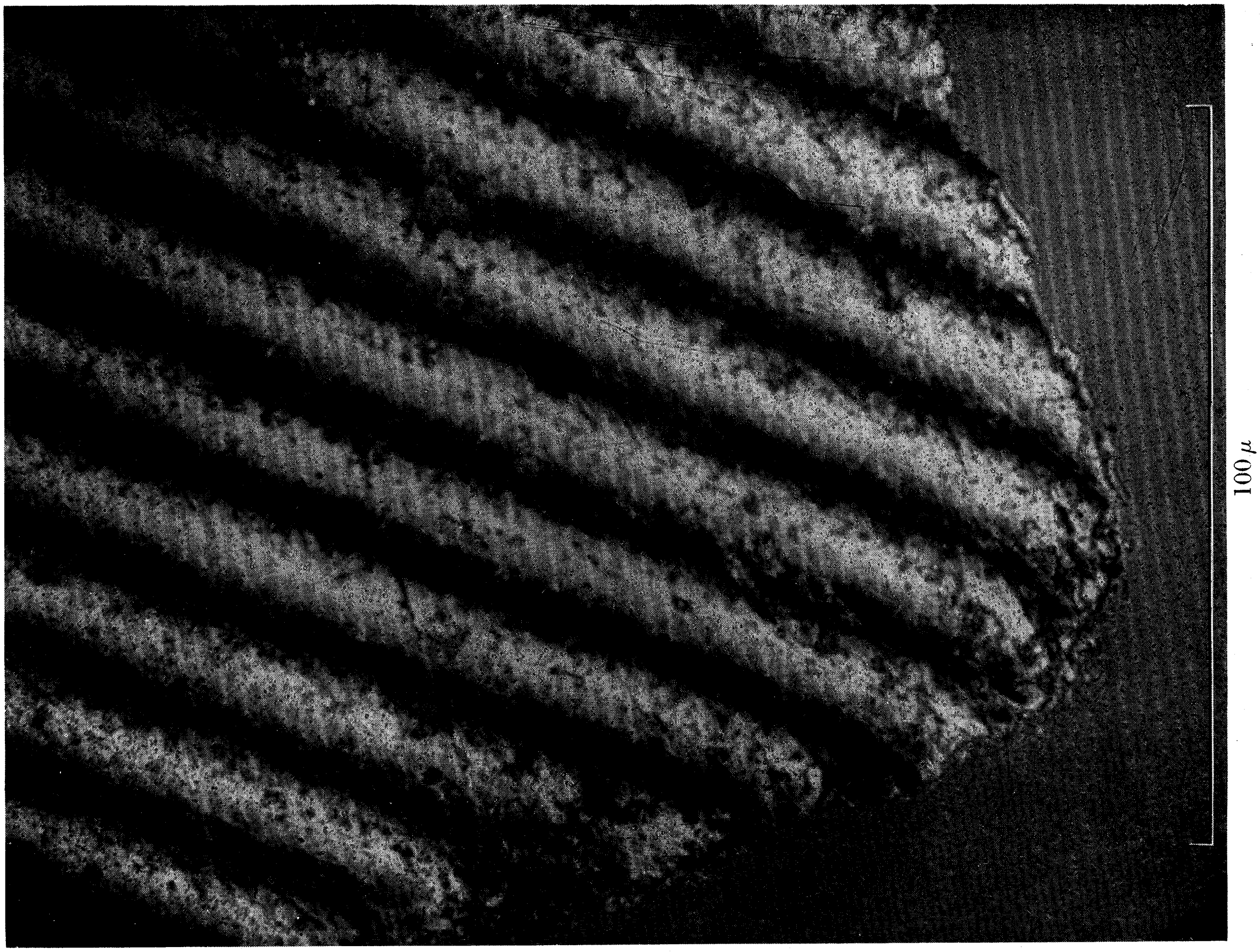

FIGURE 3. Photograph of corner of cube taken with interference microscope.

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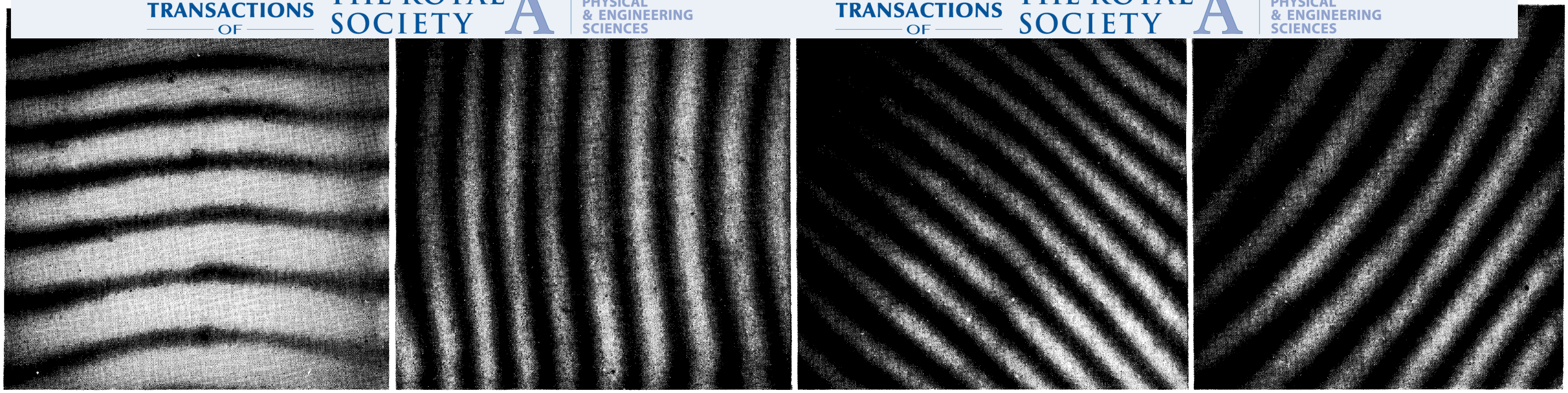


FIGURE 5. Set of four photographs (face 1) of interference fringes obtained with liquid-surface interferometer.

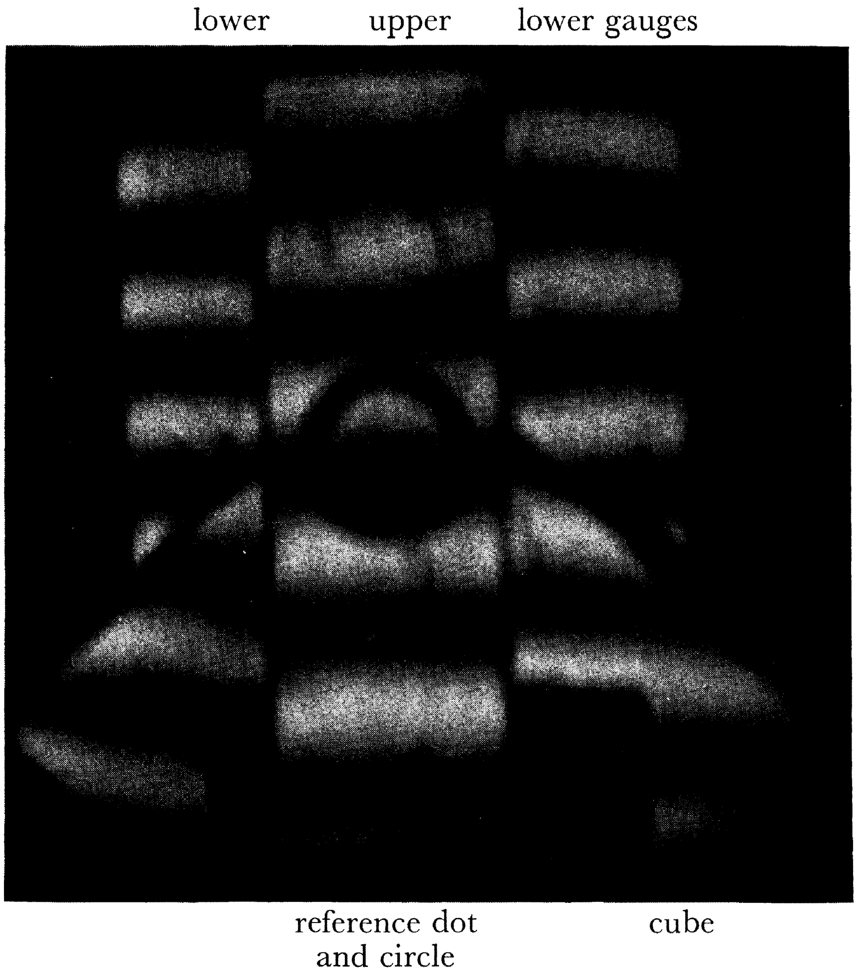


FIGURE 9. Photograph of field of Kösters–Zeiss interferometer showing slip gagues wrung on to cube.

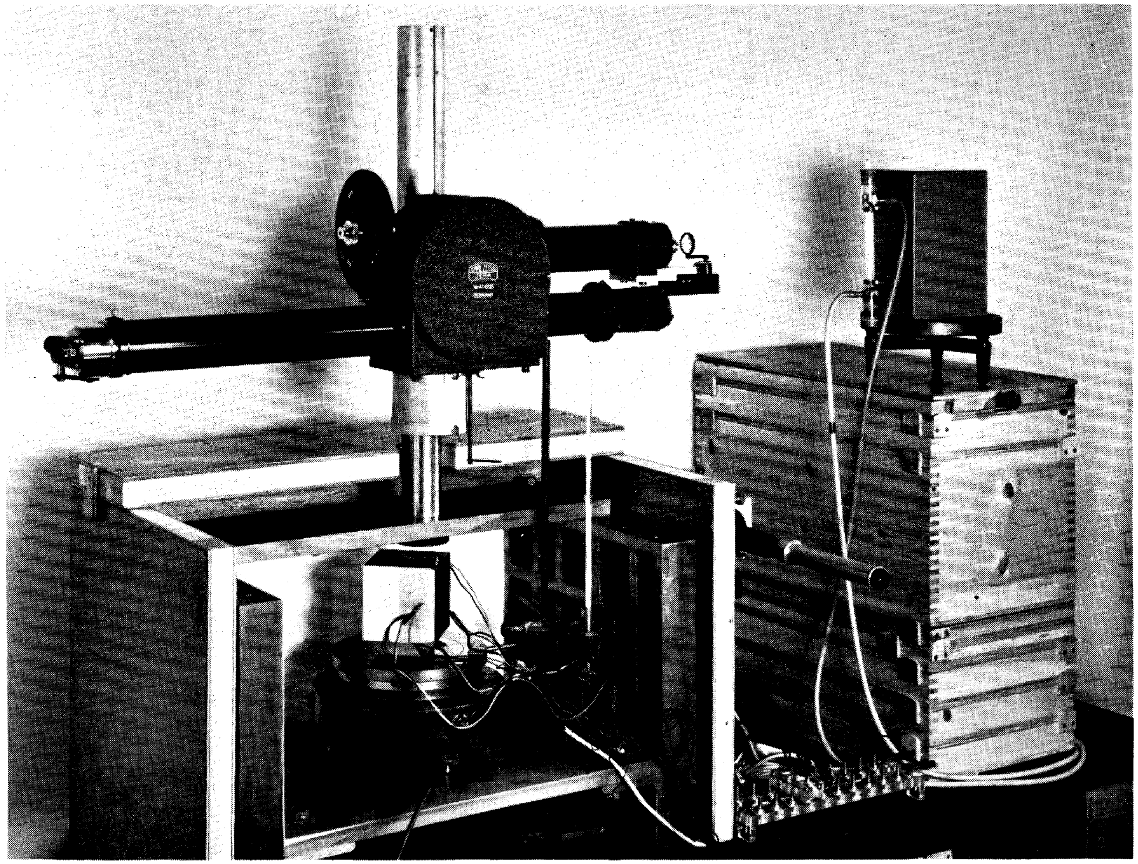


FIGURE 10. Cube set up under Kösters–Zeiss interferometer.

The areas of different appearance are used to distinguish the different faces of the cube which are numbered from 1 to 6 so that the sum of the numbers of opposite faces is 7.

The cube is slightly ferromagnetic and, by weighing it near a permanent magnet of known moment, the value of $(\mu-1)$ was found to be 1·6.

The permanent moments were similarly found to be:

normal to faces 1 and 6:	120 e.m.u.
3 and 4:	15 e.m.u.
2 and 5:	5 e.m.u.

The forces exerted on the cube by neighbouring ferromagnetic material when it is being weighed either in mercury or in air are less than 1 dyn. (See also § 5 (*c*).)

The following values of the elastic moduli were determined in the Physics Division of the Laboratory from measurements of the velocity of sound through the cube:

	rigidity modulus:	$2{\cdot}11\times10^{12}$ dyn/cm^2;
	Poisson's ratio:	0·23.
Hence,	Young's modulus:	$5{\cdot}2\times10^{12}$ dyn/cm^2,
	bulk modulus:	$3{\cdot}2\times10^{12}$ dyn/cm^2.

When immersed in mercury the cube is under a mean pressure of about 60 mm Hg or nearly 10^5 dyn/cm^2. The change of volume is therefore about 0·03 p.p.m. and is ignored.

The shear strains caused by the method of supporting the cube during measurements of its dimensions may affect the results of those measurements; they are discussed in § 3 (*e*) (i).

In addition to the measurements described below, the angles between faces have been measured by means of a method utilizing auto-collimating telescopes; the standard deviation of a measured value of a cube angle is 0·14 s and only two angles depart by more than 1 s from 90° and two more by more than 0·5 s, differences which are quite unimportant in calculating the volume of the cube.

3. The volume of the cube

(*a*) *Definition of the dimensions of the cube*

In order to correlate the various measurements of the cube and to enable the volume to be calculated from them in a straightforward manner, the values should all be referred to a common geometrical framework which is precisely defined with reference to the actual methods of measurement that are used. For this purpose, the physical edges of the cube are not satisfactory and are not directly accessible by the optical interference methods used for the measurements. In examining the form of the faces it was convenient to consider 100 points on each face, each point being at the centre of one of 100 equal small squares into which the whole area of the face is divided, and the four such points nearest the corners of each face, twenty-four in all, form a suitable geometrical framework for the measurements. The distances between opposite faces at these points are defined with a precision limited only by the reproducibility of the optical contact of lapped metal surfaces and can be measured very accurately by optical interference, while the form of a face can be expressed as the depth of any point on it below the plane defined by three of the four corner reference points. The distances between the corner reference points on opposite faces are conveniently called 'edge-lengths', although they are not in fact equal to the relatively ill-defined lengths of the physical edges.

The separation of two faces as measured by the interference methods is in effect that between the plane surfaces of two polished blocks in optical contact with the opposite faces, and because of the irregularities of the surface of the cube a small volume is included between the cube and these planes; the volume per unit area of this space was called the mean depth of the surface below the wringing plane.

(*b*) *Mean depth of the surface below the wringing plane*

This quantity was determined directly by a method used by Rolt & Barrell (1927) to investigate the thickness of the wringing film between lapped and polished surfaces. A drop of paraffin oil of known volume was placed on the grease-free surface of an optically flat polished glass proof-plane, which was then wrung into optical contact with one of the faces of the cube, this also being free of grease; the area to which the oil spread was measured through the glass.

TABLE 2. MEASUREMENTS OF WRINGING FILM THICKNESS

face	number of measurements	mean volume per cm^2 (nm)	s.d. of single observation (nm)
1	5	28·9	3·3
2	4	28·6	2·4
3	4	30·2	1·7
4	4	27·8	3·0
5	5	30·6	2·9
6	4	31·0	4·0

mean, all faces:	29·5 nm;
variance between faces:	1·6 nm^2;
s.d. of mean:	0·5 nm.

The drops were formed by dipping a copper wire, of 0·7 mm diameter, into a pool of paraffin on a flat plate and then touching the tip on the glass surface. It was found, as Rolt & Barrell state, that the volume of the drop formed was not sensitive to the depth of the oil pool; it does, however, seem to depend on the cleanness of the surface. The mass of an individual drop was found by weighing thirty drops placed on a clean weighed watch glass.

The surfaces were cleaned with swabs of cotton wool soaked in *iso*propyl ether. Great care must be taken that dust or grease particles do not settle on the surfaces after they have been cleaned and before they are wrung together. The film must be left to spread for at least an hour before its area is measured. It was not convenient to measure the area with a travelling microscope as Rolt & Barrell did; instead it was found that the outline of the film could be traced in indian ink on the top of the glass plate and the area estimated by putting the outline over a piece of squared paper. The parallax errors in tracing are much less than the scatter between wringings.

The results are collected in table 2.

It is probable that most of the variation is due to the variation in the sizes of the individual drops. There is no evidence that the mean depth differs from face to face. It was found that there was no difference between the areas of different appearance; the most direct evidence of this is that when drops were placed on the boundary between areas of different appearance, they spread uniformly at the same rate into the two areas. Two glass planes were used but there is no significant difference between the results obtained with them. Fine scratches which, in the course of the experiments, appeared on the surfaces wrung to the cube, may have increased the apparent film thickness.

(c) *The form of the faces*

The contours of the faces of the cube were determined with the liquid-surface interferometer described by Barrell & Marriner (1948). The easier method of comparing the faces with a glass or quartz optical flat could not be used because a large enough flat was not available at the time, but despite some inconveniences the liquid-surface method is probably the better to use because the temperature of the cube is more uniform when the cube is immersed in liquid than when it is in air.

