Precise Measurements of the Density of Mercury at 20 degrees C II. Content Method

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PRECISE MEASUREMENTS OF THE DENSITY OF MERCURY AT 20 °C

II. CONTENT METHOD

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[Plates 1 and 2]

CONTENTS

The determinations described in this paper are complementary to earlier ones (Cook & Stone 1957) in which the density of mercury was found from the mass of mercury displaced by a solid cube of measured volume (displacement method). In the present work (content method) the density was calculated from the mass of mercury filling a hollow cube formed of optically worked blocks of fused silica, the internal dimensions of which could be measured by optical interference. The densities of three samples have been measured by both methods, the mean difference between methods being 0·45 p.p.m. (part per million).

The silica cube consists of six optically worked blocks adhering by molecular forces without any cement. The separations of the internal faces are about 7·3 cm, the internal volume is about 390 cm^3 and the mass of mercury contained in it is about 5·3 kg. The mean separations of the internal faces have been measured with standard deviations of about 2 nm but changes in the separation over periods of 6 months or so are nearly ten times this. The uncertainty of the measured volume of the cube is therefore predominantly due to the changes in dimensions; it corresponds to a standard deviation of 0·18 p.p.m.

The cube was filled with mercury under vacuum through a capillary tube in the top face and mercury could be withdrawn through a hypodermic tube inserted through the capillary. The volume of mercury in the cube was found from the height of the meniscus in the capillary when the cube was immersed in a thermostatic bath which had been kept at a temperature constant to 1 to 2×10^{-3} deg C for 18 to 24 h. The mass of mercury in the cube was found by weighing the cube empty and full against a similar empty cube as counterpoise. The overall uncertainty of the mass of mercury filling the cube at a specified temperature has a standard deviation of 0·35 p.p.m.

The standard deviation of the measured density of any one sample is about 0·3 p.p.m., depending on the number of determinations on the sample.

The densities of six samples were measured; three had been prepared for the measurements by the displacement method, one was a sample used to fill primary barometers at the N.P.L., one was supplied by the National Standards Laboratory, Australia, and the sixth by the National Bureau of Standards, Washington, on behalf of the International Union of Pure and Applied Physics. The range of all measurements by both content and displacement methods on all samples is 1·7 p.p.m. The differences between samples are significant; the mean of all measurements is

13·545884 g/cm^3

at 20 °C and 1 atm pressure.

The corresponding value at 0 °C and 1 atm calculated from the expansion formula of Beattie, Blaisdell, Kaye, Gerry & Johnson (1941) is

13·595080 g/cm^3.

The values assigned to the standard wavelengths used in the interferometry measurements were changed between the displacement and content methods and the results of the former have been recomputed accordingly.

1. INTRODUCTION

In a previous paper (Cook & Stone 1957, referred to as I) the reasons for undertaking new measurements of the density of mercury in absolute units were given and previous measurements were reviewed. Briefly, the density of mercury is required to about one part in a million in order that the temperature at which water boils under a pressure of one standard atmosphere as measured by a mercury barometer may be realized to 0·0001 deg C. The density should be known in absolute units (grams per cubic centimetre) so that pressures established in a mercury barometer may be measured in dynes per square centimetre and to avoid the uncertainty in the density of water inherent in previous measurements involving the comparison of the density of mercury with that of water. Previous measurements showed a scatter of about 10 p.p.m. and it was found that our absolute measurements were subject to smaller random and systematic errors than were comparisons of the densities of mercury and water. Paper I was devoted to a description of absolute measurements in which the mass of mercury displaced by a solid cube of measured volume was determined; in the present paper the results of a second method are given wherein the mass of mercury filling a hollow box of measured volume is found.

The largest source of uncertainty in the determinations with the solid cube was considered to be the ignorance of the thickness of grease films remaining on the surface of the cube when it was immersed in mercury. Such films would make the apparent density too great because a volume of mercury larger than that of the optically measured volume of the cube would be displaced; such films on the inside of the hollow cube would, on the other hand, make the apparent density too small so that discrepancies between the two methods should give an idea of the order of magnitude of film effects which, furthermore, should be roughly eliminated from the mean value from the two methods.

A hollow cubical box was constructed of six fused silica blocks, the surfaces of which were polished so that they were optically flat and either parallel or perpendicular as required to allow the blocks to be assembled into a hollow cube. No adhesive was used, the blocks being in optical contact. The separation of any pair of internal faces was about 7·3 cm. The volume of mercury contained in the cube was thus about 390 cm^3 and its mass about 5·3 kg. The upper block of the assembly had a capillary hole in it through which the mercury was filled into the cube under a pressure of air of about 0·1 μb. The internal volume of the cube was obtained from measurements of the separation of the faces by optical interference, together with estimates of the extra volume due to small chips on the internal edges of the blocks. After the cube was filled with mercury under very much reduced pressure, it was placed in a jacket of mercury to equalize the pressures on the inner and outer faces of the cube, and the whole assembly was placed in a thermostatic bath and the height of the mercury in the capillary tube at the temperature of the bath was observed. This enables the volume of mercury in the cube at that temperature to be calculated. The cube was then removed from the bath and weighed with the mercury it contained, a second similar cube being used, empty, as a counterpoise. Finally, the mercury was drawn out of the cube through a hypodermic tube and the cube was weighed empty, again against the second cube as a counterpoise.

The mercury samples, A, B and C described in paper I were again used in the hollow cube and a further sample E similar to D, but not identical with it, was available. In addition samples were measured for the National Standards Laboratory, Australia, and for the National Bureau of Standards on behalf of the International Union of Pure and Applied Physics.

The purification of mercury and the evidence for the purity of our samples A, B, and C were discussed in paper I. Sample E, from mercury that was filled into the primary barometers I and IA of the N.P.L., was prepared in the same way, namely, by washing with dilute nitric acid and distilling three times in air at a pressure of about 20 mb. The samples from the N.B.S. and N.S.L. were purified at those institutions by similar methods.

As in the previous work, the density is found in grams per cubic centimetre at 20 °C on the International Temperature Scale (1948) and the standard of mass is the International Prototype Kilogramme through the British copy kept at the N.P.L. We have, however, used a different standard of length, namely, the wavelength of the orange line (6056 Å) of the atomic spectrum of krypton-86; formally this is consistent with the wavelength of the red line of cadmium taken as the standard in paper I, but in the meantime the wavelengths assigned to the radiations of certain lamps containing mercury-198, which were the actual interferometric sources in that work, have been altered and accordingly the results found in paper I require adjustment to make them comparable with those of the present work.

As in paper I, it is convenient at this point to summarize the uncertainties, expressed as standard deviations, to which the various measurements are liable.

Uncertainty in volume of the cube

wavelengths of interferometric sources (0·0001 Å)	0·6 part in 10^7
volume of defects of internal edges	1
measurement of volume	0·6
changes of volume	1·4
resultant	1·8

Additional uncertainty in volume and mass of mercury contained in the cube

gauging of volume of mercury contained	1 part in 10^7
standards of mass	0·4
mass of mercury	2·5
temperature	2·0
resultant	3·5

Although the object of the measurements was to determine the density of mercury at 20 °C, it was in fact necessary to work at around 21 °C in order to maintain the temperature of the thermostatic bath sufficiently above ambient temperature, controlled at 20 °C, for the thermostat to behave properly. The volume of the cube was accordingly also determined at about 21 °C so that in effect the density was determined at about 21 °C. The reduction to 20 °C was made by using the expansion formula of Beattie, Blaisdell, Kaye, Gerry & Johnson (1941).

2. Description of the hollow cube of fused silica

(a) *Construction and history*

A photograph of the cube is shown in figure 1 (plate 1) and a diagram showing the arrangement of the blocks of fused silica in figure 2. The silica blocks were supplied by the Thermal Syndicate Limited and are of C quality fused silica. This is not the highest optical quality but is quite good enough to see through the blocks, as is necessary in the measurements of the internal dimensions and in observing the height of mercury in the capillary tube. The top and bottom blocks are 12·5 × 12·5 × 2·5 cm, two of the side blocks are 12·5 × 7·3 × 2·5 cm, and the other two side blocks are 7·3 × 7·3 × 2·5 cm. Although only one cube was measured, two were in fact made: an additional quantity of silica equal to one cube was in any case wanted as a counterpoise for the weighings and it seemed a wise precaution to prepare the spare blocks and finally to make them into a spare cube in case of damage to the other. This proved in fact very valuable.

The staff of the optical workshop of the Light Division of the National Physical Laboratory worked and assembled the blocks. After some preliminary difficulties it was found that the blocks could be assembled under *iso*propyl ether and easily moved into their correct positions and that when they were removed from the ether and had dried out, the blocks were in firm optical contact. Similarly, when it was necessary to dismantle a cube, this also could readily be done under *iso*propyl ether. Attempts to assemble and dismantle the blocks dry were, on the other hand, often unsuccessful.

In order to throw off stray reflexions during the interferometric measurements each outer face should be at a small angle (a few minutes of arc) to the inner face of the same block but for ease of working, the blocks were made with parallel faces. Initially, therefore, a separate silica plate with a suitable wedge angle was placed on the appropriate outer face and optical contact was made by a film of glycerine between it and the block. However, during preliminary experiments the cube collapsed, apparently because glycerine had seeped between the blocks and the pressure outside the cube was increased temporarily relative to that inside

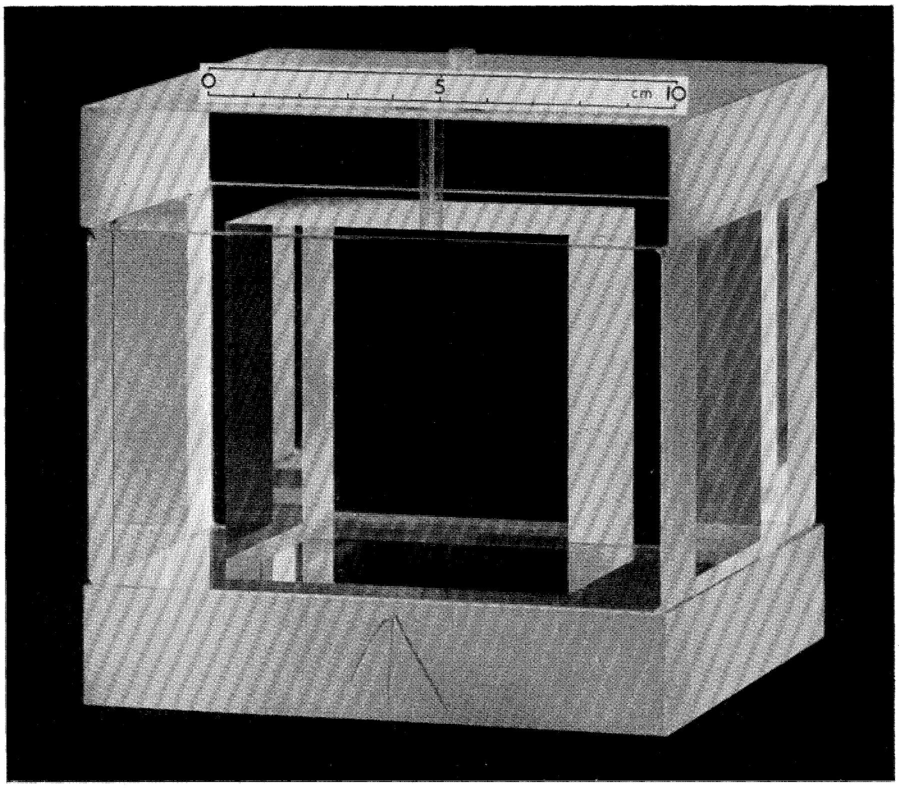


FIGURE 1. Photograph of the hollow cube of fused silica (before attachment of stainless-steel fitting).