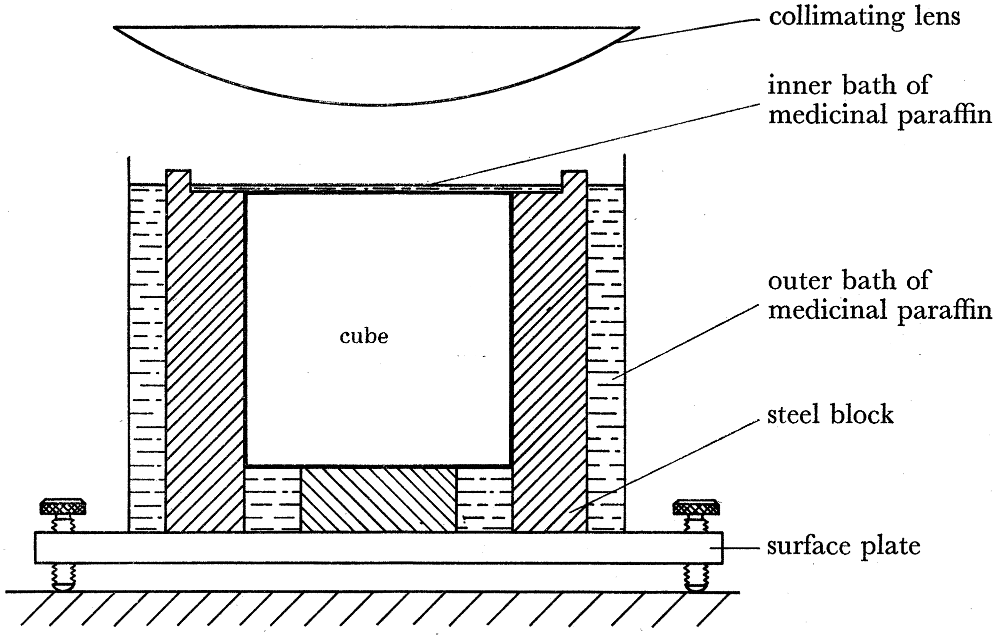


FIGURE 4. Liquid-surface interferometer.

Fringes of constant distance between the liquid surface and the face of the cube were obtained in a Fizeau interferometer system and were photographed in the mercury green light ($\lambda = 5461$ Å).

The cube was supported as shown in figure 4, on a glass block resting on a surface plate and was surrounded by four closely fitting steel blocks which were ground so that together with the upper face of the cube they formed a tray to contain medicinal paraffin. It was not possible to prevent paraffin leaking from this tray and the cube and blocks were therefore surrounded by an outer bath of medicinal paraffin the level of which was made equal to that of the paraffin in the tray. This is important in preventing a slow change of level of the paraffin in the tray with consequent drift of the fringes. The surface of the inner paraffin bath must extend so far beyond the cube face that it is not distorted by surface tension over the cube, and the depth of the layer beyond the cube must be the same as that over the cube, for if it is different, convection currents may disturb the surface. The arrangement used meets these conditions.

The pool of paraffin was 0·3 cm deep. If it is less deep, the liquid flows very slowly to its stable position, while if it is much deeper, the surface is sensitive to vibrations of the apparatus.

The cube may be distorted mechanically because of the way in which it is supported and it may be distorted thermally by non-uniform temperatures. Mechanical distortion was considered to be minimized by the choice of the area of the block supporting the cube, and evidence that it may be ignored is discussed below (§ 3 (*e*) (i)). Temperature gradients were reduced as far as possible by working in a room of which the temperature was controlled to 0·2° C; in addition, the great thermal inertia of the cube, steel blocks and paraffin ensured that the temperature of the cube was uniform and changed slowly. Further, after the cube was set up in the interferometer, it was left for 24 h before taking photographs. However, the apparatus was close to one wall of the room and it is possible that there were temperature gradients at right angles to the wall. Accordingly, after one set of observations had been taken, the cube was turned through a right angle about its vertical axis and the observations repeated.

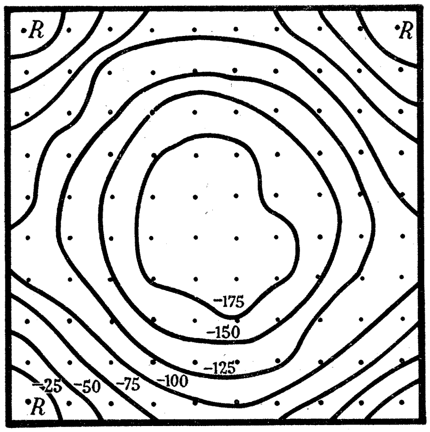


FIGURE 6. Diagram of face 4 showing reference dots for measurement of liquid-surface interferograms and contours on face at 25 nm intervals relative to reference plane (*RRR*). (25 nm = 25 × 10^{-9} m ≃ 10^{-6} in.)

Photographs of the interference pattern were taken with the fringes crossing the face in the two directions parallel to edges and in the two directions at 45° to edges. The face was covered by about ten fringes. A set of four photographs is reproduced in figure 5, plate 3. Each group of four photographs forms a set and at least three sets were obtained for each face. The apparatus was completely dismantled and reassembled between sets and the cube was turned through a right angle about its vertical axis.

For measurement, the photographs were projected on to a translucent screen on which was drawn the outline of the cube face and 100 dots at the centres of the 100 small squares into which each face was divided (§ 3 (*a*)). The magnification of the projected photograph was adjusted so that the edges of the picture coincided with the edges of the diagram and the fringe value at each dot was estimated by eye. From these values, the depth of the face below the face reference plane (§ 3 (*a*)) was calculated for each reference point.

Contours on one of the faces, drawn at intervals of 25 nm (10^{-6} in.) are shown in figure 6 and the mean depths of the faces below the reference planes are given in table 3.

A value for the mean depth was obtained from each photograph of a set, and hence the variance of the mean depth within each set could be calculated. Similarly, the variance between sets may be calculated and can be compared with the value expected from the 'within-set' variance. These variances are included in table 3.

The depth of the fourth-corner point below the reference plane defined by the other three is also required (§ 3 (*e*) (ii)) and it is given for each face in table 4.

TABLE 3. MEAN DEPTHS OF FACES BELOW REFERENCE PLANES

face	mean depth (nm)	variance within sets (nm^2)	variance between sets (nm^2)	standard deviation of mean depth (nm)
1	81·8	39·2	72·2	4·9
2	89·0	44·0	8·7	1·7
3	113·2	16·6	85·4	5·3
4	114·9	166·5	72·4	4·9
5	50·3	154·8	19·4	2·5
6	85·0	39·3	7·7	1·7
	means	76·7	44·3	3·9

The standard deviation of the mean depth is derived from the 'between-sets' variance.
For definition of reference planes, see table 4.

TABLE 4. DEPTHS OF FOURTH-CORNER REFERENCE POINTS BELOW REFERENCE PLANE THROUGH THE OTHER THREE

face	fourth corner	depth (nm)	variance within sets (nm^2)	variance between sets (nm^2)	standard deviation of mean depth (nm)
1	(2, 4)	21·5	207	345	11
2	(3, 6)	15·3	790	367	11
3	(5, 6)	6·1	282	219	9
4	(1, 2)	13·8	1062	1016	18
5	(3, 6)	23·0	1213	593	14
6	(3, 5)	−21·5	370	49	4
		means	637	454	12

Sign convention: the depth of the centre of the face below the reference plane is positive.
Notation of fourth corner: the corner is labelled by the numbers of the adjacent faces which include it.
The reference plane is defined by the other three corner reference points.

Let the three corner points, by which the reference plane is defined, define also axes of Cartesian co-ordinates so that any of the 100 points may be specified by co-ordinates ranging from 0 to 9, the co-ordinates of the three fundamental corner points being (0, 0), (0, 9) and (9, 0). Let the fringe values at the point (x, y) be f_{xy}; then the depth of the surface at this point below the reference plane is

$$f_{xy}-[f_{00}+(f_{90}-f_{00})\,x/9+(f_{09}-f_{00})\,y/9].$$

The depth of the fourth-corner point (9, 9), is then $[f_{99}+f_{00}-f_{90}-f_{09}]$ and the variance of this depth is $4v$ where v is the variance of a single fringe value. The average depth of the surface below the reference plane is

$$f_{\text{av.}}-\sum_{x}\sum_{y}[f_{00}+(f_{90}-f_{00})\,x/9+(f_{09}-f_{00})\,y/9]/100,$$

that is, $f_{\text{av.}}-\frac{1}{2}(f_{90}+f_{09})$, where $f_{\text{av.}}$ is the average value of f_{xy}. Since the variance of $f_{\text{av.}}$ is $v/100$, the variance of the average depth is very slightly greater than $\frac{1}{2}v$.

The 'within-set' variance will be due in the main to errors in reading the fringe values at each dot and to short period disturbances of the liquid surface. The reading errors were evaluated by two observers each making all the 100 readings on the same photograph three times and the standard deviation of a single reading was found to be 0·055 fringe or 10·2 nm, variance 104 nm^2. This is to be compared with the 'within-set' variances as follows:

of mean depth: $\frac{1}{2}v = 76{\cdot}7, \quad v = 153\ \text{nm}^2$;

of fourth corner: $4v = 637, \quad v = 159\ \text{nm}^2$.

These two estimates of 'within-set' variance are in excellent agreement and their magnitude suggests that errors other than reading errors have occurred.

If there are no additional sources of variation affecting a set as a whole, the variance between sets should be one-quarter of the variance within sets because the mean value for each set is calculated from four photographs. The observed variance between sets is in fact three times this expected value, showing that the apparent form of a face does change with the dismantling and reassembly of the cube between sets and in particular, perhaps, with turning it through a right angle so that it is oriented differently with respect to the temperature gradients in the room. In these circumstances it is the variance between sets which determines the uncertainty of the final results.

TABLE 5. COMPARISON OF LIQUID-SURFACE AND OPTICAL-FLAT MEASUREMENTS

	maximum depth below reference plane (nm)	
face	by liquid surface	by optical flat
3	195	145
4	195	188

Another possible source of variation, which, however, may not contribute much to the 'between-sets' variance, is that the cube may not have been left long enough to reach thermal equilibrium before it was photographed. This was checked by leaving the cube undisturbed while photographs were taken on three successive days. No evidence of any change over the 3 days was found and the residual variance of mean depth, 62·5 nm^2, was in reasonable agreement with the values of 'within-set' variance given in table 3 and with the value of 52 nm^2 to be expected from the reading errors.

Analysis of the fourth-corner measurements led to conclusions essentially the same as those above.

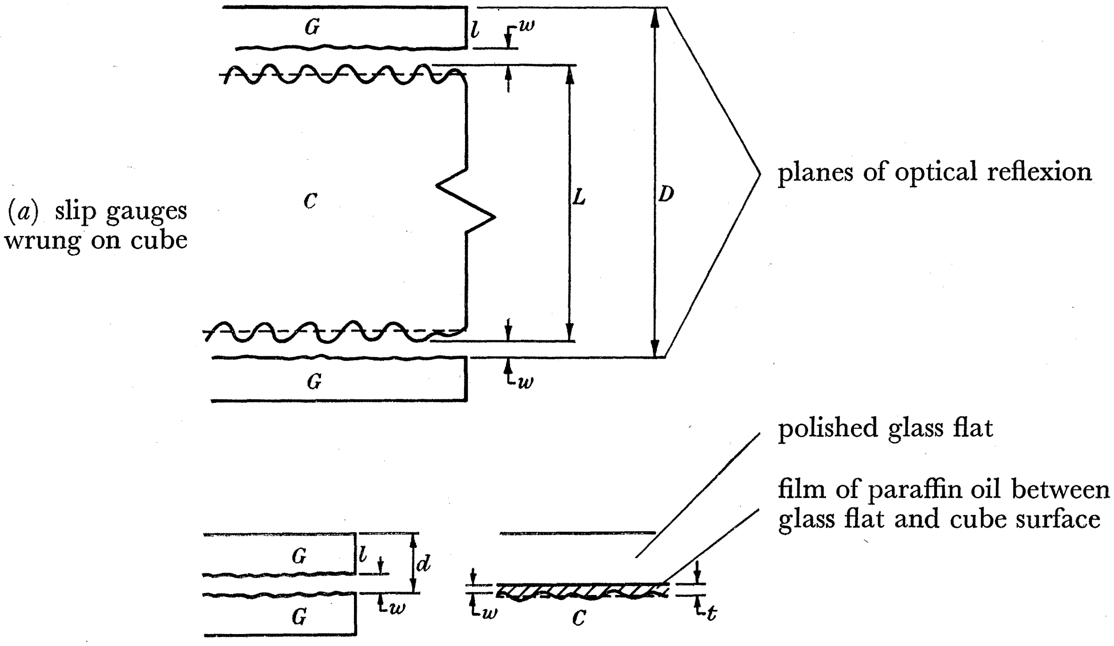
Two checks on the above results have been obtained. After the observations had been completed, a large optical flat became available and two of the cube faces were compared with it in a Fizeau interferometer. Although the results were not expected to be as reliable as the liquid-surface measurements because the cube was more liable to changes of temperature, and because the measured irregularities of the glass flat have to be allowed for, nevertheless, the agreement between the two methods is quite satisfactory (table 5).

The variation in the separation of corresponding points of opposite faces has also been measured directly by pneumatic gauging methods (Evans & Morgan 1956) with results that agree to within 0·6 p.p.m. of the volume of the cube calculated with the liquid-surface measurements, a discrepancy that is within the uncertainty of the pneumatic method.

(*d*) *Measurements of the edge-lengths*

(i) *Geometry of the measurements*

The measurements were made by optical interferometry, adapting a technique used for measuring engineers' end gauges (see Barrell & Puttock 1950). Consider the diagrammatic section through the cube shown in figure 7. When a slip gauge is wrung on to the cube, its wringing plane will be separated from the crests of the irregularities of the cube surface by the distance w equal to the thickness of a wringing film of paraffin oil. Then if L is the distance between the crests of opposite faces of the cube, and l is the distance between the faces of a slip gauge wrung on to the top of the cube, the distance, D, between the top surface of this slip gauge and that of another wrung on to the base of the cube is $(L+l+2w)$. Now let the two slip gauges be wrung together and let the distance, d, equal to $(l+w)$, between their two upper surfaces, be measured.



(*a*) slip gauges wrung on cube

(*b*) slip gauges wrung together

(*c*) glass flat wrung on cube for measurement of the average depth, t, of the surface irregularities of the cube

FIGURE 7. Diagrammatic section through cube (C) and slip gauges (G) showing the lengths D and d measured in the Kösters–Zeiss interferometer, the distance L between the planes touching the outermost points of the cube surfaces, the wringing film thickness, w, and the average depth, t, of the surface irregularities of the cube.

Then $L = D - d - w$ and the exact meaning of l is immaterial. The optical phase shifts due to differences between the surfaces of the two slip gauges are included in both D and d and they are therefore eliminated from $(D-d)$, the measured length of the edge. $(D-d)$ will be denoted by L'.

If the volume of the cube is calculated from the length L it will be overestimated, since the volume defect due to the surface irregularities is not allowed for. Now the mean depth

t of the surface below the polished surface of an optical flat (§ 3 (a)) is equal to the mean depth of the cube surface below the crests of the irregularities plus the wringing film thickness w. The length needed for calculating the volume displaced by the mercury is therefore $\{L-2(t-w)\}$ which is equal to $(L'+w-2t)$.

Rolt & Barrell (1927) have found the wringing film thickness to be 5 nm.

In practice, one tungsten carbide slip gauge was wrung on to the top face of the cube and two similar gauges were wrung on to the bottom face. The disposition of the gauges is shown in figure 8. The cube was supported under the head of a Kösters–Zeiss interferometer and the disposition of the fringes on the gauges will be seen in figure 9, plate 3. The advantage of the Kösters–Zeiss interferometer for measurements of this sort is that the image of the reflecting plane in the reference arm of the Twyman–Green arrangement falls midway between the upper and lower gauges so that all the fringes are of equal contrast, and the visual estimation of the fractional fringe difference between the upper and lower gauges is as easy as possible.

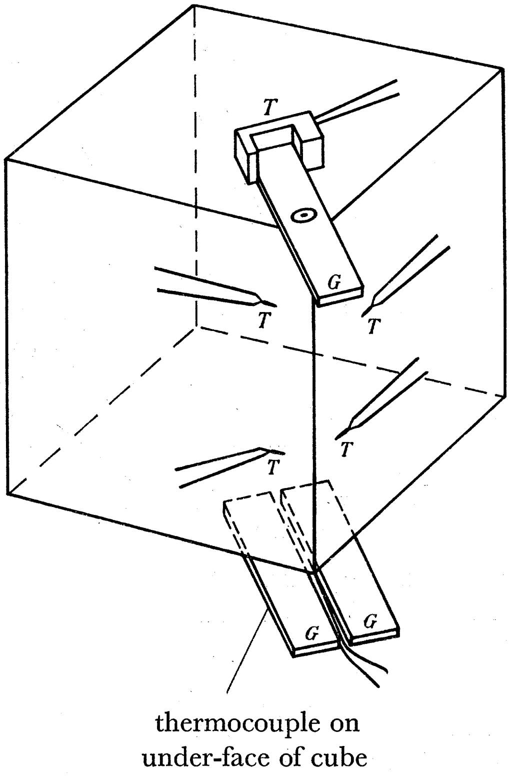


FIGURE 8. Arrangement of slip gauges and thermocouples on cube. G, slip gauge; T, thermocouple.

Because the faces of the cube are slightly concave, the distance between the slip gauges wrung on to opposite faces varies with the position on the upper gauge at which the fractional fringe difference is estimated. A fiducial dot was therefore marked on the top surface of the upper gauge (this may be seen in figure 9) and, for the purpose of measuring fringe fractions, a fringe on the upper gauge was arranged to lie on this dot. The fractional difference from the lower gauges was estimated for the position of the dot, and the position of the dot relative to the edges of the cube face was determined from a photograph such as figure 9. The slopes of the faces near the corners were estimated from the measured contours (§ 3 (*c*)) and a correction was obtained by which each length L' was reduced to the adjacent corner reference point. In this way the measured distances were related to the fundamental framework defined in § 3 (*a*).

(ii) *Experimental details*

The interferometer head was supported on a massive steel framework which also carried a table on which the cube was placed on the same glass block as was used in the liquid-surface interferometer. The effects of possible distortion of the cube due to the way in which it was supported are discussed in § 3 (*e*) (i). The framework was covered with double-walled wooden panels for thermal insulation and the apparatus was placed on a slate bench in a room of which the temperature was controlled to $\pm\frac{1}{4}°$ C near 20° C.

The temperature of the cube was measured by six copper constantan thermocouples, one junction of each being affixed to the cube by Sellotape as shown in figure 10, plate 3, with the other junction in contact with a light-gauge copper tube surrounding the bulb of a mercury-in-glass thermometer placed in the lagged enclosure. The thermometer was divided to 0·01° C and estimated to 0·001° C with a microscope. The copper leads of the couples were connected to pairs of copper rods mounted on a Perspex panel and could be connected in turn to a loop galvanometer by means of copper contacts on a sprung Perspex mount.† This type of selector switch, which is also used as a reversing switch, is free from the troubles that often beset accurate thermocouple measurements. The couples were calibrated over a range of 0·5° C by comparison with two mercury thermometers. The accuracy of measurement of temperatures near 20° C is estimated to be about ±0·005° C.

The slip gauges and the faces of the cube on to which they were to be wrung were carefully cleaned with petrol and small drops of paraffin oil were put on the gauges to help wringing.

In the neighbourhood of certain corners there are slight imperfections of the edges of the cube which, though otherwise undetectable, kept the gauge from wringing down properly as was shown either by the feel of the gauge on the cube or by the appearance of the interference fringes on the gauge. It was sometimes necessary to lap the edge of the cube with a fine stone before the gauge would wring properly; such lapping, carried out over a small area, has a negligible effect on the volume of the cube.

After the cube with the gauges wrung on had been set up under the interferometer, it was left for at least 3 h for its temperature to become steady and uniform. Satisfactory results were obtained if the cube and thermometer temperatures differed by less than 0·1° C (they usually agreed to 0·05° C) and if the six thermocouples differed by less than 0·05° C (they usually agreed to 0·03° C).

The observer first took the thermometer and thermocouple readings and then estimated the fractional fringe difference on the fiducial dot for the four radiations specified below. He repeated the fringe estimations in the reverse order and finished by reading the thermometer and thermocouples again. The air pressure and humidity were noted. Each combination of the cube and gauges was measured by at least two observers, and finally the cube and gauges were photographed through the interferometer so that the position of the

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† The design of this switch is due to Mr C. R. Barber.

fiducial dot on the upper slip gauge could be measured relative to the cube edges. The cube was then removed from the interferometer, the gauges were interchanged, and the cube was replaced in the interferometer so that the face which was previously on top was now underneath.

The lengths were measured in terms of four monochromatic radiations of the mercury-198 spectrum emitted from a water-cooled electrodeless lamp excited by a 100 Mc/s electrical discharge. The following wavelengths have been determined at the National Physical Laboratory, and were checked on the actual lamps used:

yellow (1)	0·579 069 30 μ
yellow (2)	0·576 962 83
green	0·546 078 17
violet	0·435 836 03.

These values are for air at 20° C at 760 mm Hg pressure with 0·03 % by volume of carbon dioxide and a water-vapour pressure of 10 mm Hg. Corrections for departures from these standard conditions were obtained from the following equation:

$$\frac{\lambda_a-\lambda_s}{\lambda_s}=\left\{A+\frac{Bh'}{1+\alpha t}+C(f-10)\right\}\times 10^{-6}.$$

The symbols have the following meanings:

λ_a is the wavelength in an atmosphere with temperature t° C, pressure h mm Hg and water-vapour pressure f mm Hg.

λ_s is the wavelength in the standard atmosphere.

$\alpha = 0{\cdot}003\,661/°$ C.

$h' = h(1+\beta_t h)$, where $\beta_t = (1{\cdot}049 - 0{\cdot}0157\,t)\times 10^{-6}$ and the average values of A, B and C for the four wavelengths are:

A,	273·561;
B,	0·386 088;
C,	0·0558 (Barrell 1951; Edlén 1953).

Average values were used for A, B and C because the final lengths are the means of the measurements in the four wavelengths.

The measured lengths were reduced to 20° C using the coefficient of linear expansion of the cube determined in the course of the first series of measurements (§ 3 (*d*) (iii)).

(iii) *Results*

The results are collected in table 6. The cube edge is identified by the numbers of the faces that meet in it and the direction in which the measurement was made by the number of the face on top. The lengths tabulated are the distances, D, as measured in the interferometer less the measured length, d, of the upper slip gauge and they have been reduced to distances between reference points by the corrections for the slopes of the faces near the corners. These corrections range from +11 to −31 nm and are almost all negative because the fiducial dot on the upper slip gauge usually fell outside the reference point.

The values of the measured length, *d*, of the upper slip gauge are as follows:

1953	March	2539830 nm
	June	2539818
1954	November	2539817
		gauges re-lapped
1955	October	2529991
	November (1)	2529982
	(2)	2529981
	(3)	2529980

The standard deviation of any of the above values is about 3 nm. The values of *d* used in obtaining the results in table 6 are:

1953		2539824 nm
1954		2539817
1955	October	2529986
	November	2529981.

The 1953 and 1955 measurements suggest that the gauge shortened by about 10 nm during the first ten or fifteen wringings after lapping.

Not all measurements are given in table 6, some having been rejected because it appeared from the photographs of the fringes that one of the gauges was not in proper contact with the cube. Such an imperfection increases the measured length.

In the 1953 and 1954 observations, all six thermocouples were stuck to the cube and it was assumed that the air temperature used in correcting for the refractive index of the air was the same as the temperature of the cube; but in 1955 two of the thermocouples were used to measure the air temperature and it was found that the air temperature was more variable than that of the cube. It is estimated that errors in the 1953 and 1954 measurements from this cause are unlikely to exceed 6 nm and the statistics given below indicate that the actual errors are appreciably less.

Each value in table 6 is the mean of two observations by different observers and the standard deviation of a single observation on a given gauge combination is estimated from the discrepancies between observers to be 11 nm, the separate mean values for 1953, 1954 and 1955 being almost identical. Since the air temperature usually changed appreciably between the two observations of a combination, this figure includes some contribution from the air temperature uncertainty mentioned above and the fact that the discrepancies between observers were not significantly less in 1955 than in 1953 and 1954 indicates that this source of uncertainty was not important in 1953 and 1954.

At least six measurements of each edge-length have been made, two in each year, and the standard deviation of a single measurement about the overall edge mean is 13·4 nm, the standard deviations of the measurements between the different pairs of faces not differing significantly. Since each measurement is the mean of at least two observations by different observers, the expected standard deviation is $11/\sqrt{2}$ nm or about 8 nm. The larger value actually found may be accounted for by variations in the contact between the gauges and the cube and by actual changes in the dimensions of the cube in the course of the $2\frac{1}{2}$ years covered by the measurements. The variations do in fact appear to be quite random and there is no evidence of any systematic change in the dimensions of the cube, even the changes of −26 nm in the measured length of edge (3, 5) and of −25 nm in that of edge (3, 6) between 1953 and 1954 almost certainly being due to variations in contact. It may be significant that these edges meet in the corner (3, 5, 6) and burrs on the edges near this one corner may have caused the changes.

TABLE 6. MEASURED DISTANCE, L', BETWEEN FACES OF CUBE AT CORNER REFERENCE POINTS

Unit: 1 nanometre (nm)

number identifying configuration	edge	upper face	measured distance			mean 1954, 1955
			1953	1954	1955	
(A) Between faces 1 and 6, distances are 88 868 000 nm +						
I	4, 2	1	360, 364	343	346	351
II		6	347	360	354	
III	2, 3	6	380	390	366	375
IV		1	358	374	369	
V	3, 5	1	257, 306	281, 250	264	259
VI		6	285, 278	245	262	
VII	5, 4	1	265	282	271	274
VIII		6	302	281	260	
(B) Between faces 2 and 5, distances are 88 865 000 nm +						
IX	6, 4	5	435	446	435	442
X		2	439	440	450	
XI	4, 1	5	402	430	398	411
XII		2	423, 397	399	417	
XIII	1, 3	5	427	467	414	437
XIV		2	431	435	432	
XV	3, 6	5	471	449	448	446
XVI		2	467	438	450	
(C) Between faces 3 and 4, distances are 88 865 000 nm +						
XVII	2, 6	3	792, 772	777	783	778
XVIII		4	791	777	775	
XIX	6, 5	3	721	712	716	713
XX		4	697	688	737	
XXI	5, 1	3	836	820	842	833
XXII		4	811	831	838	
XXIII	1, 2	3	917	869	867	883
XXIV		4	879	906	889	

The distances are those directly measured in the interferometer less the measured length of the upper slip gauge. No allowance has been made for the thickness of wringing films nor for the roughness of the cube surface.

It is slightly more satisfactory to calculate the volume of the cube from the mean of the 1954 and 1955 measurements rather than from that of the mean of the measurements of all 3 years, but it makes very little difference which is used, since the greatest differences between such means for any edge are both 8 nm (edges (3, 5) and (3, 6)), all the others agreeing to 5 nm. Four measurements of each edge are combined in the 1954/5 means and the standard deviation of each mean edge-length should therefore be $\frac{1}{2}\times 13{\cdot}4$ or 6·7 nm. This figure contains no allowance for the standard deviation of the length of the upper slip gauge which is about 3 nm.

The coefficients of linear expansion of the cube were measured by repeating observations of one edge in each direction at 20 and 36° C. The values so found are given in table 7. The linearity of the expansion of the cube was not checked by observations at a third temperature, but all the definitive observations of the volume of the cube and of the mass of mercury displaced were made so close to 20° C that slight non-linearity is unimportant.

Table 7. Coefficients of linear expansion of the cube

between faces 1 and 6:	$5{\cdot}210 \times 10^{-6}/°$ C	s.d. 0·008
2 and 5:	5·185	s.d. 0·006
3 and 4:	5·181	s.d. 0·007
mean value:	$5{\cdot}192 \times 10^{-6}/°$ C	

(e) *Combination of the observations*

(i) *Elastic distortion of the cube*

When the cube is hanging in mercury the mean dilatation under the body forces and the pressure of the mercury on the faces may be calculated from a formula for average strain given by Love (1920, p. 173). The mean dilatation due to the body forces is $+W/6Ak$, where W is the weight of the cube, A the face area and k the bulk modulus, and amounts to 0·005 p.p.m. The pressure dilatation is $-p/k$ where p is the mercury pressure at the level of the centre of gravity of the cube, about 0·1 bar. The pressure dilatation is thus about −0·03 p.p.m. and the net dilatation, about −0·025 p.p.m., is negligible.

When the cube is supported on its glass block under the Kösters–Zeiss interferometer, the mean change of length in the vertical direction is $\frac{1}{2}W/Ea$ where E is Young's modulus and a is the side length (Love, p. 173). This is equal to 1 nm, or about one-tenth of the standard deviation of the observations of the lengths of the edges. However, it is not the mean change of length that is required but that at an edge. Love's discussion of a prism supported by a uniform tension over the upper face (Love, p. 125) indicates that if the cube were supported by a uniform pressure over the lower face, the change of length of any vertical filament would be equal to the mean change. For any practical method of support, this will not be true but St Venant's principle suggests that if the mean change is negligible, the actual edge-length change for any method of support is not likely to be important.

An experiment has been done which confirms this surmise. The length of a particular edge was measured by the Kösters–Zeiss interferometer, first with the cube supported on the glass block in the usual way, secondly with it supported by a single small glass disk at the face centre, and thirdly with it supported by three or four small glass disks near the edge (see figure 11). Leaving the wrung slip gauges undisturbed, the cube was supported in the various ways and the length of the edge measured. The results are shown in figure 11 and it will be seen that they do not differ significantly—the r.m.s. departure from the mean is 3 nm compared with a standard deviation of a single observation, based on scatter between observers, of about 5 nm.

When the cube is supported by uniform pressure on the lower face, the displacement at the centre of the top face is less than that at the corners by $\sigma W/Ea$, about 0·5 nm. Superposed on this distortion is that due to the plate-like flexure of the cube on its support but this is less than 1 % of the body force distortion.

Elastic distortions of the cube therefore affect by negligible amounts the measurements needed to obtain the volume.

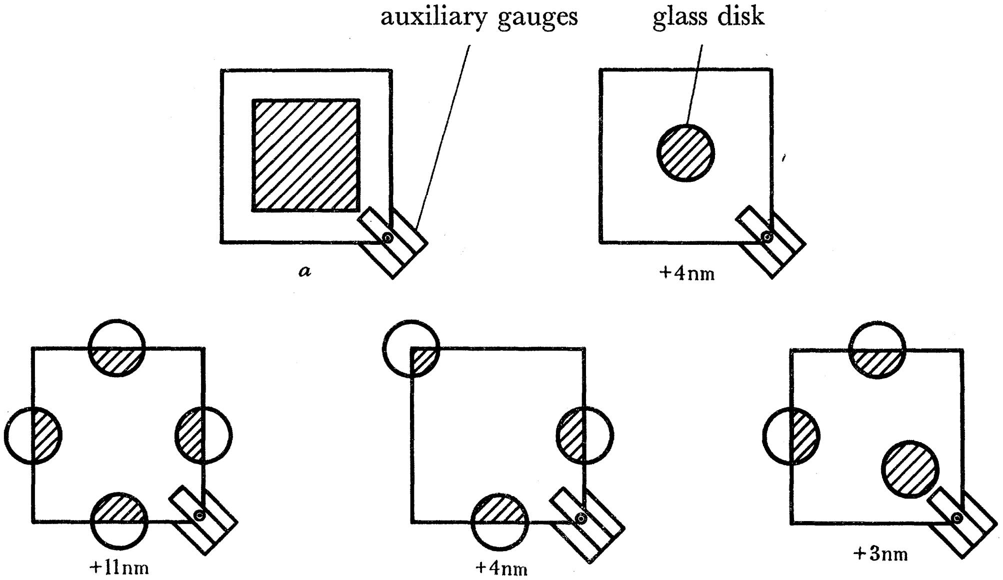

Figure 11. Measurement of length of an edge of the cube with different methods of support. The figures are the differences from the length measured in the standard arrangement (*a*).

(ii) *Combination of edge-length and face-form measurements*

Since the measurements of face contours were referred to planes defined by reference points near three of the corners of each face, the volume of the cube is conveniently calculated by first finding the volume enclosed by the reference planes, and then subtracting the volume represented by the mean depths below the reference planes. To calculate the volume enclosed by the reference planes, it is sufficient to know the distances between three pairs of opposite reference points on each pair of planes, and the measurements of the fourth-edge lengths together with the measurements of the heights of the fourth reference corners above the reference planes give redundant observations.

The measured edge-lengths, L', have therefore been combined with the fourth-corner measurements by the method of least squares to obtain the most probable values of the distances between the mid-points of opposite reference planes. The planes are so very nearly parallel that in these calculations the lack of parallelism may be ignored.

Consider figure 12 in which the four vertical faces are lettered k, l, m and n; the vertical edges can then be denominated by the letters of the faces that intersect in them. Let $L'_{k,l}$ be the measured length of edge (k, l) and let Λ be the separation of the mid-points of the reference planes of the top and bottom faces. The distances between the opposite corners of the reference planes of the upper and lower faces may be put in the form

$$\begin{array}{ll} (k, l): & \Lambda-\alpha_1, \\ (l, m): & \Lambda-\alpha_2, \\ (m, n): & \Lambda+\alpha_1, \\ (n, k): & \Lambda+\alpha_2, \end{array}$$

where α_1 and α_2 are parameters determining the angle between the planes.

Let the fourth corner of the upper plane be at edge (k, l) and that of the lower plane at edge (m, n) as shown in the figure and let the depths of these corners below the reference planes be δ_1 and δ_2 respectively. Then the measured lengths, L', and the measured depths, d, of the fourth corners can be written in the following parametric forms:

$$\begin{aligned} L'_{(k,l)} &= \Lambda - \alpha_1 - \delta_1, \\ L'_{(l,m)} &= \Lambda - \alpha_2, \\ L'_{(m,n)} &= \Lambda + \alpha_1 - \delta_2, \\ L'_{(n,k)} &= \Lambda + \alpha_2, \\ d_1 &= \delta_1, \\ d_2 &= \delta_2. \end{aligned}$$

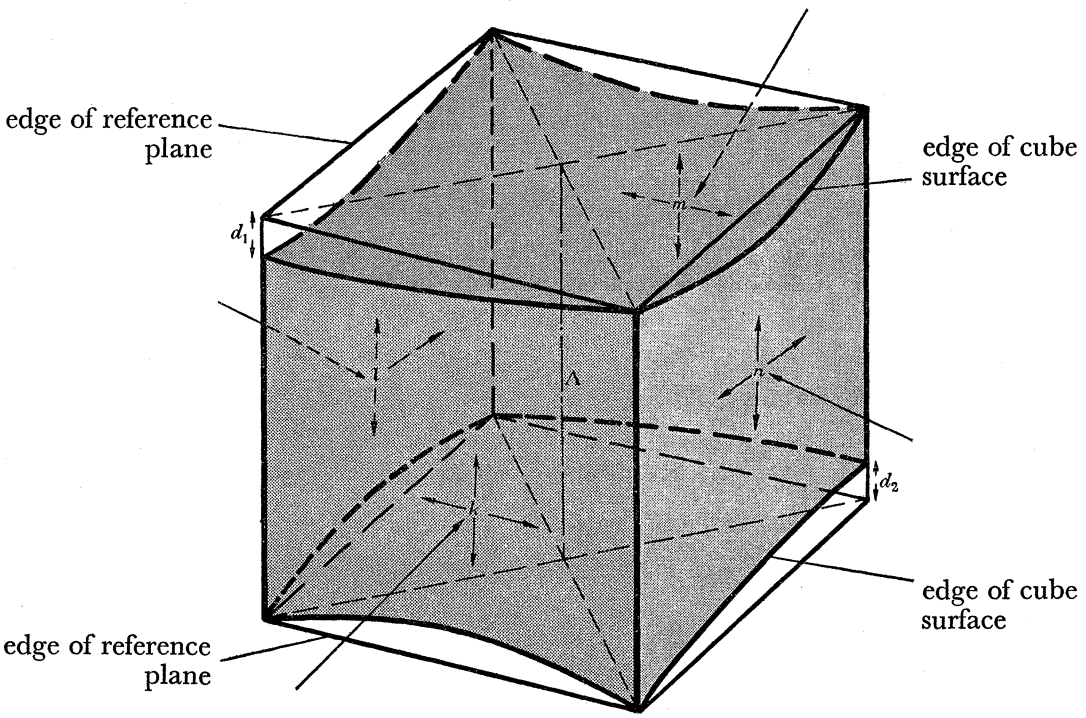

FIGURE 12. The combination of edge-length and fourth-corner measurements.