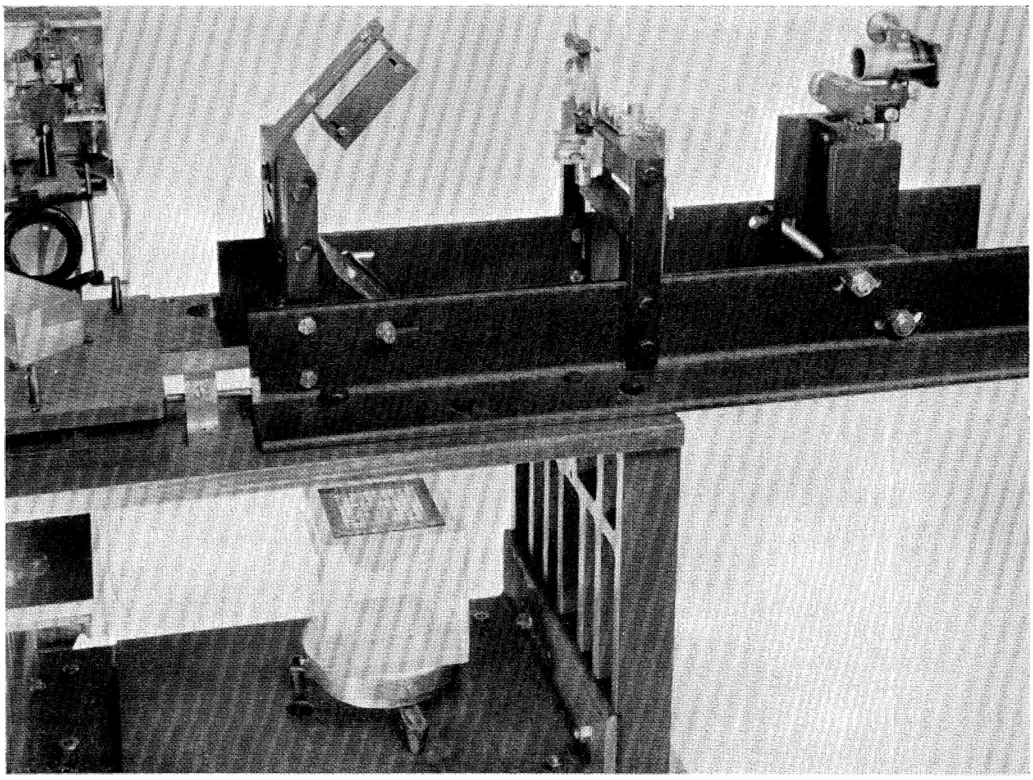
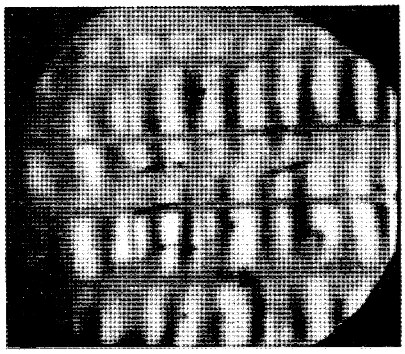


FIGURE 5. Cube in interferometer for observation of three-beam interference fringes, showing graticule on cube. For clarity the cube has been removed from its vacuum vessel.



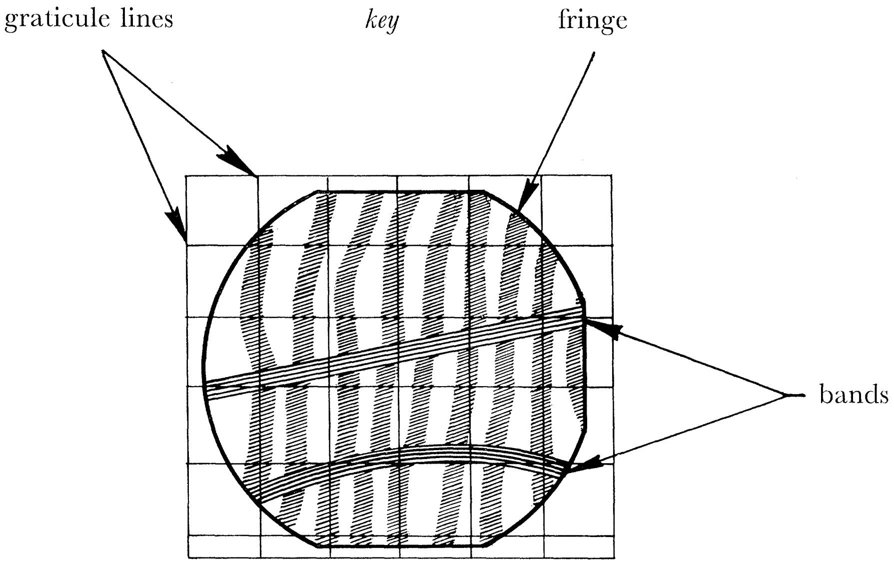


Figure 6. Appearance of three-beam fringes.

when air was admitted too rapidly into the pot in which the cube was placed for measurements under vacuum. After this accident, which caused damage to the internal edges of the blocks, wedge plates were permanently cemented with Araldite to all the outer faces except the top and bottom: the latter was itself made with a wedge and it was impossible to look downwards through the top block because of the fittings on it that are described below. The outer surface of the top block was given a matt finish to destroy reflexions from it.

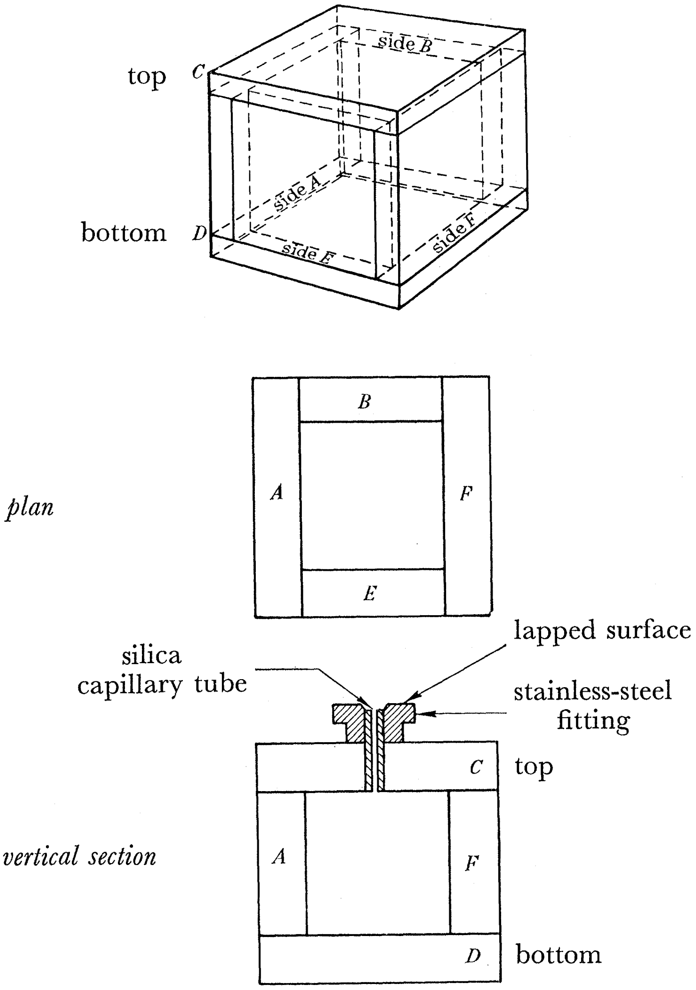


Figure 2. Diagrams of cube showing arrangement and lettering of blocks.

The upper block of the cube was drilled to accept a capillary tube cemented in with Araldite, and the inner surface was finally polished after the tube was inserted. The tube projected above the top surface of the block and a non-magnetic stainless-steel fitting (see figure 2) was slid over it and cemented on to it and the top of the block with Araldite. This fitting, the upper surface of which was lapped flat, served two purposes: it provided a connexion to the vacuum system for filling the cube with mercury under reduced pressure (see §4(*b*)) and it was used in gauging the height of mercury in the capillary tube, as described in §4(*d*).

(*b*) *Volume of the capillary tube*

The volume of the capillary tube between its inner surface and various heights was found by measuring the length of a thread of mercury at different positions along the tube, the mercury being weighed after it had been removed from the tube. This work was done after the cube had been assembled; the thread was viewed with a microscope through one of the sides of the upper block. The results are given in table 1 where the value of $\Delta v/\Delta l$ is given against the interval of length. The corresponding formula for the volume of the capillary is

TABLE 1. CAPILLARY VOLUMES

intervals, length measured from inside surface of cube (mm)	$\frac{\Delta v}{\Delta l}$ (mm^2)
10·5 to 3·5	0·777
14·0 to 7·5	0·767
19 to 12	0·765
23 to 16	0·762

$$v = 0{\cdot}787l - 0{\cdot}68l^2 \times 10^{-3},$$

where v mm^3 is the volume from the inner face of the cube to a distance l mm up the capillary.

This formula gives the volume of the capillary tube and the volume of the meniscus has to be taken into account to get the volume of the mercury in the capillary.

(*c*) *Volume of chips*

The volume of the chips on the inside edges of the component blocks was estimated from measurements of the areas of the chips projected on to the faces of the adjacent blocks, these measurements being made through the blocks with a low-power microscope. A sketch of a typical chip is shown in figure 3 and it is clear from this that the estimation of the volume of the chip depends on assuming a form for the surface of fracture. It was, in fact, assumed that this was plane, but it is more likely to be conchoidal so that the volumes given below may be rather too great.

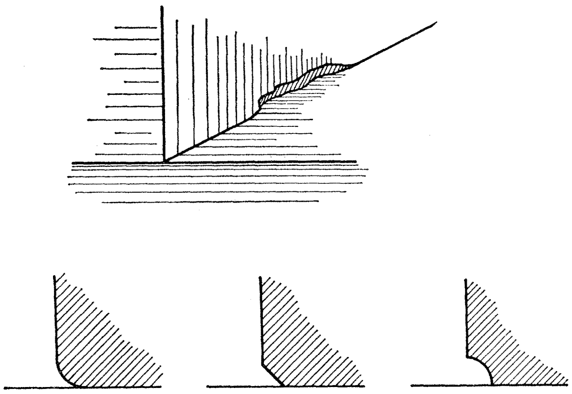


FIGURE 3. Sketch of a chip showing possible forms of fracture.

All but eight chips can be ignored. The volumes of these are as follows, in order of magnitude:

0·653 mm^3	0·105 mm^3
0·176	0·075
0·130	0·036
0·127	0·008

The total volume is 1·310 mm^3, or 3×10^{-6} of the volume of the cube.

The major contribution to the uncertainty of measurement comes from the largest chip for which two observers estimated values of 0·624, 0·694 and 0·639 mm^3, a range of 0·07 mm^3 or 1×10^{-7} of the cube volume. In addition, the total volume may perhaps be overestimated by up to 10% (3×10^{-7} of the cube volume) because of ignorance of the form of the fractures; we shall represent the overall uncertainty due to these two sources of error by a standard deviation of 1×10^{-7} of the cube volume.

(*d*) *Contact of mercury at edges and corners*

Surface tension prevents the mercury filling the edges, corners and chips of the cube completely but the error in assuming that the filling is complete may be neglected. The radius of curvature of the cylindrical surface of the mercury along an internal edge of the cube under a pressure of 1 atm will be about 5 μm and the total empty volume between the cube and the mercury along the edges will therefore be about 4×10^{-6} cm^3 or 1×10^{-8} of the cube volume. The empty volume at the corners and chips is even less.

On looking through the sides of the cube the mercury always appears to fill the edges, corners and chips.

3. VOLUME OF THE CUBE

(*a*) *Methods, wavelength standards*

It was hoped when the cube was designed that it would be possible to measure all the internal dimensions by making use of the fringes of equal inclination (Haidinger rings) formed by the interference of light reflected from opposite internal faces. For this to be possible, two conditions are necessary—the reflexion coefficient of the surfaces must be reasonably high and the surfaces must be very nearly parallel. The coefficient of reflexion at a fused silica surface *in vacuo* is about 4% which means that effectively there are no multiple reflexions between the surfaces, and the interference fringes formed have a sinusoidal distribution of intensity. It was thus not possible to achieve the accuracy of measurement normally expected with a Fabry–Perot interferometer with highly reflecting surfaces, but nonetheless the fringes could be measured to a hundredth of a fringe spacing or so. The method of construction of the cube ensured that the top and bottom surfaces were at a very small angle indeed (0·1″) and good fringes could be seen all over them, but the long side faces were at a greater angle, up to 1·3″, and the fringes formed over some parts were rather indistinct, while the short side faces had such a relatively large angle between them (4·5″) that Haidinger rings were not seen. A different system of interference had therefore to be used for the short side faces and it was found that when the cube was set up in a Michelson interferometer a three-beam system of interference fringes was formed consisting of fringes crossed by bands of constant separation between the faces (Cook 1957).

To observe the Haidinger rings the cube was viewed through a prism spectrometer of sufficient resolution to separate the two yellow lines of mercury. It was illuminated by an electrodeless lamp containing mercury-198 excited by a high-frequency discharge and, as shown diagrammatically in figure 4, the fringes were seen in reflected light. The diameters of the Haidinger rings were measured with a micrometer in the eyepiece of the telescope of the spectrometer and the fractional part of the order of interference was calculated by least squares from the equation for the Haidinger rings,

$$kd^2 = p+\epsilon,$$

where d is the diameter of the pth ring counted from the centre of the pattern and ϵ is the fractional order of interference at the centre. k is a constant. A phase change of π at the reflexion from the silica/air interface at one surface has to be allowed for.

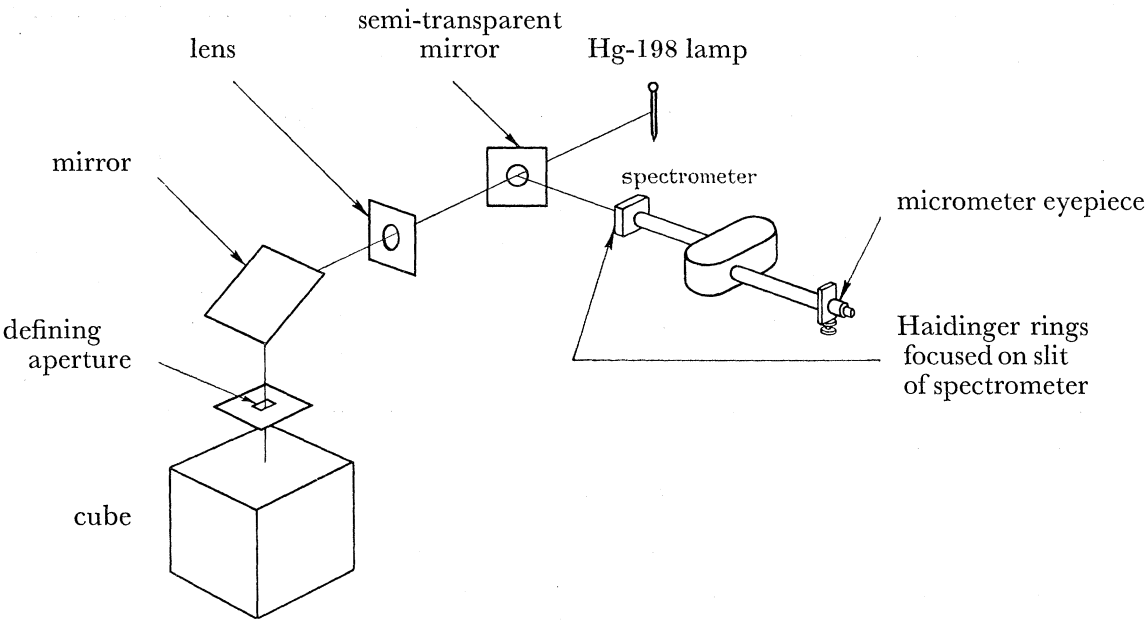


Figure 4. Arrangement for viewing Haidinger rings.

Measurements were made at the centres of 100 equal areas into which the faces were divided.

Since a great deal of computation was involved, the observations were punched on Hollerith cards and the least-squares calculations were carried out in the DEUCE computer. The results included not solely the fractional orders of interference but also the residuals of the observations and the uncertainties of the computed fractional orders.

Because the bore of the capillary tube in the top of the cube was quite small it was feared that it would not be possible to estimate the pressure and temperature of the air inside the cube very exactly from those of the air outside and accordingly all measurements of the dimensions of the cube were done *in vacuo*. The cube was placed in a brass vessel closed with a glass lid and O-ring seal and evacuated to about 100 μb with a mechanical pump. The residual pressure was measured with a Vacustat Macleod gauge. The temperature of the cube was measured with thermocouples which were stuck to the six faces with adhesive tape. The leads of these thermocouples were taken through vacuum seals in the side of the cylinder without any electrical joints and the temperature of the reference junctions was measured to 0·01 deg C with a mercury-in-glass thermometer. The thermocouples were calibrated on a number of occasions and the uncertainty in the calibration factor at any time was about 5 %. Since the temperature of the cube was always within 1 deg C of that of the reference junctions, the measured temperature of the cube was in error by less than 0·05 deg C, corresponding to less than 2 nm in the separation of a pair of faces. It will be seen below, however, that this is significant.

For the Haidinger ring measurements, the cube in its container was placed on a coordinate stage so that it could be adjusted under the interferometer to enable a specified area to be observed. The field of view of the interferometer was limited by a square diaphragm placed above the cube in the parallel beam of light; the area of the diaphragm was one-hundredth of the area of an internal face.

The three-beam interference fringes were observed when the cube was placed under the head of a Kösters–Zeiss gauge interferometer—a form of Twyman–Green interferometer. The field of view was rather more than one-ninth of the cube face and so the cube had to be put into nine different positions for a whole face to be covered. Since the fringes are localized on the cube face the points at which measurements are made have to be defined by a graticule on the cube face and a grid of copper wires on a brass frame was made which was laid on the upper face of the cube as shown in figure 5 (plate 1). The appearance of the fringes with the graticule superposed is shown in figure 6 (plate 2). The observations consist in estimating by eye the fractional order of interference at each of the grid nodes.

The measurements of the diameters of the Haidinger rings can be made with an uncertainty corresponding to a few hundredths of an order and so it is sufficient if two observers make independent measurements in the same radiation—the green line (λ 5461 Å) of mercury-198. The estimation of the order of interference of the three-beam bands is, however, much less accurate, and to improve the final accuracy estimates were made by two or more observers in three wavelengths, for the most part the green and two yellow lines ($\lambda\lambda$ 5771 and 5792 Å) of mercury-198 but on occasion lines of krypton-86 were used.

The integral orders of interference were determined by the method of exact fractions starting from measurements of the separation of the faces made with a travelling microscope. With care settings could be made on the edges of the faces to 0·5 μm. The integral orders of interference were determined at about six points distributed over each face, as many wavelengths as possible being used. The Haidinger rings were photographed simultaneously in the two yellow lines, the green and a violet line (λ 4359 Å) of mercury, these being sufficient on account of the accuracy of measurement. The three-beam bands were observed by eye and in addition to the four lines of mercury, a green (λ 5571 Å) and a yellow line (λ 5872 Å) of krypton were used.

The standard of length has been taken to be the wavelength *in vacuo* of the orange line in the spectrum of krypton -86(λ 6056 Å) excited at 63·14 °K; this is

$$0{\cdot}605\,780\,211\ \mu\text{m} \quad \text{(I.A.U. Commission 14, 1958).}$$

Referred to this wavelength, that of the green line of mercury-198 is nominally

$$0{\cdot}546\,227\,063\ \mu\text{m}\ \textit{in vacuo}.^*$$

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[*] The value adopted by Commission 14 of the I.A.U. is 0·546 227 07 μm; the value quoted is based on later information obtained at the National Physical Laboratory.

However, the wavelength emitted by the high-frequency electrodeless lamps used in this work depends on the pressure of the argon gas used to carry the discharge and it was found that the three lamps used gave different wavelengths. The differences between them were measured by Dr W. R. C. Rowley and Mr R. G. Hitchins using a pressure-scanned Fabry–Perot interferometer with photoelectric recording (Cook 1960).

The values of the yellow lines also vary from lamp to lamp and the wavelengths of these were compared by Mrs P. Anderton using a Fabry–Perot interferometer with photographic recording. The measured vacuum wavelengths (Å) are as follows:

lamp		M43	H20	43918/2
yellow 1	5792	·2685	·2689	—
yellow 2	5771	·1985	·1989	—
green	5462	·27063	·27081	·27105

The uncertainties of the differences of the wavelengths of the green line are about 2×10^{-5} Å and of the yellow lines, 2×10^{-4} Å.

Yellow and green lines of ^{86}Kr excited at 77·2 °K (the boiling point of nitrogen) were also used; the wavelengths *in vacuo* are

yellow	5872·5414 Å
green	5571·8353 Å.

It will be noticed that the wavelengths involved in the three-beam interference observations are less precisely known than those used in the Haidinger ring observations.

The nominal values of wavelengths quoted above for lamp M 43 differ from the values given for the lamps used in the previous work with the tungsten carbide cube (paper I), namely, M 26, M 42 and a lamp from the National Bureau of Standards. The vacuum wavelengths used for these lamps were

yellow 1	5792·2680 Å
yellow 2	5771·1978
green	5462·2702
violet	4359·5619

(the values given in paper I were wavelengths in standard air).

The differences between the two sets of values are probably to be ascribed to differences in the interpretation of the rather broad standard red line of cadmium with which all have been compared (see Barrell 1958). Many standards laboratories now appear to agree on values close to those adopted in this paper. Unfortunately, the lamps M 21, M 42 and N.B.S. had failed by the time these discrepancies had become apparent and it has not been possible to compare the earlier group directly with the later ones. The lamps M 42 and M 43 provide a link, however, because they were made at the same time in the same laboratory and it is probable that the wavelengths they emitted were the same to 0·0001 Å. The results of paper I have accordingly been recomputed on this basis (§5 (*c*)).

(*b*) *Temperature coefficients*

The coefficients of thermal expansion over the range of about 16 to 20 °C were measured perpendicular to each of the three pairs of faces. The temperature of the cube was changed by altering the room temperature by means of the setting of the air-conditioning plant;

the changes were made overnight with air in the brass container so that on starting work in the morning the temperature of the cube was nearly the same as that of the air in the room and did not change much in the course of the observations after the container was evacuated.

The observations by the Haidinger ring method were made on faces *A*, *F* and *C*, *D* (top and bottom) for each pair at sixteen points uniformly placed over the faces, and were made in mercury green light only. The observations on faces *B*, *E* by the three-beam method covered an area at the centre of the faces and were made in the green and the two yellow radiations of mercury.

The thermocouples were calibrated at the time of these observations, but since the difference between the cube and the reference junction outside the evacuated container was usually 1 deg C or less the effects of uncertainties in the thermocouple calibrations do not exceed 5×10^{-9}/deg C in the coefficient of expansion.

The observations on each of the pairs of faces *A*, *F* and *C*, *D* form an array of 96 fractional orders of interference, that is, values for six temperatures at each of 16 points. Analysis of the variances of these two sets give the following estimates of the standard deviation of a single measurement:

A, *F*	8·2 nm
C, *D*	8·6

Each is on $96 - 16 - 6$, that is 74, degrees of freedom.

The coefficients of expansion were found from the linear regression on temperature of the mean order of interference at the sixteen points. The residuals from the regression line have the following standard deviations:

A, *F*	2·5 nm
C, *D*	2·7

These agree well with the values to be expected from the analysis of variance (about 2·1 nm for the mean of sixteen points) in which no assumption was made about the form of the variation with temperature. The coefficients of expansion are given in table 2.

TABLE 2. COEFFICIENTS OF THERMAL EXPANSION BETWEEN 16 AND 20 °C.

direction normal to faces ...	*C*, *D*	*A*, *F*	*B*, *E*
method	Haidinger rings		3-beam system
coefficient, 10^{-6}/deg C	0·522	0·513	0·523
s.d. of coefficient	0·018	0·018	0·024
s.d. of single observation, nm	8·6	8·2	7·1
s.d. of length at one temperature (*a*) (nm)	2·7	2·5	3·4
s.d. of length at one temperature (*b*) (nm)	2·2	2·1	4·1

mean value $0{\cdot}519 \times 10^{-6}$/deg C
s.d. 0·010

(*a*) s.d. determined from departure from linear relation with temperature.
(*b*) s.d. determined from scatter of observations at fixed temperature.

The observations on faces *B*, *E* were treated rather differently. The mean order of interference over the area of observation (16 points) was found in three radiations at each of five temperatures. Analysis of the variance gave for the standard deviation of the mean of observations 7·1 nm on 10 degrees of freedom. The coefficient of expansion was found from the linear regression on temperature of the mean length from all three radiations, and the standard deviation of the residuals from the regression line is 3·4 nm on 4 degrees of freedom compared with 4·1 nm to be expected from the analysis of variance.

The coefficient of expansion is given in table 2.

The mean coefficient for all three directions is $0{\cdot}519 \times 10^{-6}$/deg C at 21 °C and the differences between directions are not significant.