Five parameters, Λ, α_1, α_2, δ_1 and δ_2, have been introduced and there are six measured quantities comprising four edge-lengths and two fourth-corner depths. Normal equations have therefore been formed and solved for the parameters, the fourth-corner observations being given half weight in the adjustment in accordance with the variances of the various observations. The calculations are summarized in table 8.

The standard deviations of the calculated distances L' between the reference planes given in table 8 are determined from the residuals on one degree of freedom each and are therefore not very well determined, nor are they, in themselves, a reliable basis for estimating the uncertainty of the calculated volume of the cube. However, they are consistent with the standard deviation of a measured edge-length and lead, as will be seen below, to much the same value for the uncertainty of the volume.

TABLE 8. COMBINATION OF EDGE-LENGTHS AND FOURTH-CORNER DEPTHS

edge or corner	parametric form	observed value	obs. − calc.
(A) Separation of faces 1 and 6. Edge-lengths are 88868000 nm + tabulated values			
(4, 2)	$\Lambda+\alpha_1-\delta_1$	351	− 5
(2, 3)	$\Lambda+\alpha_2$	375	+ 5
(3, 5)	$\Lambda-\alpha_1-\delta_2$	259	− 5
(5, 4)	$\Lambda-\alpha_2$	274	+ 4
(1, 2, 4)	δ_1	22	−10
(6, 3, 5)	δ_2	−22	−10
standard deviation of observation of unit weight:		14 nm	
calculated separation of mid-points of planes:		88868320 nm	
standard deviation:		8 nm	
(B) Separation of faces 2 and 5. Edge-lengths are 88865000 nm + tabulated values			
(6, 4)	$\Lambda+\alpha_1$	442	−2·5
(4, 1)	$\Lambda-\alpha_2$	411	+2
(1, 3)	$\Lambda-\alpha_1$	437	−2·5
(3, 6)	$\Lambda+\alpha_2-\delta_1-\delta_2$	446	+2
(2, 3, 6)	δ_1	15	+4·5
(5, 3, 6)	δ_2	25	+4·5
standard deviation of observation of unit weight:		6·4 nm	
calculated separation of mid-points of planes:		88865442 nm	
standard deviation:		4 nm	
(C) Separation of faces 3 and 4. Edge-lengths are 88865000 nm + tabulated values			
(2, 6)	$\Lambda-\alpha_1$	778	−0·5
(6, 5)	$\Lambda-\alpha_2-\delta_1$	713	+1
(5, 1)	$\Lambda+\alpha_1$	833	−0·5
(1, 2)	$\Lambda+\alpha_2-\delta_2$	883	+1
(3, 5, 6)	δ_1	6	+1
(4, 1, 2)	δ_2	14	+1
standard deviation of observation of unit weight:		1·9 nm	
calculated separation of mid-points of planes:		88865806 nm	
standard deviation:		1·1 nm	

(iii) *The volume of the cube and its uncertainty*

It has already been explained in § 3 (*d*) (i) that the effective edge-length to be used in calculating the volume of mercury displaced by the cube is $(L'+w-2t)$. The corresponding distance between the mid-points of a pair of reference planes is $(\Lambda+w-2t)$ which will be denoted by Λ^*. The wringing film thickness, w, is 5 nm (Rolt & Barrell 1927) and t has been found to be 29·5 nm (§ 3 (*b*)); thus $\Lambda^* = \Lambda - 54$ nm.

Let the mean depth of a face below its reference plane be T; the volume deficit of, say, face 1 is then

$$T_1 \times \Lambda^*(2, 5) \times \Lambda^*(3, 4)$$

and the volume of the mercury displaced by the cube is

$$\Lambda^*(1, 6) \times \Lambda^*(2, 5) \times \Lambda^*(3, 4) \times [1-(T_1+T_6)/L(1, 6)-(T_2+T_5)/L(2, 5)-(T_3+T_4)/L(3, 4)],$$

where, in the small terms in the brackets, the precise meaning of L is not important.

The numerical values are:

(1) Effective mean distances between reference planes at 20° C (table 8)

$\Lambda^*(1, 6)$: 88868266 nm
$\Lambda^*(2, 5)$: 88865388
$\Lambda^*(3, 4)$: 88865752.

2) Ratios of mean depths of faces to distances between faces (table 3)

$$T_1/L(1,\,6):\quad 0{\cdot}920\times10^{-6}$$
$$T_6/L(1,\,6):\quad 0{\cdot}956$$
$$T_2/L(2,\,5):\quad 1{\cdot}002$$
$$T_5/L(2,\,5):\quad 0{\cdot}566$$
$$T_3/L(3,\,4):\quad 1{\cdot}274$$
$$T_4/L(3,\,4):\quad 1{\cdot}293.$$

The volume of mercury displaced by the cube at 20° C is therefore

$$\mathbf{701{\cdot}796\,434}\ \mathrm{cm}^3.$$

If V is the volume of the cube, then

$$\delta V/V = \Sigma\delta\Lambda/L - 6\delta t/L - \Sigma\delta T/L$$

and so

$$\mathrm{var}(\delta V/V) = (\Sigma\ \mathrm{var}\ \Lambda + 36\ \mathrm{var}\ t + 6\ \mathrm{var}\ T)/L^2,$$

where var t, the variance of the mean value of t over all faces, is equal to 0·25 nm^2 (table 2) and var T is the variance of the mean value of T for a single face and is equal to 15 nm^2 (table 3).

Σ var Λ can be estimated in two ways.

First, the sum of the variances of the calculated distances between planes given in table 8 is 88 nm^2 to which must be added 3×9 nm^2 for the variance of the length of the slip gauge. Σ var Λ is therefore estimated to be 115 nm^2, but it has already been seen that the calculated variances in table 8 depend each on one degree of freedom and are therefore only poorly determined.

Alternatively, Σ var Λ may be estimated from the variance of a measured edge-length about the mean of all six measurements of a given edge. On this basis, the variance of the 1954/5 mean of an edge-length is 45 nm^2. To estimate the variance of the mean distance between planes, the edges associated with fourth corners should be ignored and the variance of the mean distance is then nearly the variance of the mean of two opposite edge-lengths or 23 nm^2. The sum for the three directions is 69 nm^2 to which again 3×9 nm^2 has to be added for the uncertainty of the length of the top slip gauge, making a total of 96 nm^2.

The difference between the two estimates is statistically insignificant and on either basis the estimated standard deviation of the volume of the cube is $1{\cdot}5\times10^{-7}$ of the volume.

4. The mass of mercury displaced by the cube at 20° C

(a) *The mass of the cube*

The cube has been weighed five times against a 10 kg standard weight of the National Physical Laboratory, the weighings being interspersed among weighings of the cube in mercury. The standard deviation of the weight on a single occasion, as calculated from the scatter of the five values, is 0·25 mg and there is no evidence of a change in the difference between the standard and the cube.

Before being weighed, the cube was cleaned with swabs of cotton wool soaked in *iso*propyl ether. The usual corrections were applied for the mass of air displaced by the cube and the weights.

The estimated errors due to possible magnetic forces on the cube are negligible, but as a precaution the cube was placed on the balance pan so that every face was at some time on top.

The value of the standard 10 kg weight, 10_8, has twice been determined in terms of the 1 kg standards of the National Physical Laboratory, different routes being followed on the two occasions. The results are as follows:

1955 March $10_8 = 10$ kg $-24{\cdot}3$ mg, standard deviation 1·3 mg

1955 November $10_8 = 10$ kg $-22{\cdot}1$ mg, standard deviation 0·8 mg.

The 1 kg standards are very well known and thus the source of the greatest uncertainty in the mass of the cube is the determination of the 10 kg standard in terms of the 1 kg standards. A mean value of (10 kg −23 mg) was adopted for 10_8, and assigned a standard deviation of 1 mg.

The mass of the cube is then

$$\mathbf{9723{\cdot}2649}\ \mathrm{g},$$

also with a standard deviation of 1 mg.

(*b*) *Apparatus and procedure for weighing the cube in mercury*

The balance used to weigh the cube in mercury is an ordinary knife-edge balance which can take loads up to 1 kg. The load when the cube, immersed in mercury, is attached to it is about 250 g, but the inertia of the cube in mercury is equivalent to that of a mass of about 15 kg and the frictional forces are very much greater than those with such a load in air, so that the balance is heavily overdamped when adjusted to the sensitivity normally used for loads in air; accordingly, the sensitivity had to be decreased to reduce the damping below critical. The balance pointer was then observed through a microscope with a scale in the eyepiece. When weighing the cube in mercury the logarithmic decrement of the balance was 0·8, the period was about 30 s and one small division in the microscope eyepiece was equivalent to 2·5 mg. The position of the pointer could be read to between one- and two-tenths of a small division.

The mercury container, surrounded by blocks of cork, was carried on a trolley by which it could be adjusted horizontally and the balance was supported over it on a slate bench with a hole in it through which the cube was suspended. The container could also be raised or lowered so that the stainless-steel bar shown in figure 13 was either supported in two V-hooks attached to the rod hung from the balance arm or alternatively was supported on a V-rest standing on the lid of the container. Thus, the balance could be poised either with or without the load of the cube, disk, wire and bar and accordingly this load could be found by difference. The load of the disk in mercury, the wire and bar, was similarly found in another measurement.

The rest-point of the balance was found by observing seven successive extreme readings of the balance oscillations.

The mercury container was a box, 13 cm cube, made of five glass plates cemented together. The open top was covered by a glass lid, made in two parts so that it could be placed on the box when the cube and its supporting wire were in position. The glass box was placed in a close-fitting aluminium box, again with a lid in two parts, and blocks of cork 2 in. thick for thermal insulation were assembled around the aluminium box. Holes were drilled near the corners of each lid to accommodate the glass tubes containing the thermocouples for measuring the mercury temperature (see § 4 (*c*)).

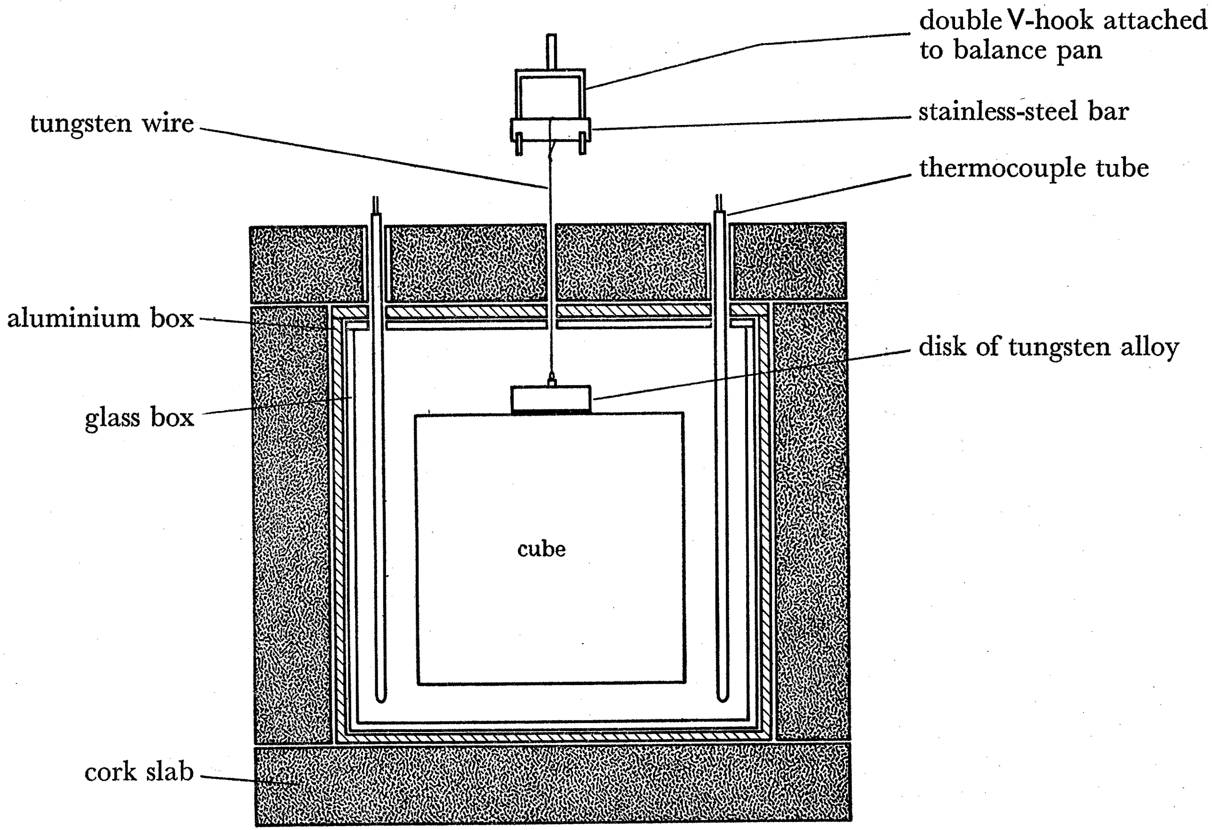

FIGURE 13. Mercury container and support of cube by tungsten alloy disk.

All equipment which came into contact with mercury was cleaned very thoroughly. To remove grease and adsorbed ions the glass box was steamed out with grease-free steam (see Barber, Handley & Herington 1954) and then dried *in vacuo*. The thermocouple tubes were washed successively with dilute nitric acid, distilled water and acetone. The cube itself and the supporting disk or cage were swabbed with *iso*propyl ether on fresh cotton wool. It was found that *iso*propyl ether left no residue and that swabbing was, for this purpose, as satisfactory as distilling the solvent on to the cube surface and was much more convenient. Methods which might involve warming the cube were not tried lest the heating should change the dimensions of the cube.

If mercury is poured round the cube in air at atmospheric pressure, quite large volumes of air adhere to the cube, and it was found that if the weight of the cube in mercury is not to vary by more than a few milligrams, the mercury must be poured round the cube at an air pressure less than about 25 μb. Since, with the apparatus available, it was as easy to attain a pressure of between 2 and 3 μb, the mercury was always poured round the cube at such a pressure, which is slightly greater than the vapour pressure of mercury at 20° C.

The following arrangements were therefore made for immersing the cube in mercury. The top of the trolley which carried the mercury container was a disk of brass on which a large bell jar could be placed. A mercury diffusion pump was fixed to the plate and there was a connexion for a Pirani gauge. The aluminium box, with the cork insulation removed, was first supported on the base-plate by a temporary framework arranged so that after the mercury had been run into the inner glass container, the bottom cork slab could be placed under the aluminium box which was then lowered on to it. The cleaned cube with the supporting disk wrung on was then placed in the glass container which had previously been steamed out and dried, and the glass lids were placed in position.

A mercury reservoir was then assembled above the glass box. It was a stainless-steel bowl, and it had a stainless-steel unlubricated drain tap that could be turned by a shaft passing through an O-ring seal in the brass base-plate. The reservoir and tap were cleaned by steaming. After mercury had been poured into this reservoir it was usually found that a little dust or grease had accumulated on the surface and it was removed by sucking it off through a fine glass tube. The bell jar was then placed over the apparatus and after reducing the pressure to between 2 and 3 μb as read on a Pirani gauge, the drain cock of the reservoir was opened allowing the mercury to run into the glass box and cover the cube. The reservoir contained rather more mercury than was needed in the box and so, by drawing the mercury from the bottom of the reservoir, any surface contamination that had not been sucked off or had accumulated subsequently, was left behind, while by allowing the mercury to splash on to the cube in a high vacuum, any moisture was removed. Air was now admitted, the bell jar and reservoir were removed and the surface of the mercury in the box was examined and any dust sucked off. Finally, the aluminium lids were screwed down, the cork insulation assembled and the cleaned thermocouple tubes passed through the holes in the covers into the mercury.

The mercury in its lagged container was left for at least 24 h before any weighings were made.

The weight of the cube and disk in mercury was found by substitution weighings. The cube was suspended from a balance pan on which weights could be placed and the whole was counterpoised by a load suspended from the other arm of the balance. The mercury container was first raised so that the stainless-steel bar rested on the fixed vees free of the balance hooks, the balance was poised by placing appropriate weights on the pan, and two rest-points of the balance were determined. The container was then lowered, bringing the stainless-steel bar on to the V-hooks and applying the load of the cube to the balance and, weights having been removed from the balance pan to poise the balance, four more rest-points were determined at the same time as thermocouple readings were taken for the mercury temperature. Finally, two more rest-points were taken with the stainless-steel bar off the balance. With this scheme, no error is caused by any inequality in the lengths of the arms of the balance, while the effects of steady changes in the lengths of the arms are also eliminated. Corrections were applied for the errors of the poising weights and for air buoyancy. Two sets of observations were usually made in a day.

When a satisfactory series of weighings had been completed, the cube was removed from the mercury, cleaned and the support disk re-wrung, after which the cube was re-immersed in mercury and a further series of weighings made. The detailed results are given in § 5.

(*c*) *Temperature measurement and control*

Thermocouples were used to compare the mercury temperature with the temperature of an oil bath in which two platinum resistance thermometers were immersed. This scheme was adopted because it was inconvenient to place the thermometers directly in the mercury.

Each group of thermocouples consisted of five pairs of copper/constantan junctions in series. The five junctions in the mercury were embedded in paraffin wax in a glass tube which projected vertically into the mercury through the lids of the container (see above). The junctions were arranged to be spaced equally throughout the depth of the mercury so that the temperature indicated by the five junctions in series was the mean temperature throughout the depth of the mercury. The other junctions were inserted into holes in a brass block which also had two vertical holes to receive the platinum resistance thermometers. They lay in the horizontal plane passing midway through the windings of the thermometers, and were so disposed in a rectangular array that the mean temperature of each group of five junctions was equal to that of the two platinum thermometers, assuming that temperature gradients in the block were linear. The block was immersed in a cork-lagged bath of well-stirred paraffin oil and its temperature normally changed by less than 0·005° C in the course of observations lasting $\frac{1}{2}$ h.

The temperature difference to be measured by the thermocouples should be as small as possible so that errors associated with temperature gradients in the leads should be small, and by good fortune it was found that the temperature gradients in the room were such that the bath temperature was always lower than the mercury temperature at the beginning of the morning so that the bath could be heated until its temperature was within about 0·05° C of the mercury temperature.

The thermojunctions were connected in series with a suitable galvanometer through a selector switch like that described in § 3 (*d*) (ii) and the system was calibrated against the two platinum resistance thermometers.

The platinum resistance thermometers are those used by Sears & Barrell (1932) in their determination of the metre and the yard in terms of wavelengths of light, and the same potentiometer and standard coils were used to measure the resistances (50 Ω) at 20° C. An additional standard coil was provided to measure the resistances at 0° C to enable the zero point to be determined frequently (a water triple-point cell (see Barber *et al.* 1954) was used for this purpose).

During the course of the measurements, it was found that the measured resistance of a thermometer depended on the region of the potentiometer dials being used, despite the fact that the dial resistances had been carefully calibrated and corrections were applied for their errors. This effect appears to be connected with the fact that the standard coils were not matched closely to the thermometers so that different parts of the potentiometer dials were used when comparing with the standard and with the thermometer. Therefore, a set of standard coils, closely matched to the thermometer resistances, was prepared (by Mr C. R. Barber of the Physics Division) and when they were used it was found that the measured resistances of the thermometers at the triple point of water agreed well with the values determined with the Smith bridge in the Physics Division (see Barber, Gridley & Hall 1955). Unfortunately, the matched coils were not available until all the measurements with the cube had been completed, but by intercomparing them with the unmatched standard coils and with the thermometers at 0 and 20° C, it was possible to arrive at corrections (of the order of 0·002° C) to be applied to temperatures determined from measurements with the unmatched coils. These observations also show that the standard deviation of a single observation of temperature is between 0·0005 and 0·001° C and that the corrected temperatures may still be subject to a systematic error of up to 0·001° C.

The resistances of the thermometers at 0° C have remained very stable, neither having changed by more than the equivalent of 0·001° C in the course of 3 years and each being within the equivalent of 0·002° C of the values recorded by Sears & Barrell (1932).

The temperature of the mercury was kept sufficiently steady by working in the air-conditioned room with the temperature controlled to about ±0·1° C and by the 2-in. cork lagging around the mercury container. A single group of four rest-points of the balance with the cube freely suspended in mercury took about 10 min to observe, and in this time the temperature of the mercury rarely changed by more than 0·004° C, corresponding to 0·7 p.p.m. of the density of mercury. Since thermocouple readings for the mercury temperature were taken simultaneously with the balance observations, the mean temperature corresponding to the mean of the group of four rest-points is well determined even with the most rapid changes that occurred.

The mercury container under the bench on which the balance stood had the wall of the room at the back and a brick pillar to one side. The temperatures recorded by the thermocouples at the four corners of the box almost always differed systematically, those at the back being about 0·002 or 0·003° C less than those at the front and because of this the mean temperature of the box is probably uncertain by about 0·0005° C.

The temperature errors may be summarized as follows: the thermocouple errors are probably unimportant; the standard deviation of the mean temperature of the two platinum resistance thermometers is about 0·0007° C (but may exceptionally be greater if the oil-bath temperature changed appreciably); the time and space averages of the mercury temperature each have a standard deviation of about 0·0005° C.

The standard deviation due to all random sources of error is therefore about 0·001° C. In addition, there may be a systematic error of up to 0·001° C.

(*d*) *Surface tension forces*

As was mentioned in § 1 (*c*), it was possible to choose the volume and mass of the cube so that it weighed only 217 g in mercury and could be suspended by a tungsten wire about 0·05 mm in diameter, so that, assuming the surface tension of mercury to be 500 dyn/cm, the surface tension force at small contact angles would be about 7 dyn, corresponding to about 0·7 p.p.m. of the density of mercury. Since the angle of contact of mercury against a solid may be very variable, its value for the tungsten wire was measured while the wire was moving up and down through the mercury as the balance was swinging. The contact of the mercury with such a fine wire could not of course be observed directly, but the general form of the deformed mercury surface around the wire can be calculated and from observations of the surface figure and an assumed value of the surface tension the angle of contact may be inferred.†

Let θ be the angle of inclination of the surface to the horizontal at a distance x from the axis of the wire and let α be the angle of contact of the mercury against the wire. If θ_c is the inclination of the surface to the horizontal at the contact, $\theta_c = \alpha - \frac{1}{2}\pi$. It may then be shown that

$$\sin\theta = \sin\theta_c\, K_1(bx)/K_1(ba).$$

K_1 is the modified Bessel function of order unity, a is the radius of the wire and $b = (g\rho/\gamma)^{\frac{1}{2}}$ where g is the value of gravity, ρ the density of the mercury and γ the surface tension.

θ_c was calculated from measured values of the radius at which θ attained a specific value. A diagram of the apparatus used is shown in figure 14.

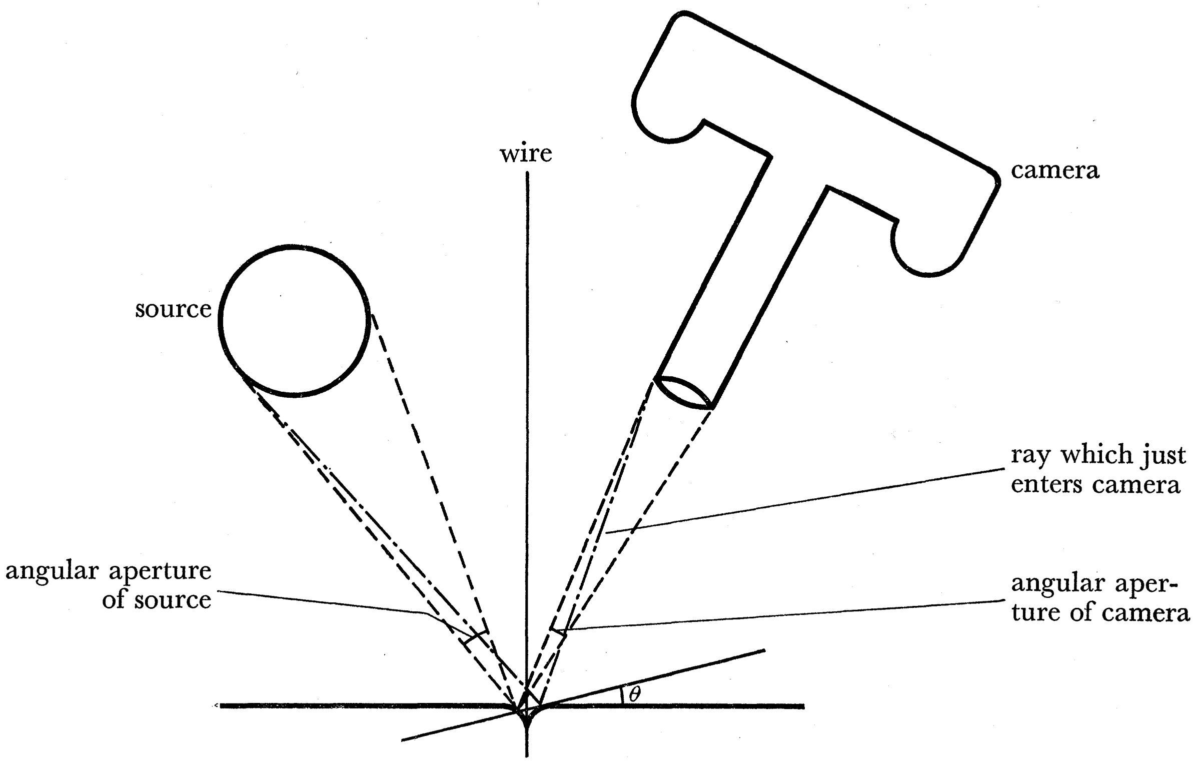

FIGURE 14. Diagram of apparatus for measurement of contact angle of mercury against wire.

A source of light illuminates the mercury surface which is photographed through a microscope system. Let ϕ_1 be the angular semi-aperture of the source and ϕ_2 that of the camera objective. Then if θ, the inclination of some region of the surface to the horizontal exceeds $\frac{1}{2}(\phi_1+\phi_2)$, no light from the source will be reflected into the camera objective from that region, while if θ is less than $\frac{1}{2}(\phi_1-\phi_2)$, all light from the source incident on that region will be reflected into the objective. Accordingly, the image of the mercury surface formed in the camera should show a dark region surrounding the point of entry of the suspension wire, a penumbral band in which the surface inclination is between $\frac{1}{2}(\phi_1+\phi_2)$ and $\frac{1}{2}(\phi_1-\phi_2)$ and an outer bright area where the inclination is less than $\frac{1}{2}(\phi_1-\phi_2)$.

The photographs actually taken show no penumbral zone but a sharp division between the bright and dark regions, no doubt because the range of contrast in the image is too

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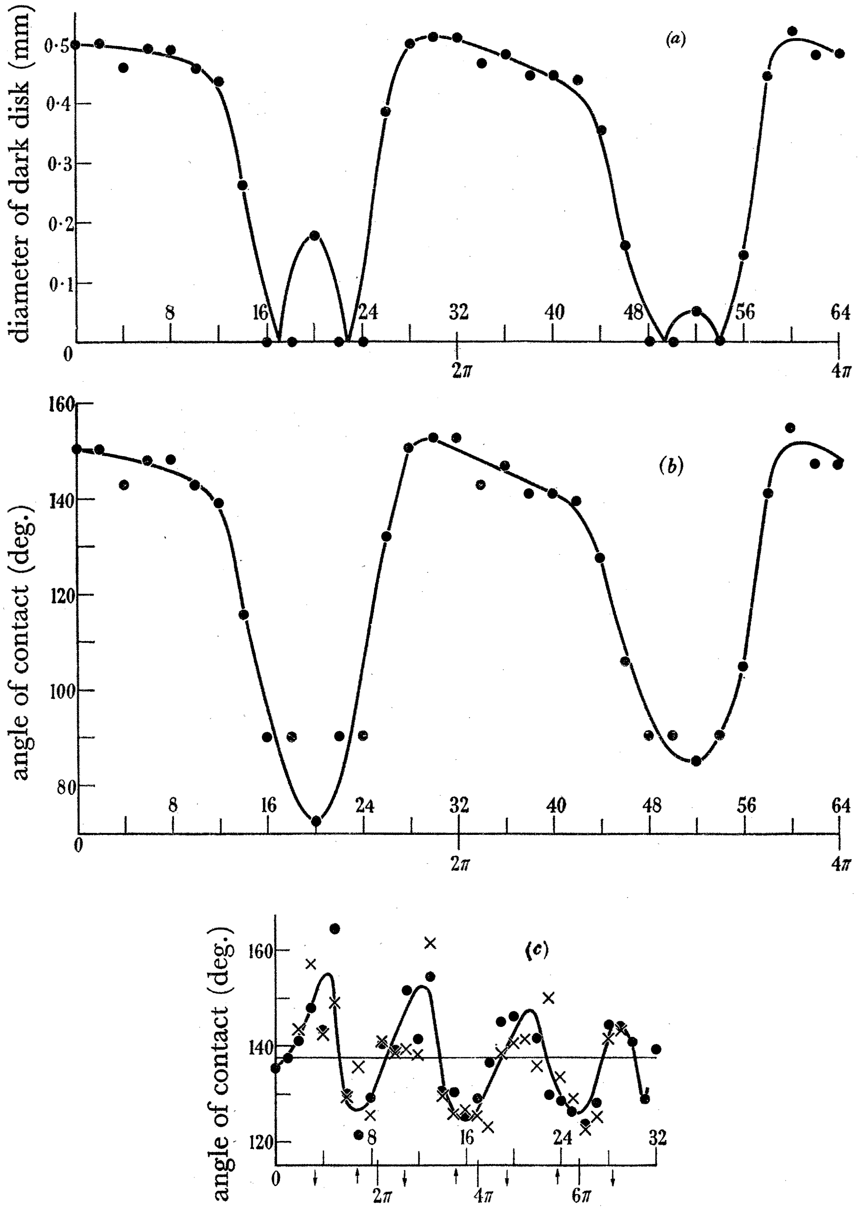
† A brief account has already been given by Cook & Stone (1954).

great for the emulsion used. This makes the interpretation of the results somewhat uncertain because the observed diameter of dark area might correspond to any angle between $\frac{1}{2}(\phi_1+\phi_2)$ and $\frac{1}{2}(\phi_1-\phi_2)$. However, various considerations limit the indeterminacy and



Abscissae in each diagram: {upper scale, time (sec)
lower scale, phase

FIGURE 15. Measurement of the angle of contact between the mercury and the suspension wire. (*a*), (*b*) Period of oscillation 32 s. (*c*) Period $8\frac{1}{2}$ s; arrows indicate direction of motion of wire; ●, ×, results of separate runs.

useful conclusions can be obtained. The variation of the measured diameter of the dark area when the cube was hung from the balance, and the period of oscillation was 32 s, is shown in figure 15(*a*) and the calculated angles in figure 15(*b*). The results shown in figure 15(*c*) were obtained with the heavy alloy cage alone and a period of 8 s.

The most interesting feature of these results for the cube is that for a short period the contact angle falls below 90°, that is, that the mercury surface is raised above the horizontal. This conclusion is unaffected by the boundary inclination chosen in reducing the results.

To correct the weighings of the cube or cage in mercury, the mean upward force on the wire averaged over a complete period of oscillation is required. The values calculated from the curves of figure 15 are:

cage alone, period 8·5 s, mean force:	5·5 dyn;
cube and cage, period 32 s, mean force:	3·5 dyn.

The variation in the observed static angles corresponds to a range of force of from 5·0 to 5·5 dyn.

In applying these results to actual weighings, two differences in conditions must be allowed for. The first is that most weighings were made not with the cage but with the disk; however, the period of the balance with the disk alone in mercury is not very different from that with the cage alone and the cage figures should apply to weighings of the disk. More important is the difference of amplitude of oscillations. The results above were obtained with amplitudes, read on the microscope scale, of about four divisions, whereas definitive weighings were made with amplitudes generally less than two divisions. It is, therefore, considered that the mean upward force on the balance when weighing the cube did not differ by more than 2 dyn and probably by not more than 1 dyn from the mean upward force when weighing the cage or disk alone. This conclusion is supported by the fact that no indication has ever been observed that the rest-point of the balance when the cube is being weighed depends on the amplitude of oscillation up to two scale divisions.

It has, therefore, seemed best to apply no correction for surface tension forces to the difference between the weight of the block and cube and that of the block alone.

(*e*) *Reduction of weighings to* 20° C *and calculation of the density at* 20° C

It is convenient to express the results of the weighings of the cube in mercury as the corresponding weight of the cube alone in mercury at 20° C; this is equal to the weight of the cube and heavy alloy disk in mercury together with the tungsten wire and stainless-steel bar, less the weight of the heavy alloy disk in mercury, tungsten wire and stainless-steel bar, all reduced to 20° C. The weight of the disk in mercury, plus wire and bar, was determined at intervals throughout the observations and the results are given in table 9. Since the variation of the disk weight is so small despite occasional breakages of the wire the mean value, 12·3952 g, has been used in reducing all the weighings of the cube. The temperature coefficient of this weight was calculated from the coefficients of expansion of mercury and the heavy alloy to be 6·4 mg/° C.

TABLE 9. WEIGHT OF HEAVY ALLOY DISK IN MERCURY TOGETHER WITH WIRE AND SUPPORT BAR

date	weight at 20° C (g)
30 September 1954	12·3943
19 April 1955	12·3952
8 July 1955	12·3960
19 September 1955	12·3951
mean:	12·3952 g

s.d. of single weighing: 0·7 mg

The temperature coefficient of the weight of the cube in mercury was calculated from the following formula for the expansion of mercury (Beattie *et al.* 1941):†

$$10^8\alpha = 18144{\cdot}01 + 0{\cdot}7016t + 2{\cdot}8625\times10^{-4}t^2 + 2{\cdot}617\times10^{-6}t^3,$$

where α is the mean coefficient of expansion between the temperatures of 0 and t °C int.