Previous measurements of the coefficient of thermal expansion of fused silica up to 20 °C range from 0·2 to $0{\cdot}52 \times 10^{-6}$/deg C with the most reliable values about 0·4 to $0{\cdot}5 \times 10^{-6}$/deg C (Cook 1956). The variability of the expansion of fused silica is undoubtedly real and is apparently correlated with the heat treatment that the specimen has undergone.

The errors of the observations are discussed further below (§3 (*d*)).

(*c*) *Compressibility of the cube*

The linear dimensions of the cube are measured under vacuum, whereas the volume required is that when the cube is under a hydrostatic pressure of about 1·1 atm. The compressibility had therefore to be measured, for although the elastic constants of fused silica are fairly well known from, for instance, ultrasonic measurements, yet it seemed possible that the compressibility of the assembled cube might not be the same as that of fused silica because of the strains introduced by forcing the blocks of silica into contact.

The compressibility was estimated from the difference of the separation of a pair of faces in vacuum and in air at atmospheric pressure. This is about half a wavelength of mercury green light but superposed on it is one of some 60 orders of interference due to the change of refractive index of the air. It is therefore rather difficult to get reliable results. The procedure was to measure the cube in vacuum as described above and in air at atmospheric pressure, assuming that the pressure inside the cube was the same as that of the air in the room. Results at first were unreliable and the reason appeared to be that the humidity of the air inside the cube differed from that in the room; the cylinder in which the cube was placed for measurements was therefore always filled with air dried by passing it over phosphorus pentoxide and it communicated with the outside air through a phosphorus pentoxide trap. The wavelengths in air were then computed on the supposition that the air was dry and contained the standard amount of carbon dioxide (0·03 %). The refractive index formula of Barrell (1951) and Edlen (1953) was used. Corrections were also applied for the pressure of residual air under the evacuated conditions. For the parallel sides A, F and C, D measurements were made with mercury green light at sixteen points evenly spaced over the faces, and were made in the sequences: vacuum, atmospheric, atmospheric, vacuum. Measurements on the faces B, E were made with the green and the two yellow radiations of mercury at each of the 100 measuring positions and only one set of observations was made under vacuum and one at atmospheric pressure.

The results on the three pairs of faces are collected in table 3. The standard deviation of the observed changes of length are found from the scatter of results at the different points of observation and the standard deviation of the pressure coefficient is just the standard deviation of the mean change of length divided by the pressure change. There is evidently no significant difference between the coefficients in the three directions. The standard deviation of the volume coefficient, estimated from the scatter of the three values, is

$0{\cdot}032 \times 10^{-6}$ atm^{-1}. Mr G. Bradfield (Basic Physics Division, N.P.L.) informs us that the mean value of the compressibility of fused silica found from ultrasonic measurements is $2{\cdot}734 \times 10^{-6}$ atm^{-1}, almost all results lying within 1 %. Evidently our value, although less accurate, is entirely consistent with the ultrasonic measurements.

TABLE 3. MEASUREMENTS OF PRESSURE COEFFICIENTS

direction perpendicular to faces ...	*C*, *D*	*A*, *F*	*B*, *E*
mean pressure difference (mmHg)	752·9	768·3	758
mean change of length (nm)	127·5	131·2	137
pressure coefficient (10^{-6} atm^{-1})	0·883	0·895	0·922
s.d.	0·028	0·028	0·018
standard deviations:			
of single length *in vacuo* (nm)	10·7	36*	†
of single length at atmospheric pressure (nm)	27·5	42*	†
of change of length			
observed (nm)	15·6	17·1	27
expected (nm)	21	36	†
volume coefficient		$2{\cdot}700 \times 10^{-6}$ atm^{-1}	
s.d.		$0{\cdot}032 \times 10^{-6}$ atm^{-1}	

* Each of these is inflated by one very large residual. For this reason the observed s.d. of change of length is less than half the expected value. Ignoring the large residuals, the s.d. of a single length is 16 nm *in vacuo* and 20 nm in air and the expected s.d. of change of length is 18 nm.

† Data not in suitable form to determine these quantities.

(*d*) *The volume of the cube at* 21 °C; *uncertainties*

Four complete measurements of the internal dimensions of the cube were made following the procedures described in § 3 (*a*). They covered the 19 months from November 1957 to May 1959 and were interspersed among fillings of the cube with the various samples of mercury. The measurements were all made *in vacuo* at temperatures within a few tenths of a degree Celsius of 21 °C and the results were reduced to 21 °C by the use of the mean coefficient of expansion determined in § 3 (*b*).

The results are shown graphically in figures 7 and 8. The former is a set of contour diagrams of the separations of the three pairs of faces averaged over the 19 months period, while the latter is a set of contour diagrams of the changes in these separations.

A detailed analysis of the errors of the interferometric observations has been made but is not given here because, as is shown below, the uncertainty of the volume of the cube at any time is determined by the changes that have taken place in the separation of the sides, these changes being many times greater than the uncertainties of the measurements. It is, however, useful to summarize the errors of measurement; first, in order to be able to make this point, and secondly to show the capabilities of the interferometric methods we employed. The accuracy of determining the fringe fraction from Haidinger rings is about twice that from the three-beam system, but this was compensated by the greater number of observations made with the latter, so that the uncertainty of a single measurement of separation at one point by either method is about 7 nm. Internal evidence in the volume measurements and a comparison of the uncertainties of these measurements with those made for thermal expansion and compressibility show that there are additional sources of uncertainty, such as in the measurement of temperature which may be of the order of

1 nm, so that a cautious estimate of the standard deviation of the mean separation of a pair of faces, calculated from measurements at 100 points, is

$$2\ \text{nm}.$$

Before going on to consider the changes in the separations of the faces, it is first necessary to discuss the measurements on faces *A*, *F*.

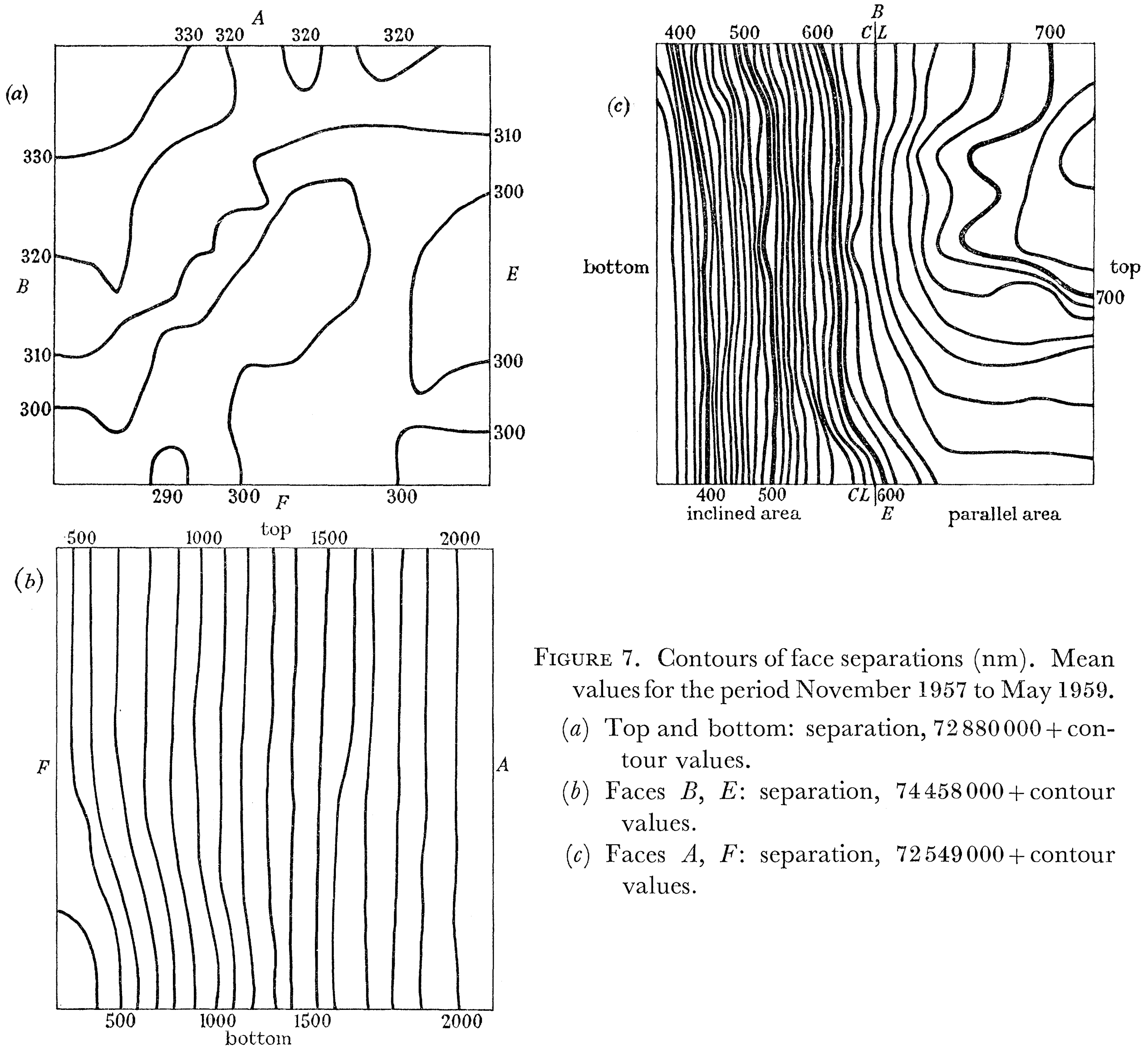

FIGURE 7. Contours of face separations (nm). Mean values for the period November 1957 to May 1959.

(*a*) Top and bottom: separation, 72 880 000 + contour values.

(*b*) Faces *B*, *E*: separation, 74 458 000 + contour values.

(*c*) Faces *A*, *F*: separation, 72 549 000 + contour values.

Figure 7 (*a*) shows that faces *C* and *D* are very nearly parallel and in practice very clear Haidinger rings were obtained when observing these faces. Faces *A*, *F*, however, are not so parallel and figure 7 (*c*) shows that the area of these faces is clearly divided into a nearly parallel part and an inclined part; the definition of the Haidinger rings observed over the inclined part was found to be impaired. We shall now discuss the effects of this inclination on the systematic errors of the observations. It will be seen from figure 7 (*c*) that the contour lines on the inclined portion run parallel to the top and bottom edges of the faces and measurements were made in two conditions, with the slit on which the Haidinger rings were focused either parallel to or at right angles to the contour lines. The formation of Haidinger rings when the two surfaces are inclined was considered by Michelson (1927) and from the theory that he gives it can be seen that when the slit of the spectrometer is parallel to the contour lines the separation of the surfaces is measured correctly, but that when the slit is perpendicular to the contours the ring diameters are increased, corresponding to measured separations which are too small. It is not possible to obtain quantitative results, since these depend on the focus conditions, which are difficult to define precisely, but the results of the measurements on faces A, F are in qualitative agreement with Michelson's results. Table 4 shows the measurements on these faces grouped according to the area and listed by date and orientation of the slit. It will be seen that no dependence on the orientation of the slit can be distinguished in the measurements on the parallel area, whereas the measurements on the inclined area with the slit parallel to the contours are greater than those with the slit perpendicular to the contours by between 30 and 35 nm. In view of Michelson's analysis the latter results must be considered to be in error and they will be rejected in calculating the volume of the cube.