If ρ is the density of mercury and V the volume of the cube at 20° C, the differential coefficient of the mass M of mercury displaced by the cube with respect to temperature is

$$\left.\frac{\mathrm{d}M}{\mathrm{d}t}\right|_{20} = -\frac{\mathrm{d}}{\mathrm{d}t}(\rho V)_{20}$$

$$= -V\left.\frac{\mathrm{d}\rho}{\mathrm{d}t}\right|_{20} - \rho V \left.\frac{1}{V}\frac{\mathrm{d}V}{\mathrm{d}t}\right|_{20}.$$

Now
$$\left.\frac{\mathrm{d}\rho}{\mathrm{d}t}\right|_{20} = -\rho_{20}\frac{\rho_{20}}{\rho_0}\left.\frac{\mathrm{d}(\alpha t)}{\mathrm{d}t}\right|_{20},$$

$$\frac{\mathrm{d}(\alpha t)}{\mathrm{d}t} = 18172{\cdot}5\times10^{-8}/^\circ\text{ C at }20^\circ\text{ C}$$

and taking ρ_{20} to be 13·5459 g/cm³ and ρ_0 to be 13·5951 g/cm³,

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = -2{\cdot}45272\times10^{-3}\text{ g/cm}^3\ ^\circ\text{C}.$$

The other numerical values are

V, volume of cube at 20° C = 701·80 cm³,

$(\rho V)_{20}$, displaced mass of mercury = 9506·5 g,

$$\left.\frac{1}{V}\frac{\mathrm{d}V}{\mathrm{d}t}\right|_{20} = 15{\cdot}576\times10^{-6}/^\circ\text{ C}\ (\S\ 3\,(d)\ (\text{iii})).$$

Hence
$$\left.\frac{\mathrm{d}M}{\mathrm{d}t}\right|_{20} = 1{\cdot}5732\text{ g}/^\circ\text{ C}.$$

(Sears's (1913) quartic formula for the expansion of mercury leads to a value of 1·5743 g/° C.)

The coefficient has also been measured directly by weighing the cube in mercury at temperatures between 19·24 and 20·73° C. The result, 1·5766 g/° C with a standard deviation of 1·1 mg/° C, differs from the calculated value by about three times its standard deviation, but since the mean temperature of the weighings is within 0·2° of 20° C, the effect on the density of mercury of the difference between the calculated and observed coefficients is less than 0·1 p.p.m. and the calculated coefficient has been used in reducing the results.

The weight of the cube reduced to 20° C is correlated with the change of the balance rest-point between the first and last of the four rest-points of a group. As indicated above (§ 4 (*b*)) the cube was immersed a number of times in each sample and for each immersion a number of weighings was made extending over some days. The results of the weighings for some of the immersions are shown in figure 16, the mean weight at 20° C being plotted against the change of weight in 10 min (the differences of rate of change of weight in the other immersions were not great enough to display the correlation). The cause of this

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† The reasons for using the results of these authors have been discussed elsewhere (Cook 1956).

behaviour is, almost certainly, that when the mercury temperature is changing the mean temperature in the container lags slightly behind that of the thermocouples which are quite close to the walls of the container. The average regression coefficient of weight on rate of change of weight, namely 8·8 min, is close to the time constant estimated for this temperature lag. The time constant is quite well determined from the observations and has been used to reduce all weights to zero rate of change of weight.

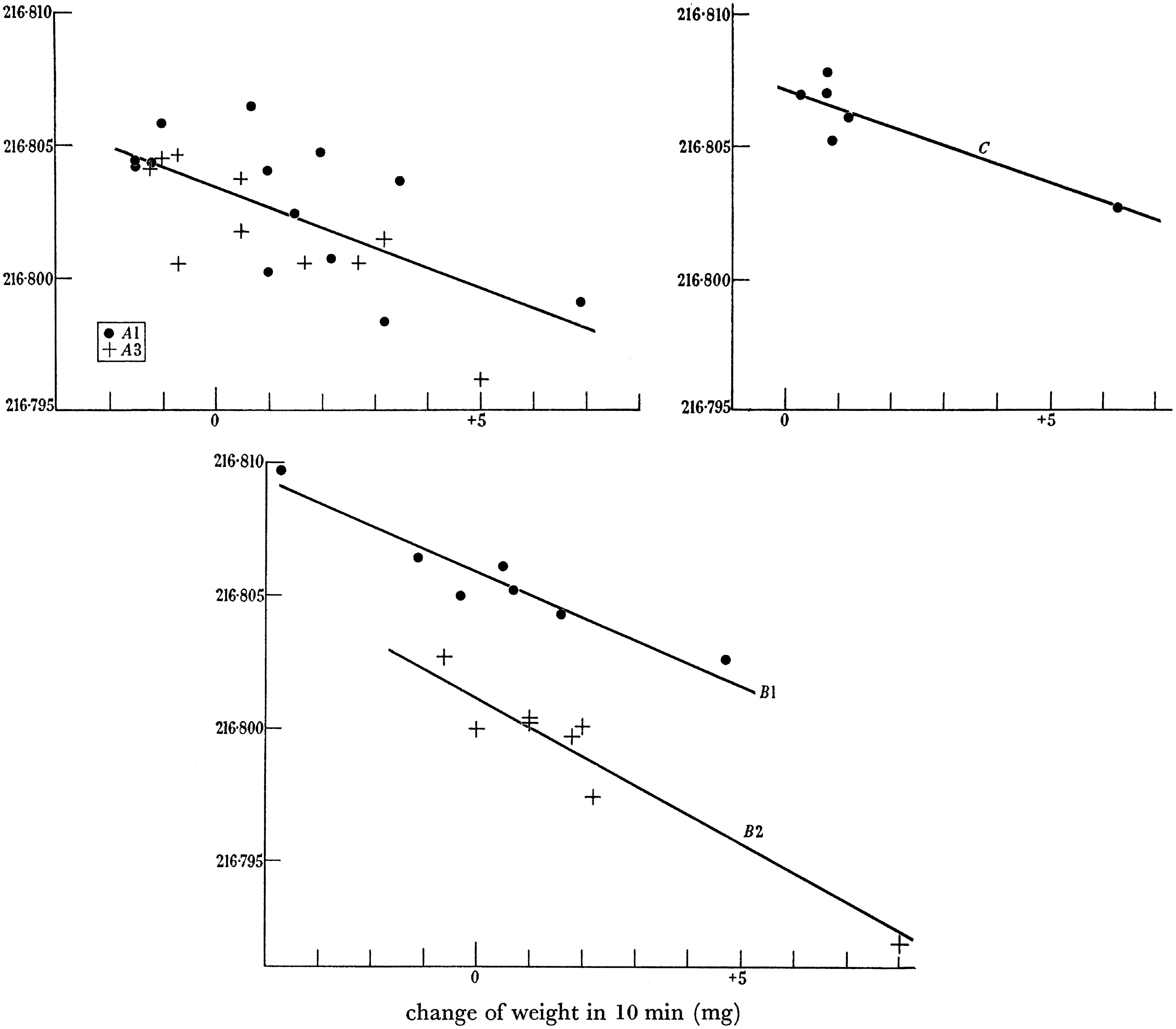

Figure 16. Dependence of the observed weight of the cube in mercury (immersions A1, A3, B1, B2 and C) reduced to 20° C on the rate at which its weight was changing.

The density of the mercury in which the cube was weighed at 20° C is then M/V, where M is the mass of mercury displaced by the cube at 20° C, corrected to zero rate of change of weight, and V is the volume of the cube at 20° C.

The density so determined is that of mercury under the pressure at the level of the centre of the cube which was about 60 mm below the mercury surface and therefore at a pressure about 80 mb above atmospheric pressure, and since the initial compressibility coefficient of mercury at atmospheric pressure is $4 \times 10^{-6}\ \mathrm{b}^{-1}$ (Bett *et al.* 1954) the measured density is about 0·32 p.p.m. greater than the density under atmospheric pressure. The measured values have therefore been reduced by this amount to correct them to atmospheric pressure.

5. The densities of four samples of mercury

(*a*) *The chemical purification and isotopic content of mercury*

Since the main reason for undertaking measurements of the density of mercury was to enable the pressure exerted by a mercury column to be calculated in absolute units, it might be thought that it would be sufficient to measure the density of the mercury, of unspecified composition, in the primary barometers of the National Physical Laboratory, just as Marek (1883) limited himself to a similar aim.

Table 10. Amounts of impurities that might produce a change of 1 p.p.m. in the density of mercury

metal	quantity (p.p.m.)	metal	quantity (p.p.m.)
Pt	2·7	Sn	1·1
Au	3·4	Fe	1·4
Ag	see note †	Na	0·13§
Zn	1·5‡	Ca	0·13
Cu	1·9	Al	0·25
Pb	4·3		

† Maey (1905) has shown that the specific volume of a solution of silver in mercury is the same as that of mercury up to nearly 30% Ag.
‡ Maey (1905).
§ Maey (1899).
Quantities of other elements are calculated for a simple mixture without change of volume.

However, if we knew nothing of the composition of our mercury, our results would be of little value because they could not be compared with those of other observers nor could they be applied to other samples of mercury, and therefore the chemical and isotopic constitution of the samples should if possible be stated with an accuracy corresponding to the precision of 1 p.p.m. aimed at in the density measurements. Unfortunately, it has so far not been possible to state the composition of our samples so accurately because the spectrochemical methods of analysis which, at our request, the Chemical Research Laboratory have been developing, are not yet sufficiently sensitive. The amounts of a number of likely impurities that would probably alter the density of mercury by 1 p.p.m. have been collected in table 10; confronted with the present sensitivity of spectroscopic analysis, it will evidently be very difficult to confirm by quantitative analysis that the density of a given sample is within 1 p.p.m. of that of pure mercury.

Our policy has therefore been to measure absolutely the densities of three carefully purified samples which were then sealed away, free from contamination as far as possible, to serve as reference standards against which to compare other samples of known composition which may be prepared in the future; in addition, a fourth sample was taken from the mercury which will be used to fill a new primary barometer at the Laboratory. At the same time we have obtained such information as we can about the chemical and isotopic constitution of the samples, and we have reviewed the published descriptions of methods of purification in order to choose the most efficient, an analytical study of the methods being of limited value because of the comparative insensitivity of chemical analysis.

All four samples were shaken with dilute nitric acid and then distilled three times in air at a pressure of about 20 mm Hg. It has been observed that shaking mercury for a few minutes with nitric acid in a bottle is much more effective than dropping it through a column of acid and also that it is possible to see an indication of the end point of the reaction. Russell & Evans (1925) found that when impure mercury was oxidized with acidified potassium permanganate solution, the end point of the reaction was shown by the surface of the mercury breaking up into a mass of small globules; the same phenomenon occurs with dilute nitric acid. Hulett & Minchin (1905) have claimed that the zinc content of mercury is reduced to less than 1 in 10^8 by shaking with mercurous nitrate in dilute nitric acid, but have detected zinc after seven passages through the nitric acid column.

The method has recently been placed on a much more secure basis by Dr F. M. Reynolds, of the Chemical Research Laboratory† who has used radioactive tracers to investigate the removal of metals from mercury by dilute nitric acid and has found that the content of many base metals is reduced to one part in 10^8 or less by shaking with dilute nitric acid for 5 or 10 min. We can, therefore, be fairly sure that the base metal content of our freshly purified mercury is negligible.

The distillation of mercury was studied by Hulett & Minchin (1905) who have shown that quite large amounts of zinc and cadmium come over when mercury is distilled in vacuum, but claim that if it is distilled in air at a pressure of about 20 mm Hg, the zinc content is less than one part in 10^{10}. Hulett (1911) has also shown that the amounts of silver, gold and platinum are reduced to a few parts in 10^8 or less after two distillations. It seems that metals with high boiling points remain in the still, while oxidizable metals are oxidized in the air, the oxides being deposited probably in the upper parts of the still. Dr Reynolds, using radioactive tracers, has effectively confirmed Hulett's results on silver and has also shown that the content of tin is reduced to less than 1 part in 10^8 after one distillation.

Our samples of mercury, when freshly prepared, are therefore probably free of any important amounts of metallic impurities, provided great care is taken in cleaning all apparatus, but it is possible that some mercury may oxidize in the still and that the oxide may dissolve in the mercury. It must be appreciated, however, that our samples have been purified in just the same way as mercury used in N.P.L. barometers and should therefore contain about the same amounts of any impurities.

Although Dr Reynolds's work enables us to be reasonably confident that our freshly prepared mercury is sufficiently pure, there still remains the problem of checking that it does not become contaminated during use or storage. Here again, Dr Reynolds's work is of great value for he has confirmed for a number of elements the observations of Wichers (1942) that the presence of a few parts in 10^8 can be detected by the appearance of the surface of the mercury. Using this criterion, our samples do not seem to have been noticeably contaminated in use, and the precautions we have taken, of storing the mercury in

† Chemistry Research (*Annual Report of the Chemical Research Laboratory*, H.M.S.O., 1956).

polyethylene bottles, using stainless-steel apparatus where possible, cleaning all equipment thoroughly and keeping it in a vacuum chamber, and being very careful to shield apparatus and mercury from dust falling from the atmosphere, appear to have been adequate. This conclusion is supported by the internal evidence of the observations (§ 5 (*c*)).

Finally, Mr H. G. Short (of the Metallurgy Division of the National Physical Laboratory) has been able to devise chemical methods of analysis for zinc and cadmium and for these elements we have a direct check on the purity of our samples.

The isotopes of mercury that occur naturally have mass numbers 196, 198, 199, 200, 201, 202 and 204 and variations of as little as 0·005 % in the abundances of one or two isotopes would change the density of a sample of mercury by one part in a million. Certain laboratories which have mass spectrometers were therefore asked if they would measure the isotopic abundances of one of our samples (A) and the results that they obtained are summarized in table 11. It seems that the agreement between the different spectrometers is better than would be expected from the uncertainties estimated for the individual measurements. The standard deviations of the mean results, calculated from the scatter of the laboratories about the mean, correspond to a standard deviation of the density of the sample of 4 p.p.m. so that it would not at present be possible to assert that the isotopic constitutions of two samples differed unless the difference corresponded to nearly 10 p.p.m. of the density. Since the densities of our four samples agree to within 1 p.p.m. the isotopic abundances of the other three samples were not determined.

(*b*) *Particulars of four samples of mercury*

The particulars of the four samples of mercury are as follows.

Mercury A

This was taken from the Metrology Division store and is believed to come from Almaden.

Gross impurities were removed by bubbling moist air through it and it was shaken in small quantities with dilute nitric acid.

It was then divided into two portions, one of which was distilled three times in air at 20 mm Hg pressure in a Pyrex glass still, the other being similarly distilled in a fused silica still. The purpose of this was to determine whether the Pyrex introduced any impurities that the silica did not, but the analytical methods were not sensitive enough for any conclusion to be drawn. All further distillations were done in the silica still.

The two portions were then put together and distilled a further three times in the silica still, so that this mercury has been distilled six times.

The results of measurements of the isotopic abundances of this mercury have been discussed above. All the laboratories analyzed the mercury after it had been distilled three times and in addition, two laboratories analyzed samples taken from the stock before any distillation. The abundances before and after three distillations differ by less than the scatter of the observations.

Mercury B and C

Both these lots of mercury were taken from the stocks of the Laboratory and their origin is uncertain except that C may come mainly from Mexico. Each was cleaned with dilute

TABLE 11. MEASURED ABUNDANCES OF ISOTOPES IN MERCURY A

mass number …	196	198	199	200	201	202	204
measured abundance (%):							
A.E.R.E.	0·18 ± 0·02	10·01 ± 0·10	16·93 ± 0·07	23·21 ± 0·10	13·19 ± 0·05	29·72 ± 0·15	6·76 ± 0·04
N.B.S.	0·156 ± 0·01	10·12 ± 0·10	16·99 ± 0·09	23·07 ± 0·12	13·24 ± 0·07	29·64 ± 0·15	6·79 ± 0·07
A. B. Atomenergi, Sweden	0·154	9·98 ± 0·01	16·95 ± 0·02	23·19 ± 0·02	13·22 ± 0·02	29·74 ± 0·03	6·78 ± 0·01
McMaster University, Canada	0·151 ± 0·001	10·00 ± 0·01	16·93 ± 0·02	23·15 ± 0·02	13·16 ± 0·03	29·83 ± 0·03	6·77 ± 0·02
mean abundance	0·160	10·03	16·95	23·16	13·20	29·73	6·78
s.d. of mean	0·007	0·030	0·014	0·030	0·018	0·040	0·006

Notes: A.E.R.E.: Atomic Energy Research Establishment, Harwell.
N.B.S.: National Bureau of Standards, Washington, D.C.
Standard deviation of mean is calculated from scatter between laboratories.

TABLE 12. RESULTS OF WEIGHING THE CUBE IN FOUR SAMPLES OF MERCURY

sample	immersion	cube face uppermost	number of weighings	mean temperature of observation (° C)	mean weight in mercury at 20° C 216·800 g +	s.d. of single weighing (mg)	mean density of sample at 20° C and 1 atm (g/cm³)	s.d. of mean density† (p.p.m.)
A	1	5	14	20·004	4·1 mg	1·5	13·545 891 6	0·07
	3	2	9	19·845	2·7	1·6		
B	1	4	7	20·165	6·0	0·6	13·545 890 6	0·18
	2	4	6	20·124	5·6	1·7		
	3	1	8	19·988	0·6	1·1		
C	1	4	6	20·050	7·5	0·9	13·545 886 4	0·13
	2	1	1	20·076	3·3	—		
	3	1	3	20·136	9·4	0·6		
	4	6	4	20·172	8·0	1·1		
D	—	—	3	20·150	−3·2	0·8	13·545 901 1	—

† This s.d. is solely that corresponding to the variability of the weight in mercury.

nitric acid and distilled three times in air in the silica still; the initial quantity of each was 3 l. and the final quantity after distillation, 1·5 l. The density of C was measured before distillation as well as afterwards.