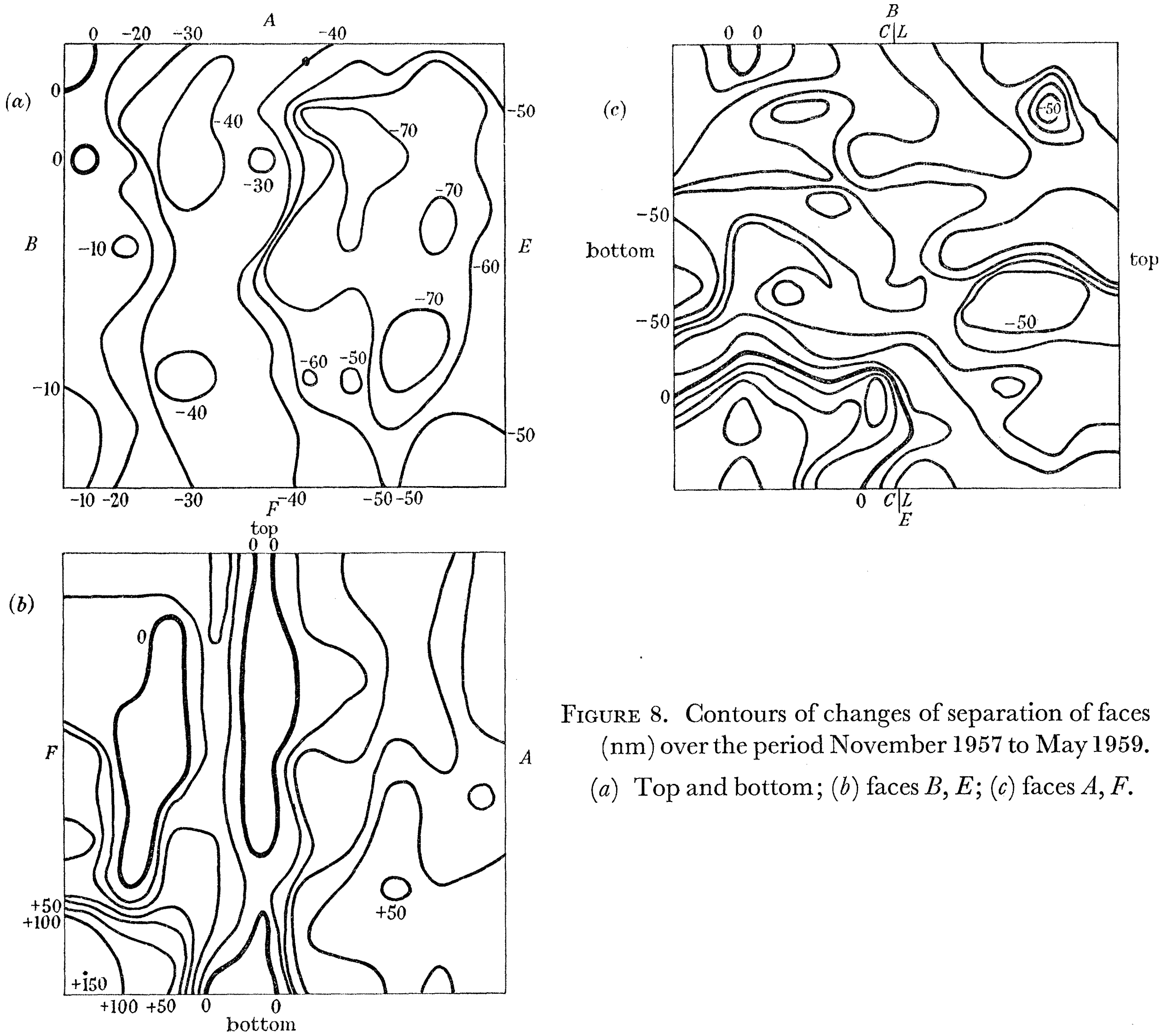

FIGURE 8. Contours of changes of separation of faces (nm) over the period November 1957 to May 1959. (*a*) Top and bottom; (*b*) faces B, E; (*c*) faces A, F.

We can now consider the changes in the separations of the face and estimate the average separations of the faces and the volume of the equivalent parallelepiped.

The first point to make is that the changes over the 19 months of the observations are real. The standard deviation of a single observation on any pair of faces is about 7 nm and that of the difference between two such observations is accordingly about 10 nm. The probability of two measurements differing by more than 30 nm due to errors of observation is thus about 1 in 400. When the diagrams of figure 8 are examined with these limits in mind, it is clear that the changes in the separations of none of the pairs of faces can be explained by random errors of observations, especially when the evident correlation of changes at neighbouring points is considered. The figures in table 5 show the same thing in a rather different way. The standard deviations estimated earlier lead to a value of 2 nm for the standard deviation of the difference between two measured values of the mean separation, and the changes of mean separation in table 5 are of the order of ten times this value. We can be quite sure that the changes are not the results of random errors of observation. Systematic errors also do not seem to be a likely cause. If the internal air pressure had been estimated incorrectly one would expect the changes to be uniform over the face of the cube and not to show the observed distortions. Non-uniform temperatures might give such effects but it would be surprising if they produced the steady changes observed in the separations of faces C, D and B, E. It seems most probable that the observed changes are due to actual distortions of the faces.

TABLE 4. MEASUREMENTS ON FACES A AND F

	Separation (nm) 72 549 000 +					
area …	parallel		inclined		whole face	
	Pa.	Pe.	Pa.	Pe.	Pa.	Pe.
Nov. 1957	688·3	685·5	514·3	487·5	601·3	586·5
May 1958	—	675·3	—	482·3	—	578·8
Sept. 1958	672·7	—	523·6	—	598·2	—
May 1959	—	663·2	—	488·6	—	575·9

Notes. Pa., slit parallel to contours; Pe., slit perpendicular to contours. Parallel area: half-face to right of line CL in figure 7 (*c*); inclined area: half-face to left of line CL in figure 7 (*c*).

TABLE 5. MEAN SEPARATIONS OF FACES

	average of all sets (mm)	differences of each set from average (nm)			
		Nov. 1957	May 1958	Sept. 1958	May 1959
faces C, D	72·880 309 3	+18·9	+1·2	−1·8	−18·2
A, F mean	72·549 588 1				
slit perpendicular to contours		−1·6*	−9·3*	—	−12·2*
slit parallel to contours		+13·2	—	+10·1	—
B, E mean	74·459 293 6				
through B		−13·1	−18·0	+14·7	+24·4
through E		−7·9	—	—	—

* Rejected, see text.

To estimate the volume of the cube, less chips, we consider first faces *A* and *F*. There is evidence of a change in the separation of the inclined portion of the faces but it is not possible to adopt for this any other than the mean value

72 549 519·0 nm (table 4).

The parallel portion seems to have contracted and we take the following values:

date		Nov. 1957	May 1958	Sept. 1958	May 1959
separation (nm)	72 549 000 +	686·8	675·3	672·7	663·2

We then get for the mean separation of these faces as a whole:

date		Nov. 1957	May 1958	Sept. 1958	May 1959
separation (nm)	72 549 000 +	602·9	597·2	595·8	591·0

With the figures in table 5 for the separations of faces *C*, *D* and *B*, *E* the volumes of the cube, less chips, are:

date		Nov. 1957	May 1958	Sept. 1958	May 1959
volume (cm^3)	393·698 +	0·000 908	0·000 742	0·000 891	0·000 827

The mean value is 393·698 842 cm^3 and the standard deviation of a single value about the mean is $7·5 \times 10^{-5}$ cm^3 or 1·9 parts in 10^7.

Since we know that the changes of volume are real and not just the result of errors of observation, we shall take the volume at any given time to be the mean of the results of the measurements immediately before and after that time, as follows:

between Nov. 1957 and May 1958	393·698 825 cm^3
between May 1958 and Sept. 1958	816
between Sept. 1958 and May 1959	859
after May 1959	827

These values are all within 0·7 part in 10^7 of the mean of the four determinations,

393·698 842 cm^3.

The standard deviation of each of these mean values will be taken to be that of the mean of two determinations as found from the scatter of the four measured values about their mean, namely 1·4 parts in 10^7.* The final scatter of the measured volumes is thus appreciably less than would be expected from the changes of the separate pairs of faces and this is because the changes in *C*, *D* and *B*, *E* largely cancel.

Three corrections have to be made to the above volumes. First, the volume of chips, 0·001 310 cm^3, has to be added. Secondly, there is a very small correction of 5×10^{-6} cm^3 to take account of the fact that during the interferometric measurements the temperature of the cube was always rising at a rate of $1·2 \times 10^{-3}$ deg C/min on the average, so that the mean temperature of the cube was always less than that of the outside surfaces to which the thermocouples were fixed. Lastly, there is an even smaller correction of $0·2 \times 10^{-6}$ cm^3 to allow for the pressure of residual air in the cube (mean value 150 μb) during the measurement.

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* The corresponding value based on the standard deviation of the measured separation of a pair of faces (2 nm) would be about 0·8 part in 10^7.

With these corrections, the overall mean value of the volume of the cube at 21 °C *in vacuo* is

$$393{\cdot}700\,157\ \mathrm{cm}^3$$

with corresponding values for the means of successive pairs of observations.

4. THE MASS OF MERCURY CONTAINED IN THE CUBE

(*a*) *Outline of procedure*

The purpose of the observations described in this section was to determine the mass of mercury contained in the cube at a known temperature and pressure from which, the coefficients of expansion and the compressibilities of mercury and of the cube being known, the density under the standard conditions of 20 °C and 1 atm may be calculated.

The sample of mercury was run into the cube under vacuum. The cube was then placed in a mercury jacket, to equalize the pressures inside and outside the cube, and this in turn was placed in a thermostatic bath in which it was held at a temperature constant to about 0·001 deg C for some 18 h so that the temperature of the mercury in the cube was certainly equal to that of the bath. After adjusting to a convenient level by drawing mercury out of the cube, the height of the mercury in the capillary tube in the top of the cube was then found by a probe gauge with reference to the top surface of the stainless-steel fitting cemented over it. In this way the volume of mercury in the cube was found at the temperature of the bath and at a pressure equal to the atmospheric pressure plus that of the mercury above the centre of the cube. The cube was now removed from the mercury jacket, mercury on the outer surfaces was carefully removed and the cube and its contents were weighed using the second, empty cube as a counterpoise. Next the mercury was drawn out of the cube through a steel hypodermic tube passed through the capillary and the empty cube was weighed, again using the second cube as a counterpoise. The mass of mercury could then be calculated. The group of weights used in the experiments comprised a 5 kg weight and a set of weights from 0·01 g to 2 kg making up 5 kg. The set of weights was used in the work with the tungsten carbide cube (paper I) and had been standardized a number of times with reference to one of the two 1 kg weights of the set which had been kept as a standard. The aggregate changes in the weights used in weighing the cubes have all been much less than 0·5 mg which is 1 in 10^7 of the mass of mercury contained in the cube. The weights of this set have not been compared with the standards of the National Physical Laboratory since 1954 lest in so doing the standards should have been contaminated with mercury, but the 1 kg reference weight has been kept apart from the rest of the set except on the five occasions when it has been used as a standard.

The 5 kg weight was compared with the standards of the National Physical Laboratory on two occasions before starting determinations of the density of mercury; the results were

1955	5 kg − 19·88 mg.
May 1957	5 kg − 19·08 mg.

After the determinations of the density of mercury had been finished the weight was compared with weights of the 5 kg set and taking the value of the 1 kg reference weight of that set to be the value it had in 1954, the value of the 5 kg weight is

Sept. 1959	5 kg − 18·99 mg.

This is consistent with the increase in mass of the 5 kg weight previously observed.

We accordingly take the value of the 5 kg weight throughout the density determination to be the mean of the 1957 and 1959 results:

$$5\ \mathrm{kg} - 19{\cdot}04\ \mathrm{mg};$$

we assign to this value a standard deviation of 0·2 mg and we infer that the values of the weights of the 5 kg set are consistent with this value of the 5 kg weight to within 0·2 mg in 5 kg.

(*b*) *Filling and emptying the cube*

The apparatus used for filling the cube with mercury is shown diagrammatically in figure 9. The cube is placed in a steel box which can be roughly evacuated so that the pressures inside and outside the cube are not very different, and the stainless-steel fitting on the lid of the cube is clamped to a vertical filling tube, the joint between them being sealed with an O-ring. The vertical tube consists of a glass liner cemented with Araldite into an outer stainless-steel tube cut away in part so that the level of mercury in the glass tube may be seen. A small diffusion pump with a silicone fluid is used to maintain a pressure of the order of 0·1 μb in the cube and filling tube.