Mercury D

This mercury was prepared from 'commercially pure virgin' mercury from Spain. It was cleaned with dilute nitric acid and the density was measured after it had been distilled twice, not three times, in air using the Pyrex glass still instead of the silica one. It is the mercury for a new primary barometer.

The results of Mr Short's analyses of the samples are as follows:

mercury A	before any treatment	Zn < 0·1 p.p.m.	Cd < 0·1 p.p.m.
	after density measurements	0·25 p.p.m.	< 0·1 p.p.m.
mercury B	after density measurements	Zn 0·2 p.p.m.	Cd < 0·1 p.p.m.
C		< 0·1	
D		< 0·1	

(*c*) *Results of the observations*

The observed weights of the cube in mercury at 20° C corrected for the rate of change of weight are shown in figure 17. The effect of the correction for rate of change of weight is to reduce the range over all four samples from 1·8 p.p.m., the greatest and least values in fact being for mercury B, to 1·4 p.p.m. of the density. The results are summarized in table 12. The number following the sample letter is that of the immersion of the cube in the sample.

The results of one immersion, A 2, have been omitted from the figure and table because in this instance the cube was not supported by the heavy alloy disk but was placed in the heavy cage (§ 1 (*c*)) and although the mean weight of the cube in mercury at 20° C, namely 216·803 g agrees excellently with A 1 and A 3, the weight of the cage in mercury has been found to be much less stable than that of the disk and accordingly this result has been excluded from the definitive values.

Figure 17 and table 12 both show that the consistency of weighings of a given immersion is excellent, the scatter, given by the column, 'standard deviation of a single weighing', corresponding to about that to be expected from the estimated temperature errors.

The standard deviation of the mean of an immersion about the sample mean is 2·6 mg and is much greater than can be accounted for by the scatter within immersions. Two of the immersion means—B 3 and C 2—appear to depart significantly from their sample means, yet if they are neglected, the standard deviation of an immersion, now 0·7 mg, is still nearly twice the value to be expected from the scatter within immersions. Discrepancies between immersions may arise from five main causes. First, the weight of the heavy alloy disk and suspension has varied slightly, the standard deviation of a single weighing being about 0·7 mg, which happens to coincide with that of an immersion if B 3 and C 2 are ignored. Secondly, the mercury may become contaminated, when the immersion means would be expected to show a progressive increase in weight as the mercury became less dense (any likely contamination would lower the density). There is no sign of this, which is valuable confirmation that no important contamination has occurred.

Thirdly, the cube has a slight permanent magnetic moment and therefore, to detect any forces associated with this, it was immersed with different faces uppermost, as indicated in table 12, but any such forces do appear to be too small to be detected. In the fourth place, different surface tension conditions might give rise to some scatter, but like the effects of contamination, such errors would be expected to progress from immersion to immersion (day-to-day surface-tension variations contribute, of course, to the scatter within immersions). Finally, the most likely reason for the discrepancies of immersions B 3 and C 2 is that the cube was not properly cleaned, so that its volume would be too large and its weight too small. The discrepancies of B 3 and C 2 are about 0·6 p.p.m. of the density and correspond to a uniform layer of about 9 nm, that is, 90 Å, in thickness, corresponding to about five layers of grease molecules, while the scatter of the other immersions corresponds to about one grease layer, assuming the thickness of a layer to be about 2 nm. Variation in the amount of grease left on the cube thus seems adequate to account for the variability between immersions.

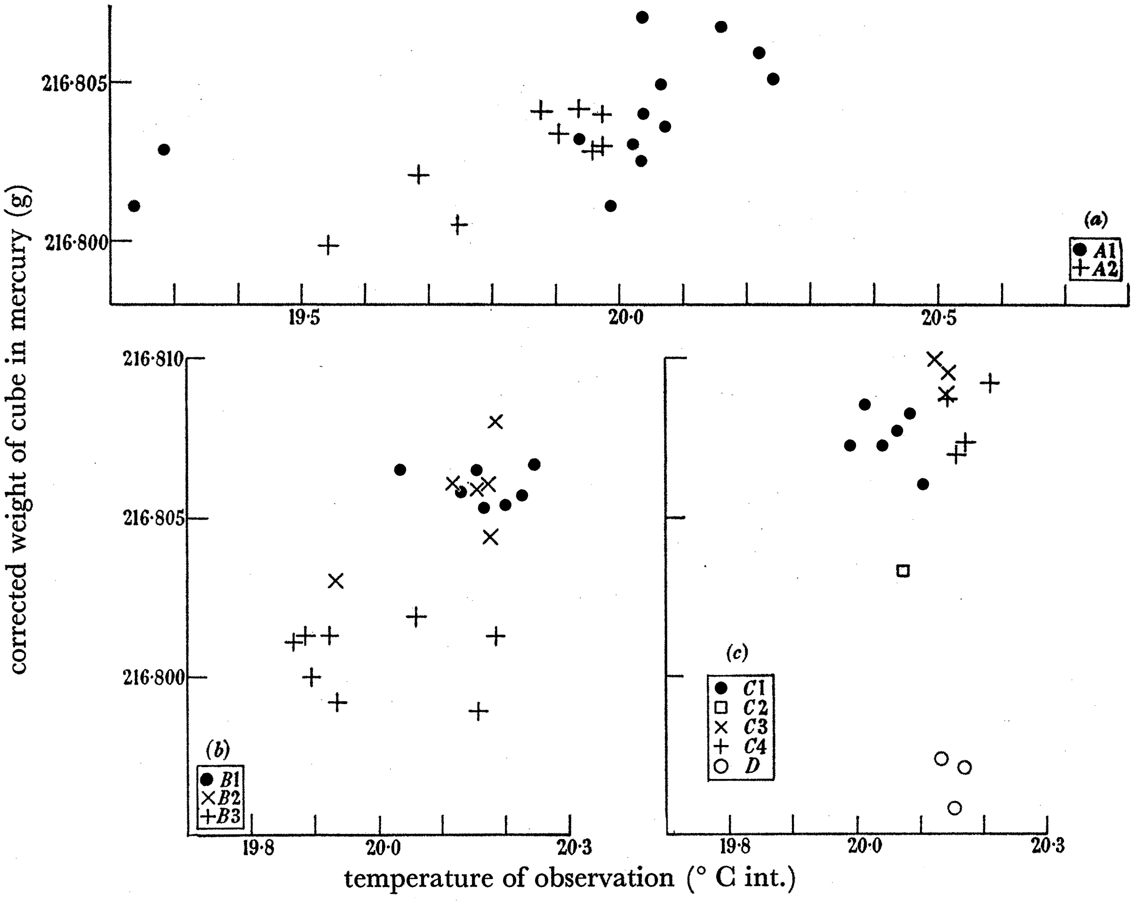

FIGURE 17. Observed weights of cube in mercury reduced to 20° C and corrected to zero rate of change of weight. A variation of 10 mg corresponds to 1 p.p.m.

It is doubtful if the results establish any difference between the densities of the samples A, B and C, and although D appears to have a density 1 p.p.m. greater, the result depends on one immersion only, so that in view of the discrepancies of B 3 and C 2, the evidence for a real difference of D is not strong.

6. Discussion

The uncertainties of the measurements have already been collected in § 1 (*c*); they fall into three groups:

(*a*) Random errors affecting all samples, namely, uncertainties of the mass and volume of the cube and to some extent, that of the surface-tension correction.

The combined standard deviation is about 0·19 p.p.m.

(*b*) Random errors affecting any given sample, namely the uncertainty of the mean weight of the cube in the sample, including that of the weight of the heavy alloy block, together with random errors of temperature measurements.

The combined standard deviation is about 0·15 p.p.m.

The unknown uncertainty arising from possible impurities in any sample is also to be included in this group.

(*c*) Systematic errors affecting all samples:

(i) the uncertainty of the absolute values of the temperatures which may amount to 0·001° C, corresponding to 0·2 p.p.m. of the density;

(ii) errors in the effective volume of the cube.

It is the possible errors in the effective volume of the cube that are the most difficult to assess. The effect of burrs at the corners of the cube on the wringing of the slip gauges to the cube for the measurement of the lengths of the edges has already been mentioned. It would make the measured volume too great and the measured density too small, but the average error in the wringing would have to be 15 nm in order to cause an error of 1 p.p.m. in the density, and it is thought that such an error would have been detected by the distortion of the interference fringes seen in the Kösters–Zeiss interferometer. An average error of 3 nm corresponding to 0·2 p.p.m. of the density, is however quite likely.

A small systematic error is possible in the measurement of surface roughness, because scratches on the polished glass surface would make the measured roughness of the cube surface too great, the apparent volume of mercury displaced too small and the density too large; this error will therefore tend to cancel the former. The whole correction for surface roughness amounts to no more than 2 p.p.m. and it is improbable that the systematic error is greater than 10 % of this although the glass flats used did become scratched in the course of the measurements.

The systematic error which is the most difficult of all to assess is that due to contamination on the surface of the cube. Air, water or grease adhering to the surface might all increase the effective volume above that measured. Of these, grease layers are most likely to have introduced an error, for by immersing the cube at 25 and 2 μb air pressure it has been demonstrated that the effect of air at 2 μb is less than 0·1 p.p.m. of the density, while the results of Bowden & Throssel (1951) show that at this pressure of water vapour, not more than one or two monolayers of water, each about 0·3 nm thick and equivalent to about 0·02 p.p.m. of the volume of the cube, would adhere to the surface. Grease, however, forms monolayers of the order of 2 nm thick, and it has already been seen that the departures of the weights of the cube for immersions B3 and C2 could be due to grease films about five layers thick. The scatter of the results of the other immersions corresponds to one or two monolayers of grease, and while it is possible that the cube was always covered with one or two layers, it might be expected that if the average thickness was four or five layers, the scatter between immersions would have been greater.

The surface of the cube was cleaned with swabs of cotton wool soaked in *iso*propyl ether until no films or streaks of contaminant were visible; dry cotton wool then 'dragged' over the surface just as it did over the polished surfaces of samples of tungsten carbide that had been thoroughly degreased in the vapour of acetone or *iso*propyl ether. This evidence, also, suggests that generally not more than one or two grease monolayers were present on the cube.

To summarize, although we did not degrease the cube in the most thorough way because we could not risk heating it lest its dimensions should change, and although we had no means of measuring the amount of grease or water on the cube, yet we believe that our circumstantial evidence is adequate for us to assert that the effects of air and water films are unimportant, while those of grease films may quite likely have led to our mean measured densities being 0·2 p.p.m. too great but are unlikely to have led to them being 1 p.p.m. too great.

Considering both systematic errors of temperature and of the volume of the cube, it will be seen that they may well amount in all to 0·5 p.p.m. but are rather unlikely to exceed 1 p.p.m.; the random errors of observation are, by comparison, unimportant.

The mean value of the density of all four samples at 20° C and 1 atm pressure is

$$\mathbf{13{\cdot}545\,8924}\ \mathrm{g/cm^3},$$

and the corresponding value at 0° C, calculated by using the expansion formula of Beattie *et al.* (1941) is

$$\mathbf{13{\cdot}595\,0861}\ \mathrm{g/cm^3}.$$

The value of 0° C is subject to an additional uncertainty of 1 p.p.m. arising from the uncertainty of the expansion measurements (Cook 1956).

Our value at 0° C differs by 6·6 p.p.m. from that of Batuecas and his collaborators. Their result is of all previous ones probably the most free of systematic errors although it is subject to whatever error there may be in the accepted value of the ratio of the litre to the cubic decimetre; at the same time, the scatter of the individual measurements is, as has been seen, quite large. The difference is only slightly greater than the estimated standard deviation of Batuecas's final mean result, and in view of evidence from our own results that variations of 1 p.p.m. may occur between samples, it seems that it is inappropriate to discuss in detail the discrepancies between Batuecas's results and ours until these variations have been further explored, an investigation we hope to undertake.

Our observations also provide some evidence of changes of density with purification. The cube was weighed in sample C after washing with nitric acid but before distillation, and the corrected weight at 20° C was 8·9 mg less than the mean value in the sample after three distillations, corresponding to a density greater by nearly 1 p.p.m. The strength of the evidence for a change of density is the same as that for a difference between sample D and the others; if it is accepted that the change is real it means that the distillation removed an appreciable quantity of dense metals (gold, platinum) or else that mercury oxide was formed during the distillation and dissolved in the mercury.

On our present information about systematic errors, differences between samples and effects of purification treatments, it seems reasonable to conclude that our results should represent the density of any similarly purified sample of mercury at 20° C to within 1 or 2 p.p.m.

A further determination of the density of mercury is now being prepared in which the mass of mercury filling a hollow cube of fused silica will be found. The internal dimensions of the cube are being measured by using it as a Fabry–Perot etalon. In this experiment, systematic errors similar to those in the edge-length measurements will be avoided and those due to grease or moisture will reduce the measured density so that the new determination will be a severe check on the present one, provided that the mercury samples do not become contaminated in storage.

The design of the experiment, to which much of the success achieved is to be attributed, is due to Mr P. H. Bigg; to him, to Dr H. Barrell, who developed the method of measuring the lengths of the edges of the cube, and to Sir Edward Bullard, F.R.S., we are indebted for continued encouragement and advice. The cube was lapped in the workshop of the Metrology Division by Mr H. Knoyle; members of the staff of the Metrology Division who have taken part in the observations include Dr Barrell, Mrs P. Anderton, Mrs F. Freshwater, Mrs M. Clough, Miss H. M. Richardson and Mr R. Marriner. We have also benefited from discussions with many members of the staff of the Laboratory, including Mr W. T. Bane who suggested supporting the cube in mercury by a disk wrung to the upper surface.

The work described in this paper forms part of the research programme of the National Physical Laboratory and the paper is published with the permission of the Director of the Laboratory.

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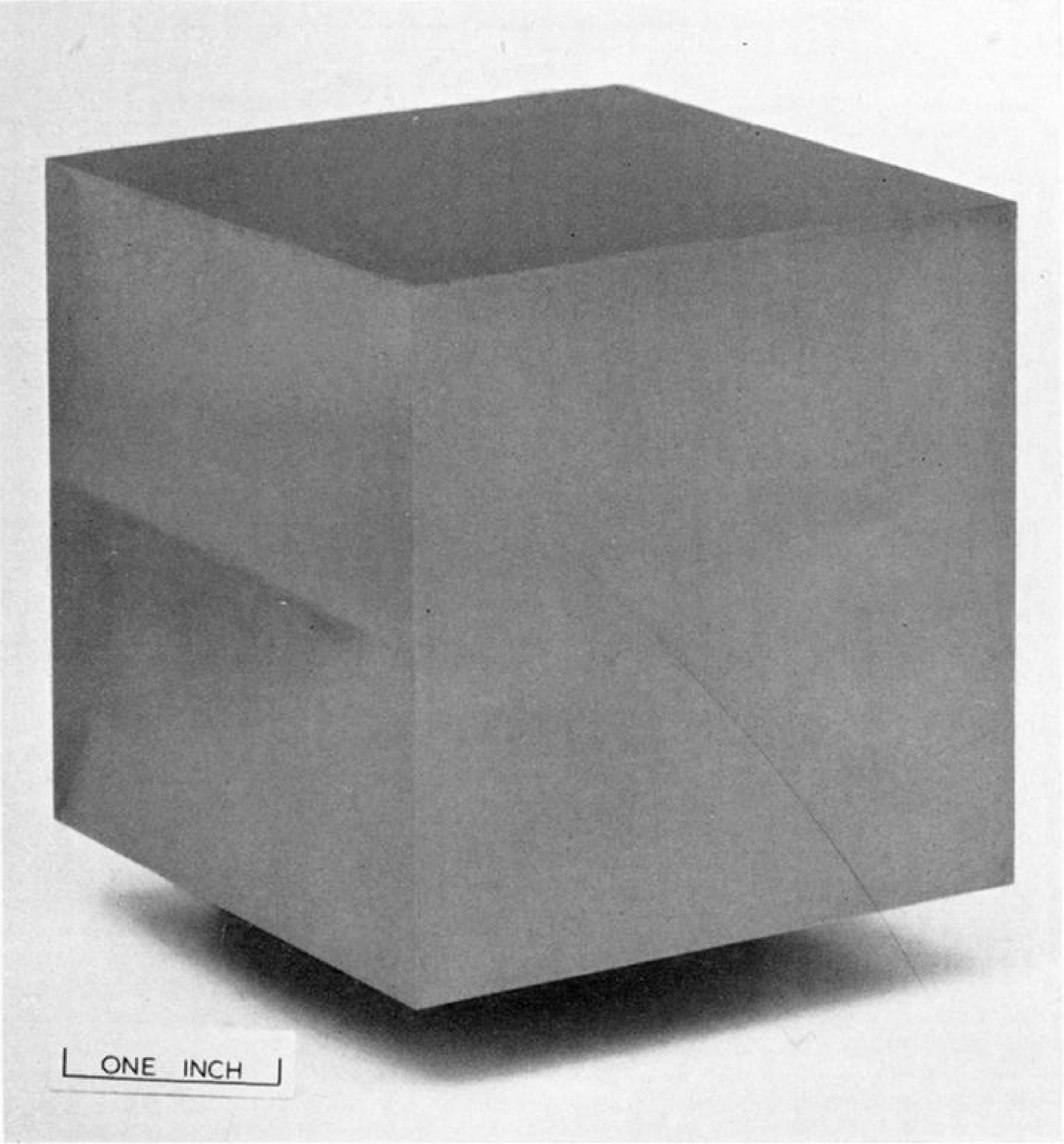