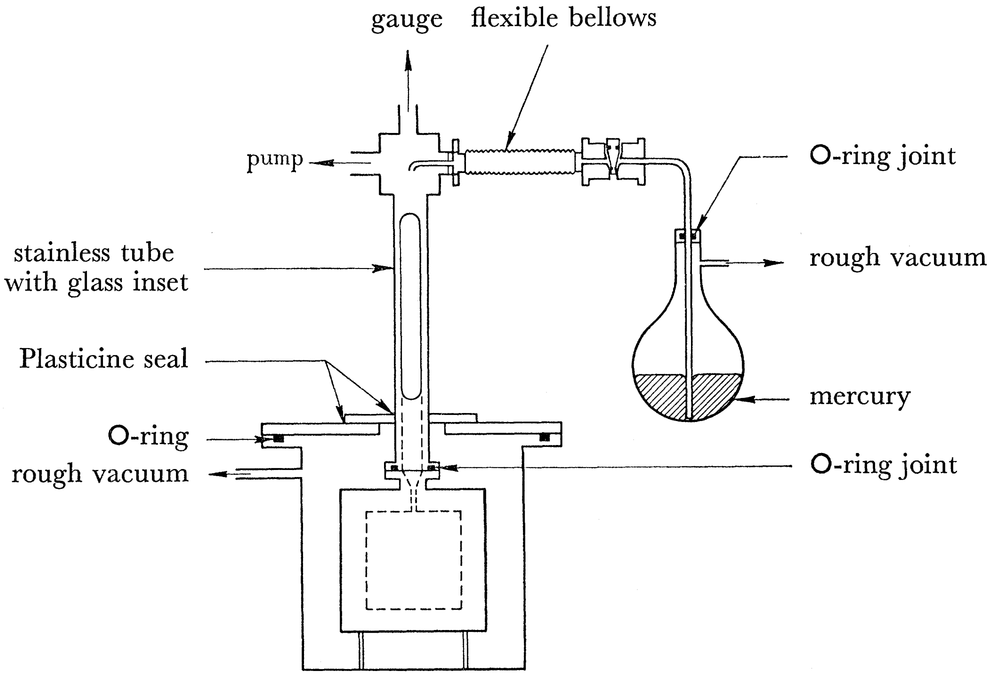


FIGURE 9. Diagram of apparatus for filling the cube under vacuum.

The mercury is contained in a glass flask and can be drawn off into the filling tube through a tube reaching to the bottom of the flask—in this way no surface contamination is drawn over into the cube. A stainless-steel tap controls the flow of mercury from the flask. The space above the mercury is roughly evacuated until the cube is to be filled, when the pressure in this space is allowed to rise to force mercury into the filling tube.

All the parts of this apparatus were made of glass or stainless steel so that they could be thoroughly cleaned, and before introducing mercury into the apparatus all the parts that came into contact with mercury were steam-cleaned as described in paper I. The cube was then assembled in its steel box and the mercury was poured into the flask, having first been filtered to remove surface contamination (the samples of mercury were not treated in any other way throughout the course of the determinations). The whole system was then evacuated with the stainless-steel tap open and a pressure of about 0·1 μb was maintained above the cube for some hours so that it was certain that despite the small conductance of the capillary tube, the pressure in the cube reached that outside. Air was then admitted to the flask and the flow of mercury into the filling tube was controlled by the stainless-steel tap so that mercury ran steadily into the cube. When the cube was nearly full, the filling tube was allowed to drain completely into the cube (with a clean evacuated system this occurred) so that any residual air trapped in the cube could be pumped out. The filling was then completed and excess mercury was left in the filling tube so that on removing the cube from the apparatus mercury stood on top of the stainless-steel fitting. Air was then let into the apparatus and the cube removed, the excess mercury ensuring that no air could enter the cube. The cube was now ready to be placed in the thermostatic bath.

After the volume and mass of mercury in the cube had been determined, the cube was emptied by drawing the mercury out through a hypodermic tube introduced through the capillary tube. The mercury discharged into an evacuated glass bottle which, in common with all other equipment, was steam-cleaned before use. It was usual to see some slight surface contamination on the mercury in the cube and this was sucked off while some mercury remained lest the surfaces of the cube should be contaminated. When not in use the mercury samples were kept in polyethylene bottles which had been steam-cleaned.

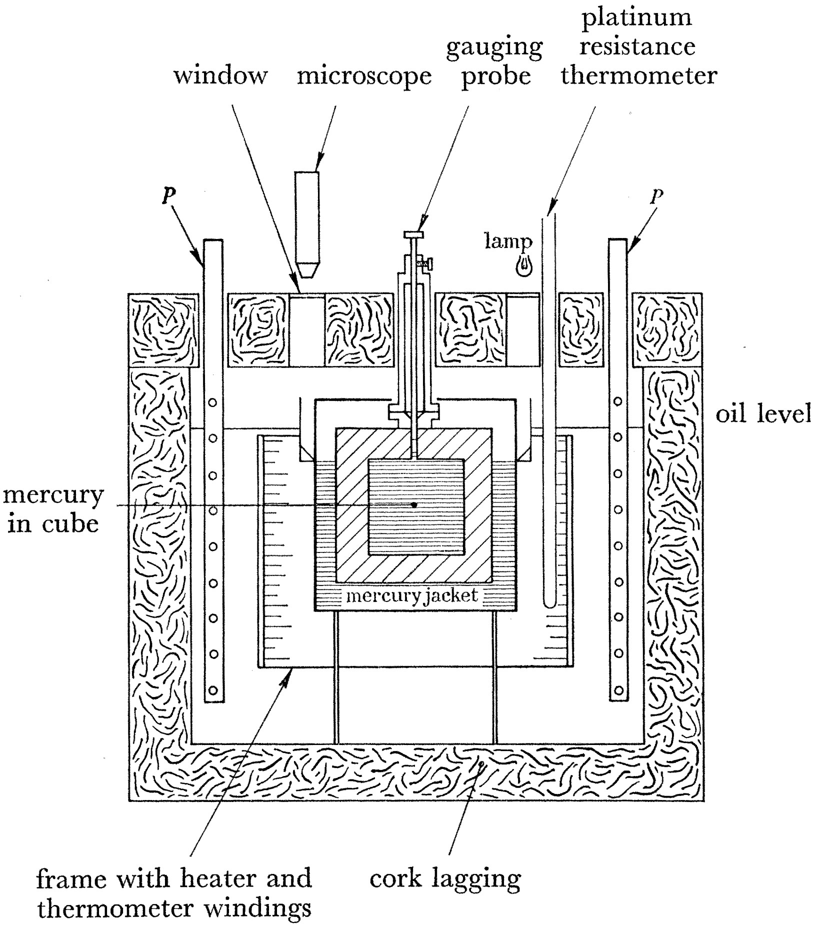
(*c*) *Temperature control and measurement*

Since the density of mercury changes by 1 p.p.m. for a change of temperature of 5×10^{-3} deg C, the temperature at which the volume of mercury in the cube is determined should be known to a few thousandths of a degree, and thus on account of the size and thermal time constant of the cube filled with mercury, it is necessary to ensure that the temperature is uniform throughout the cube and to keep it so for a time long compared with the thermal time constant. The problem is made particularly difficult because it is not possible to insert thermometers directly into the mercury in the cube and hence only the temperature of the outside of the silica cube can be measured. Furthermore, in order to keep the pressures outside and inside the cube the same, the cube was immersed in a jacket of mercury almost to the surface of the upper block and it was this whole assembly that was placed in the thermostatic bath.

The bath (see figure 10) has been described by Wilson & Stone (1957). It consists of a tank of paraffin oil in which is immersed a rectagular framework carrying resistance thermometer and heater windings. A sensitive electronic servo-controller maintains the mean temperature constant to within 1 to 2×10^{-3} deg C over 50 h at about 1 deg C above room temperature. The cube and mercury jacket assembly fit inside the thermometer-heater framework.

Early in the work with this bath it was found that very large vertical temperature gradients could occur even though the mean temperature remained constant over many hours. These gradients could not be entirely eliminated by stirring but could be reduced to acceptable values (less than 4×10^{-3} deg C over the depth of the cube) by heating the air space between the surface of the oil and the insulating lid. In use the air space heater was controlled manually according to the indications of thermocouples measuring the difference between the temperature of the top of the cube and that of the mercury in the jacket.

The mean temperature of the oil was measured by four platinum resistance thermometers used with a Smith resistance bridge of the type described by Barber, Gridley & Hall (1955). The zero-point resistances of the thermometers were checked frequently by reference to a cell containing water at the triple point (0·0100 °C). The uncertainty of the measured thermometer temperatures should be appreciably less than 1×10^{-3} deg C and the uncertainty of the estimated mercury temperature is almost entirely due to the differences, in space and time, between the temperature of the mercury and the temperatures of the thermometers.



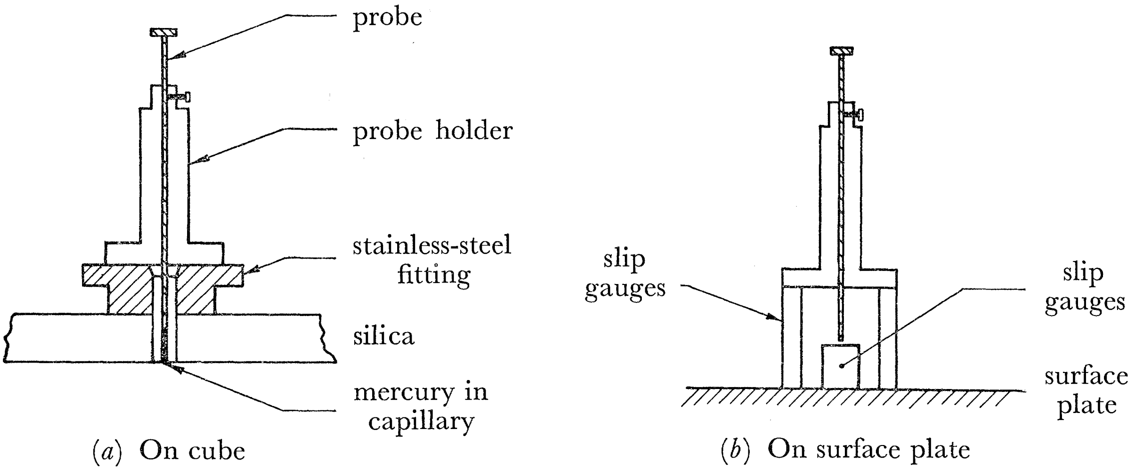
P: pumps for stirring oil

FIGURE 10. Thermostatic bath assembly.

Two of the four thermometers were placed at the level of the centre of the cube, one was placed near the level of the top, and one near the level of the bottom. Assuming, as seems justifiable, that isothermal surfaces remain horizontal whatever material boundaries they cross, the mean temperature of the four thermometers should differ from that of the mercury in the cube by less than half the difference between the upper and lower thermometers. This difference never exceeded 5×10^{-3} deg C and the average value was $3{\cdot}1 \times 10^{-3}$ deg C. The lagging time of the temperature of the mercury in the cube in the mercury jacket relative to the oil is estimated to be about 5 min, so that after keeping the cube in the bath the difference between mercury and thermometer temperatures should be negligible provided the oil temperature was changing by less than say 1×10^{-3} deg C in 10 min. The change of temperature in the 2 or 3 h before gauging never exceeded $3{\cdot}6 \times 10^{-3}$ deg C and the average change was $1{\cdot}5 \times 10^{-3}$ deg C (maximum range of all four thermometers) and, furthermore, it was always checked that the volume of the mercury, as indicated by the height in the capillary, was stationary at the time of gauging. In these circumstances, the mean temperature of the mercury was probably within 1 or 2×10^{-3} deg C of the oil temperature and this is consistent with experiments done to determine the difference of temperature between mercury in a glass cube (into which thermocouples could be placed) and the oil. On any one day, this difference had a range of about 2×10^{-3} deg C, but the average value of the daily means on 5 successive days was 0 with a standard deviation of 1×10^{-3} deg C. Since these figures are consistent with estimates of uncertainty based on the thermal time constant and the bath fluctuations, we shall take it that there is on the average no systematic temperature error and that the standard deviation of the estimated mercury temperature is 1×10^{-3} deg C, corresponding to 0·2 p.p.m. of the density of mercury.

(*d*) *Gauging and volume determination*

After the cube full of mercury had been in the thermostatic bath for some time, excess mercury was removed until the meniscus in the capillary tube was near the middle of the lid of the cube and when the temperature of the mercury was steady the position of the meniscus was found by means of a probe pushed into the capillary tube.



(*a*) On cube (*b*) On surface plate

FIGURE 11. Gauge unit (*a*) on cube, (*b*) on surface plate.

As is shown in figure 10, a microscope was arranged to view the capillary through the side of the lid of the cube and through a passage in the insulated lid of the oil bath, a similar arrangement being provided on the other side of the cube for illuminating the capillary. The probe was held in a cylinder one end of which was ground and lapped flat to rest on the upper lapped surface of the stainless-steel fitting on the cube. The cylinder was placed on this fitting (figure 11) and the probe was pushed down until it nearly touched the meniscus as seen through the microscope. The gauge was packed round with cotton wool for thermal insulation (since the large hole in the lid of the bath needed to admit it disturbed the bath temperature) and the meniscus was then observed for a while to check that it was steady. Meanwhile the temperature gradients in the bath were checked and the resistance thermometer temperatures were read, and when steady conditions were established the probe was pushed down until it touched the meniscus and was then clamped. At the same time, the atmospheric pressure was read.

The gauge assembly was removed from the bath care being taken that no mercury was removed with it, and the projection of the probe beyond the gauging surface was measured by supporting the assembly on a surface plate with piles of slip gauges as shown in figure 11. Then, from a measurement of the distance between the inner surface of the lid of the cube and the lapped surface on the stainless-steel fitting the height of the meniscus above the inner surface of the lid could be derived. Two independent measurements of the meniscus height were always made, with some hours between them and mostly on successive days.

The following data are required to compute the volume of mercury in the cube:

The volume of the cube at the temperature of the bath and under the total hydrostatic pressure of the atmosphere plus the head of mercury above the centre of the cube.

The volume of the capillary to the probe position, corrected for the meniscus volume.

The overall accuracy of the gauging and pressure measurement and correction may be estimated from the differences between the densities calculated from the two separate probe measurements of the meniscus height. The r.m.s. value of this difference was 0·14 p.p.m. of the density and the difference was not systematic. The mean of the two values should have a standard deviation of 0·1 p.p.m. This uncertainty includes a contribution from random errors of temperature and on the face of it appears to indicate that the estimated uncertainty of temperature (equivalent to 0·2 p.p.m.) is too great. However, temperature conditions on successive occasions are probably correlated and discrepancies between successive gaugings are therefore probably smaller than the error of either due to temperature. We therefore prefer to regard the temperature error as a separate contribution additional to the uncertainty of gauging.

(*e*) *Weighing; example of computations*

In weighing objects of fused silica considerable difficulties have been experienced in the past from absorption of water vapour on the surfaces and from electrostatic charging. In the present work the former difficulty was reduced by using as a counterpoise a cube almost identical with the one containing mercury while electrostatic charging was avoided by irradiating the air inside the balance case with a powerful (30 mc) source of β-rays arranged so that the operator was shielded from radiation whenever the case was open for handling the cubes or weights. These precautions appeared to be entirely adequate.

The weighing of the cubes was otherwise quite straightforward except that the corrections for the hydrostatic forces exerted by the atmosphere on the cubes and weights had to be calculated rather carefully. The cube and counterpoise cube were generally weighed with the capillaries unobstructed* and therefore when the two cubes were empty the differences in the hydrostatic forces were quite small, but when the full cube was weighed

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* On some occasions the capillaries were sealed by wringing glass plates on to the stainless-steel fittings but this did not affect the precision of the weighings and was not continued.

against the counterpoise and some 5 kg of brass weights, the differences between the hydrostatic forces were considerable and it was necessary to know the volume of the weights and of the mercury in the cube quite accurately.

On each occasion the cube, whether full or empty, was weighed twice against the counterpoise. The standard deviations of a single comparison computed from the differences of these pairs of weighings, are:

for the empty cube	0·7 mg;
for the full cube	1·7 mg.

The mass of mercury in the cube is always taken to be the difference between the mass of the full cube and the mass of the empty cube determined immediately afterwards. In this way chips knocked off the cube or globules of mercury sticking to the outside have least effect on the calculated mass of mercury. Over the period March 1958 to September 1959, the difference between the cube and the counterpoise increased by 0·16 g, the cube apparently becoming lighter, and this is probably due to small chips having been knocked off the outside of the cube (see figure 12). The damage seems to have occurred on putting the cube into the mercury jacket or on assembling the filling apparatus.

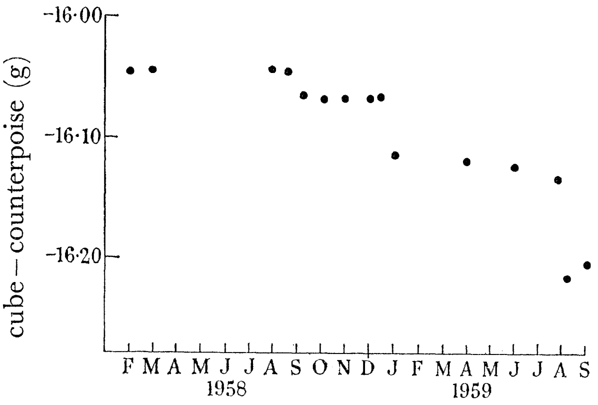

Figure 12. Changes in difference of masses of cube and counterpoise.

The standard deviation of the mass of mercury in the cube is estimated, from the above figures, to be 1·3 mg.

An example of the determination of the volume and mass of mercury contained in the cube is given in table 6.

The pressure at the level of the centre of the cube is about 7 mmHg greater inside the cube than outside because of the column of mercury of this length in the capillary tube. The mean of the internal and external pressures is used in calculating the contraction of the cube but the internal pressure is used in correcting the density of the mercury to 1 atm.

Values for the volume of the cube *in vacuo* at 21 °C were given in § 3 (*d*). The volume is that bounded by the internal plane faces and the chips but excluding the volume of the capillary. The mass of mercury is that determined by weighing the cube, full and empty, and includes the mercury in the capillary which has therefore to be subtracted to obtain the mass corresponding to the quoted volume.

Two small corrections have, with sufficient accuracy, the same value for all measurements. They allow for the volume of the meniscus in the capillary and for air drawn into the cube when the full cube is removed from the thermostat for weighing and together they increase the density by 3×10^{-6} g/cm^3.

The coefficients for correcting the density to 20 °C and 1 atm are the same as were used in paper I.*

TABLE 6. EXAMPLE OF CALCULATION OF VOLUME AND MASS OF MERCURY CONTAINED IN CUBE

Mercury for International Union of Pure and Applied Physics

atmospheric pressure	756·97 mmHg
pressure at level of centre of cube: external	793·37
internal	800·75
mean	797·06
mean temperature	21·0317 °C
volume of cube at 21 °C *in vacuo*	393·700142 cm^3
expansion to 21·0317 °C[1]	+0·000019
contraction under 797·06 mm Hg[2]	−0·001115
volume under actual conditions	393·699046
mass of mercury in cube and capillary	5332·08235 g
subtract mass of mercury in section of capillary tube 7·379 mm long	0·0781
mass of mercury in cube	5332·0043

density under conditions of observation

$$= \frac{5332{\cdot}0043}{393{\cdot}699046} = 13{\cdot}543351 \text{ g/cm}^3$$

correction for meniscus in capillary and air drawn into cube	+0·000003 g/cm^3
correction to 20 °C[3]	+0·002530
correction to 1 atm[4]	−0·000003
density at 20 °C and 1 atm	13·545881 g/cm^3

coefficients: (1) thermal expansion of cube $1{\cdot}56 \times 10^{-6}$/deg C.
(2) compressibility of cube $2{\cdot}70 \times 10^{-6}$/atm.
(3) thermal expansion of mercury—formula of Beattie *et al.* (1941).
(4) compressibility of mercury $4{\cdot}07 \times 10^{-6}$/atm.

(*f*) *Uncertainties*

In this section we summarize the uncertainties of the steps in the determination of the volume and mass of mercury contained in the cube on any one occasion, excluding, however, that of the volume of the cube itself which is common to all measurements.

The largest uncertainty is in the weighing, for the standard deviation of the measured mass of mercury in the cube has been seen to be 1·3 mg, corresponding to 0·25 p.p.m. of the density. The next largest is the uncertainty of the temperature at which the volume is determined and this has a standard deviation of 1×10^{-3} deg C, corresponding to 0·2 p.p.m. of the density.

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* The expansion formula of Beattie *et al.* (1941) as quoted in paper I is in error and should be

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

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

The measurement of the height of the mercury has been seen to lead to a standard deviation of 0·1 p.p.m. on the estimated volume and, as discussed above, we prefer to regard this as independent of temperature errors though strictly this is not the case.

The resultant of these three sources of error is 0·35 p.p.m. and the additional uncertainty of the standard of mass, 0·04 p.p.m., is negligible.

5. The densities of six samples of mercury

(*a*) *Descriptions of samples*

Three of the samples, labelled A, B and C, had been used in the measurements by the displacement method using the solid tungsten carbide cube and the sources, methods of purification, evidence of chemical purity and measurements of the isotopic constitution of sample A were described in paper I. At the end of the displacement measurements, these three samples were sealed in steam-cleaned polyethylene bottles which were not opened until the mercury was required for the hollow-cube work. When the bottles were opened, the mercury surfaces were found to be slightly mottled with what seemed to be mainly dust and grease but there was no continuous film such as would be caused by base metal oxides. When the samples were poured through filter paper pierced with a small hole, the surface contamination was removed and did not reappear in the course of the measurements. This appears to indicate that there were no significant quantities of metallic impurities in the samples, and the density is thus unlikely to have changed significantly between the two groups of measurements. As was explained in paper I, the surface appearance is a more sensitive test of base metal contamination than is chemical analysis, and we feel able to rely on the fact that surface contamination did not develop during the measurements as strong evidence that there were no significant amounts of base metals in our samples.

A fourth sample, E, came from a stock of mercury filled into the Primary Barometers nos. 1 and 1 A of the National Physical Laboratory (Elliot, Wilson, Mason & Bigg 1960). This mercury is not identical with sample D of paper I which came from mercury in the Long Range Primary Barometer of the National Physical Laboratory but was prepared in the same laboratory from similar stock and in a similar way.

The fifth sample (N.S.L.) was sent from the Division of Metrology of the Australian National Standards Laboratory. It was obtained commercially, the ultimate source being unknown. It was treated as follows at N.S.L. After gross dirt had been removed, air was bubbled through the mercury at 120 °C for 8 h and the oxides formed were filtered off. On repeating the process no oxide film formed. To remove grease the mercury was then washed with a strong solution of sodium hydroxide followed by distilled water and then to remove residual base metals it was washed with dilute nitric acid and mercurous nitrate. Finally, it was washed with distilled water, dried and distilled twice at a pressure of 0·01 mmHg. The final distillation was direct into the polyethylene bottles in which it was sent to the National Physical Laboratory. When opened at the National Physical Laboratory, the surface was quite dirty but the contamination appeared to be removed by pouring the mercury through a small hole in a cone of filter paper.

The sixth sample (N.B.S.) was provided by the National Bureau of Standards, Washington, D.C., on behalf of the International Union of Pure and Applied Physics and comes from a standard stock of pure mercury that is being established. The following details have been supplied by Dr E. Wichers.

The mercury was milled and bottled on 1 July 1958 at the Cordero Mine, McDermitt, Nevada, U.S.A. After removing rust and other foreign matter by passing through a fritted glass funnel, the mercury was extracted with dilute nitric acid for about 16 h while it was agitated by a stream of air. The acid was replaced by a fresh amount and extraction continued for a further 16 h. The mercury was then rinsed with distilled water and dried in porcelain dishes. The mercury dissolved in the nitric acid was recovered by electrolysis, extracted once more and then recombined with the main portion, thus nullifying any isotopic fractionation during the course of the chemical treatment. The mercury was then distilled, first in air at reduced pressure and afterwards under vacuum. At the end, from an original amount of about 500 kg of crude mercury, 0·010 g of a mixture of gold and silver was recovered from the residue in the second still. The mercury was stored in soda-lime bottles which had been treated with chromic, sulphuric and nitric acids before rinsing with distilled water and drying.

(*b*) *Results of measurements*

The results of all measurements on these six samples are listed in table 7.

So far as possible, mercury in the various bottles was kept distinct in case one bottle of a sample had been contaminated whilst others had not. The bottles are indicated by the Roman figures (i), (ii) against each sample. In most measurements it was not possible to use mercury from one bottle alone and small amounts from other bottles of the same sample had to be added, but where just one bottle number is given the mercury used came predominantly from that bottle.

The densities of mercury in bottles A (i), A (iii), B (i), B (ii) and N.S.L. (ii) were measured more than once, and from the departures of the values from the means for each bottle the standard deviation of a single observation is found to be 3×10^{-6} g/cm^3 on 7 degrees of freedom (variance 40×10^{-12}) or 0·5 p.p.m. of the density. This is the most direct estimate of the uncertainty of the measurements since it is not affected by differences between bottles due, for instance, to chemical impurities and can be compared with the estimate of 0·35 p.p.m. given in §4 (*f*). This latter value does not include errors in the volume of the cube, but the variability between measurements on the same bottle will include a contribution from this source on account of the long time over which some of the measurements extend so that although the observed variability seems rather large compared with the estimates of the various contributions to it, it cannot be said to be significantly so, particularly as it is based on rather few degrees of freedom.