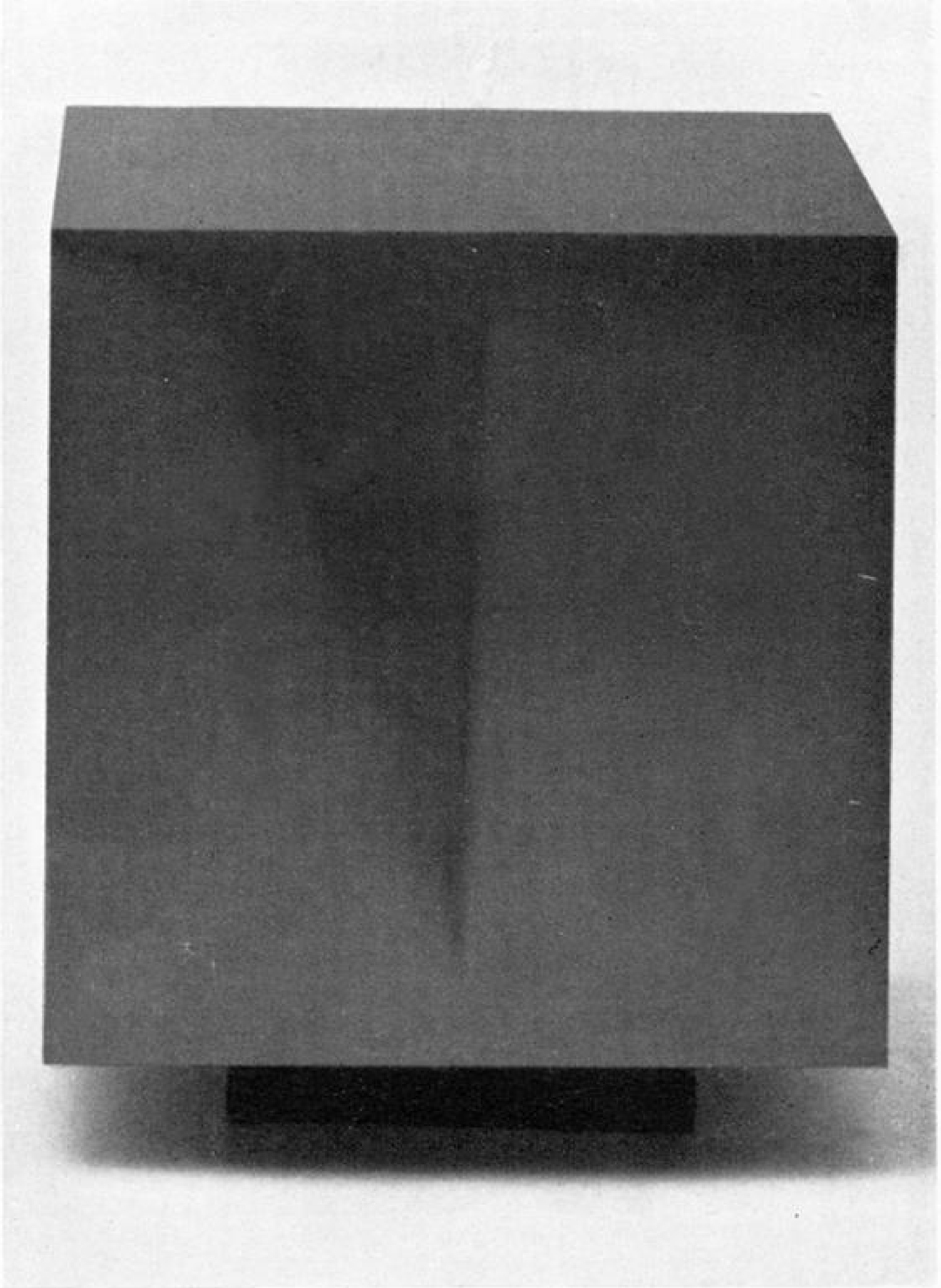

FIGURE 1. General view of cube of tungsten carbide and cobalt.

FIGURE 2. Face 1 of cube showing areas of different superficial appearance.

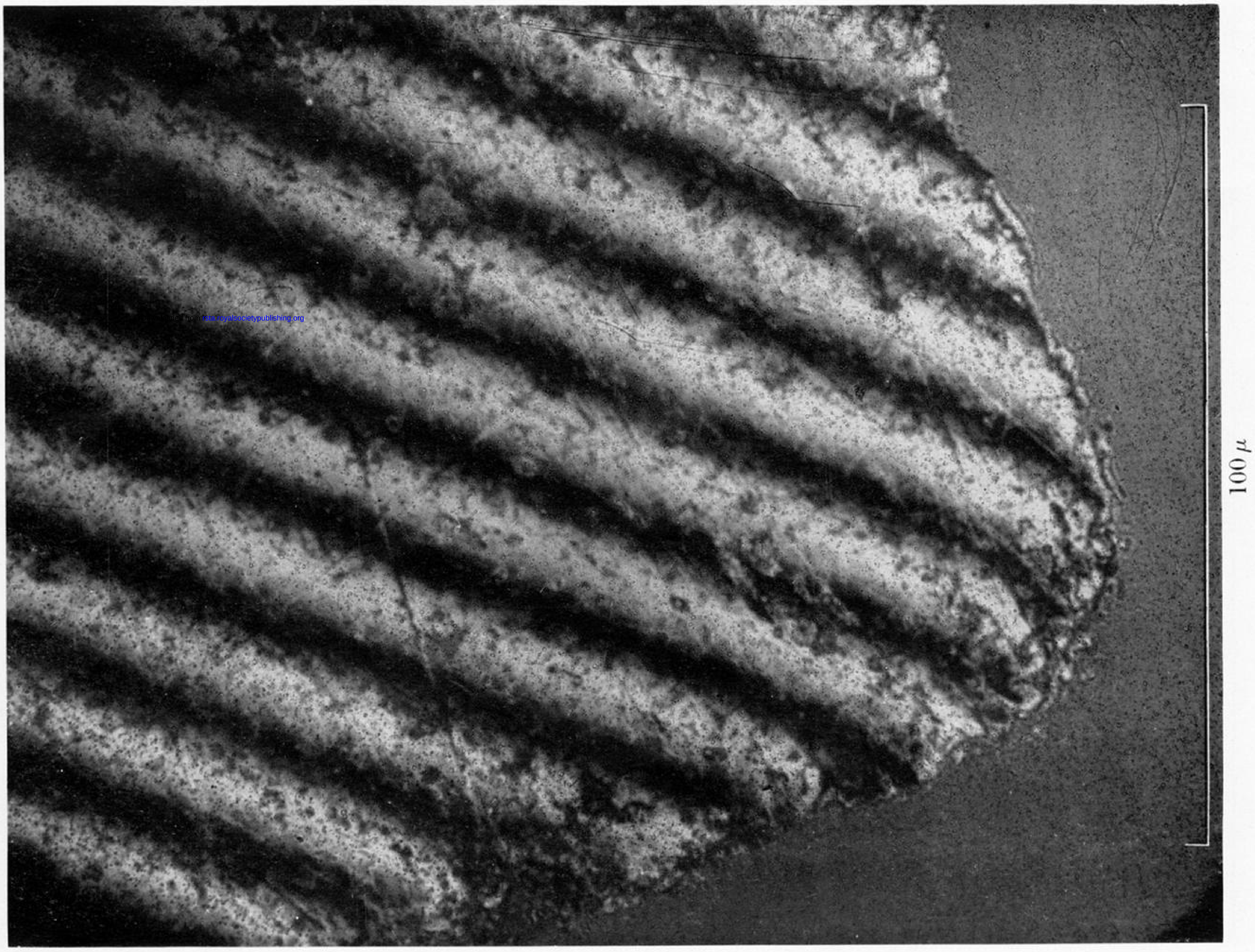

FIGURE 3. Photograph of corner of cube taken with interference microscope.

(*Facing p.* 286)

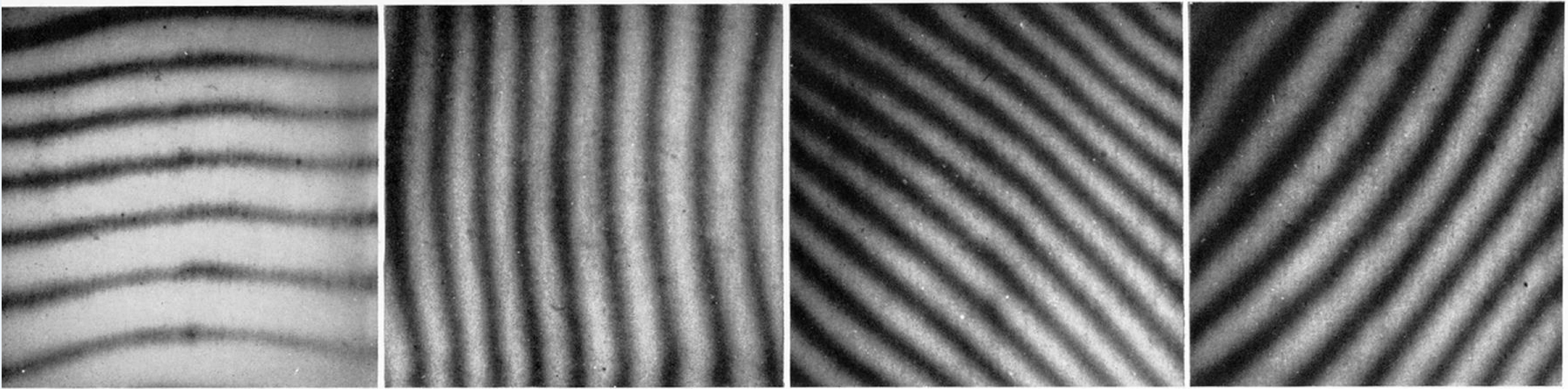

FIGURE 5. Set of four photographs (face 1) of interference fringes obtained with liquid-surface interferometer.

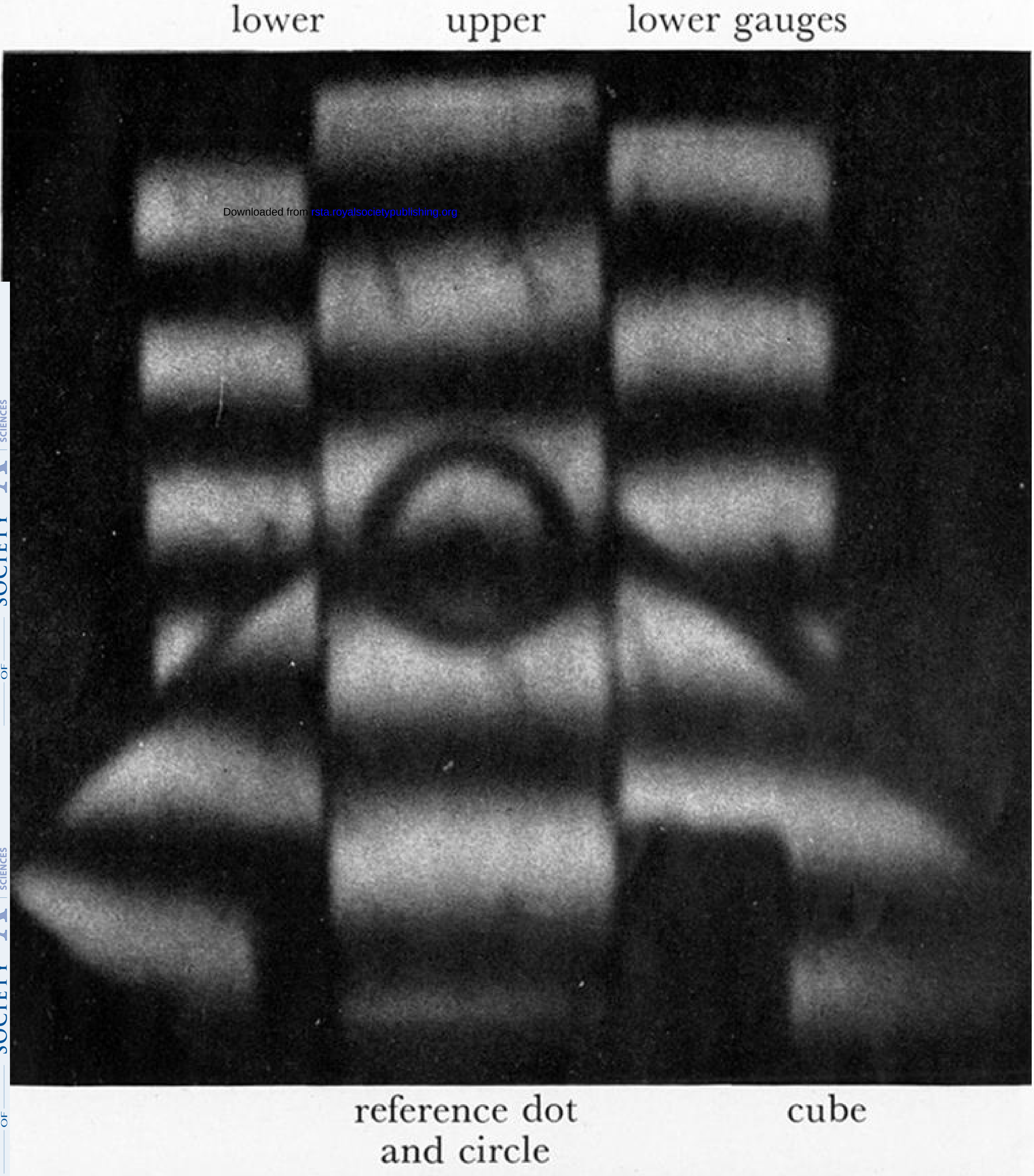

FIGURE 9. Photograph of field of Kösters–Zeiss interferometer showing slip gauges wrung on to cube.

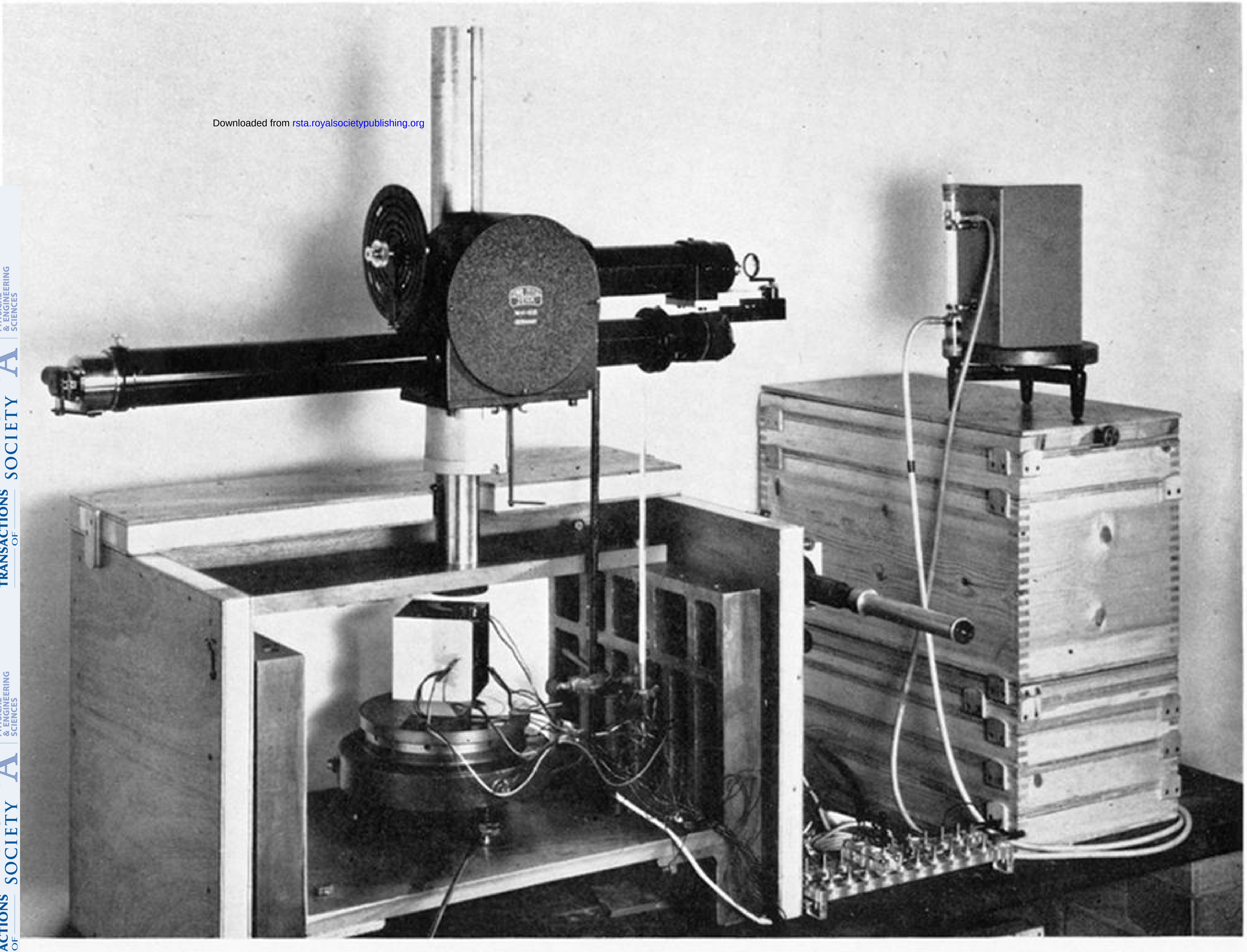

FIGURE 10. Cube set up under Kösters–Zeiss interferometer.