The standard deviation corresponding to the variability of all sample values about the sample mean is 7×10^{-6} g/cm^3 (variance 47×10^{-12}) on 18 degrees of freedom. This agrees very well with the above standard deviation of values about bottle means and there is therefore no evidence for a significant variation between bottles. The standard deviation corresponding to departures of mean values for bottles from sample means, 5×10^{-6} g/cm^3, is consistent with this.

We conclude, therefore, that there is no significant source of error or variability in the results beyond those already discussed and we accordingly take the mean value for a sample to be the straight mean of all results for the sample. These mean values are given in table 8 together with the standard deviations of the means as estimated from the variance (47×10^{-12} $(\mathrm{g/cm^3})^2$) of individual values about the sample means ((*a*) in table 8). Combining these standard deviations with that of a value of the volume of the cube, 0·14 p.p.m., the overall standard deviations (*b*) of table 8 are obtained.

Table 7. Measured values of density

date of gauging	sample	bottle	volume of cube at 21 °C *in vacuo* ($\mathrm{cm^3}$)	mean temperature of observation (°C)	mean pressure of observation (mm Hg)	density at 20 °C and 1 atm ($\mathrm{g/cm^3}$)
5 Feb. 1958	A	(i)	393·700140	21·076	797·92	13·545873
17 Feb.		(i)		21·105	805·27	882
3 Mar.		(ii)		21·111	810·85	887
10 Mar.		(iii)		21·097	793·46	889
12 Aug. 1958	B	(i)	393·700131	21·027	798·49	13·545876
20 Aug.		(ii)		21·058	789·51	868
8 Sept.		(iii)		21·070	804·38	878
15 Sept.		(i)		21·054	804·80	882
22 Sept. 1958	E	(i)		21·056	799·48	13·545894
30 Sept.		(ii)		21·000	783·73	904
27 Oct. 1958	C	(i)	393·700174	21·032	808·04	13·545871
5 Nov.		(ii)		21·036	799·04	880
18 Nov.		(iii)		21·003	809·78	882
24 Nov.		(i), (ii)		21·035	810·54	884
5 Dec. 1958	A	(i)		21·108	804·18	13·545889
15 Dec.		(iii)		21·041	769·60	896
31 Dec. 1958	B	(ii)		21·042	798·96	13·545868
1 Jan. 1959		(i)		21·042	791·40	886
5 May 1959	N.S.L.	(i)		20·996	806·91	13·545893
14 May		(ii)		21·027	808·98	891
30 June		(ii)	393·700142	21·034	801·50	882
11 Aug. 1959	N.B.S.	(i)		21·034	796·99	13·545881
19 Aug.		(ii)		21·046	803·84	882
2 Sept. 1959	A	(i), (iii)		21·044	806·41	13·545879

Table 8. Density ($\mathrm{g/cm^3}$) at 20 °C and 1 atm

sample	value by content method	standard deviations (*a*) p.p.m.	standard deviations (*b*) p.p.m.	value by displacement method	displacement − content (p.p.m.)
A	13·545885	0·23	0·27	13·545888	+0·23
B	13·545876	0·23	0·27	13·545887	+0·8
C	13·545879	0·27	0·30	13·545883	+0·30
D	—	—	—	13·545897	−0·15
E	13·545899	0·40	0·42	—	
N.S.L.	13·545889	0·30	0·33	—	—
N.B.S.	13·545882	0·40	0·42	—	—

Mean difference, displacement − content +0·30 p.p.m.
Mean difference, excluding D − E +0·45 p.p.m.

(*a*) Standard deviation excluding uncertainty of volume of cube.
(*b*) Standard deviation including uncertainty of volume of cube.

(*c*) *Comparison with results of the displacement method*

The values given in paper I have to be corrected for the change in the values assigned to the wavelengths of lines in the mercury spectrum discussed in §3 (*a*). The sample means so corrected are given in table 8.

If it is assumed that samples D and E may be compared, the mean difference between the results of the displacement method and the content method is +0·30 p.p.m., while excluding this comparison, it is +0·45 p.p.m.

It was estimated in paper I that random errors were negligible by comparison with systematic errors in the volume of the cube due to unknown grease films on it and due to temperature errors, and it was considered that these systematic errors might amount to 0·5 p.p.m.

In the present work the measured values of density, so far as they show any trend, increase with time. If films developed on the inner faces of the cube, or if the mercury were becoming impure, the density would decrease, so that there is good reason to discount these sources of error. We accordingly consider that the present work is less subject to systematic error than the earlier measurements.

Considering, then, the predominantly random errors of this work set down in table 8 and the predominantly systematic errors of the previous work, it will be seen that, individually, the differences between the displacement and content results are none of them significant, but taken together they may indicate an overall systematic difference between the two methods, which, as it happens, is in the direction to be expected if there were grease films on the solid cube.

It has been seen that the temperature is rather better known in this work than in the displacement measurements, essentially because at that time the Smith Bridge was not available. The uncertainties of the volumes of the tungsten carbide and silica cubes are almost the same but the sources of error are quite different. With the former, it was the method of measurement, especially the use of slip gauges wrung on to the cube faces to provide reference surfaces, that was the major source of error; in the latter the measurements were of considerably higher accuracy but the cube itself has been less stable than the tungsten carbide cube.

The range of values of all samples, irrespective of method, is 1·7 p.p.m. This clearly greatly exceeds the errors of the measurements and indicates real differences between samples. The mean density of all samples, except D and E*, is

$$\mathbf{13{\cdot}545\,884}\ \mathrm{g/cm^3}\ \text{at 20 °C and 1 atm,}$$

with a standard deviation of 0·2 p.p.m., and there is a high probability that the density of any sample of pure mercury will be within 1 p.p.m. of this value.

The corresponding value of the density at 0 °C and 1 atm, calculated by using the expansion of Beattie *et al.* (1941), is

$$\mathbf{13{\cdot}595\,080}\ \mathrm{g/cm^3}.$$

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* Samples D and E are excluded from this mean because they differ so greatly from the others; if they are included as one sample the overall mean becomes 13·545886 g/cm³, s.d. 0·28 p.p.m.

The original design of this experiment was due to Mr P. H. Bigg and to him and to Dr H. Barrell I am indebted for continual advice and interest. The execution of the measurements would have been impossible without the very accurate cube constructed by members of the Light Division Optical Workshop led by Mr R. T. Peters and directed by Mr K. J. Habell. Mr N. W. B. Stone was responsible for much of the preparatory experimental work and for the first determinations of density; subsequent determinations were made by Mr B. W. Jolliffe and Mrs V. P. E. R. Matthews. Mrs H. M. Dale assisted with interferometric measurements and Miss M. Ridgway with temperature measurements.

I am indebted to Dr A. V. Astin, Director of the National Bureau of Standards, and to Mr N. Esserman, Director of the National Standards Laboratory, for permission to publish particulars of the source and preparation of the N.B.S. and N.S.L. samples and the results of the measurements of their densities.

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.

References

Barber, C. R., Gridley, A. & Hall, J. A. 1955 *J. Sci. Instrum.* **32**, 213.
Barrell, H. 1951 *J. Opt. Soc. Amer.* **41**, 295.
Barrell, H. 1958 *P.V. Comm. int. Poids Més.* (2) **26**B, p. M80.
Barrell, H. 1961 *Nature, Lond.* **189**, 195.
Beattie, J. A., Blaisdell, B. E., Kaye, J., Gerry, H. T. & Johnson, C. A. 1941 *Proc. Amer. Acad. Arts Sci.* **71**, 371.
Cook, A. H. 1956 *Brit. J. Appl. Phys.* **7**, 285.
Cook, A. H. 1957 *J. Sci. Instrum.* **34**, 455.
Cook, A. H. 1960 *Proc. N.P.L. Symposium on Interferometry*, p. 389. London: H.M.S.O.
Cook, A. H. & Stone, N. W. B. 1957 *Phil. Trans.* A, **250**, 277. (Part I).
Edlen, B. 1953 *J. Opt. Soc. Amer.* **43**, 339.
Elliot, K. W. T., Wilson, D. C., Mason, F. C. P. & Bigg, P. H. 1960 *J. Sci. Instrum.* **37**, 162.
Michelson, A. A. 1927 *Studies in optics.* University of Chicago Press.
Report of Commission 14 1958 *Trans. Int. Astron. Un.* p. 10.
Wilson, W. & Stone, N. W. B. 1957 *J. Sci. Instrum.* **34**, 327.

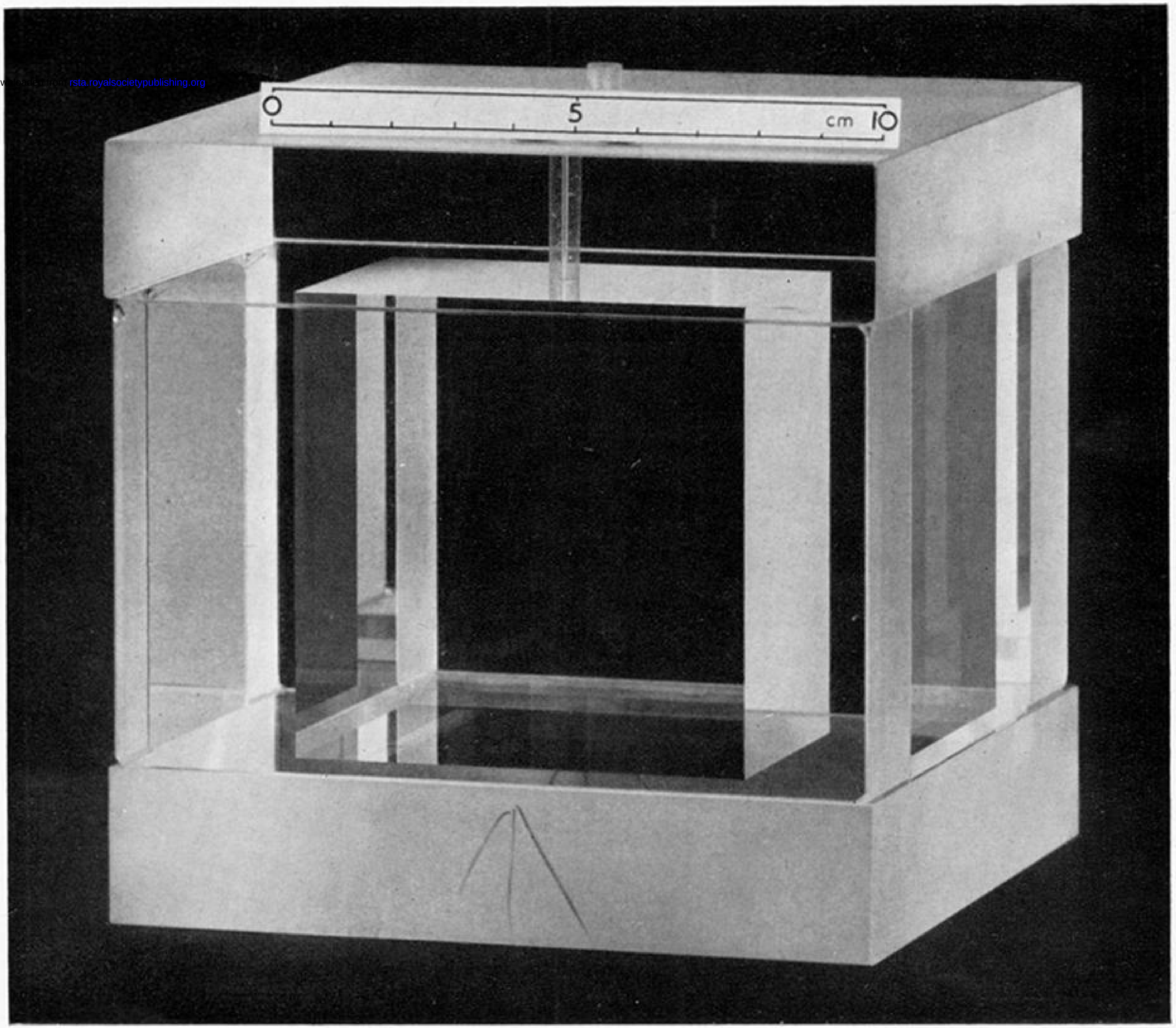
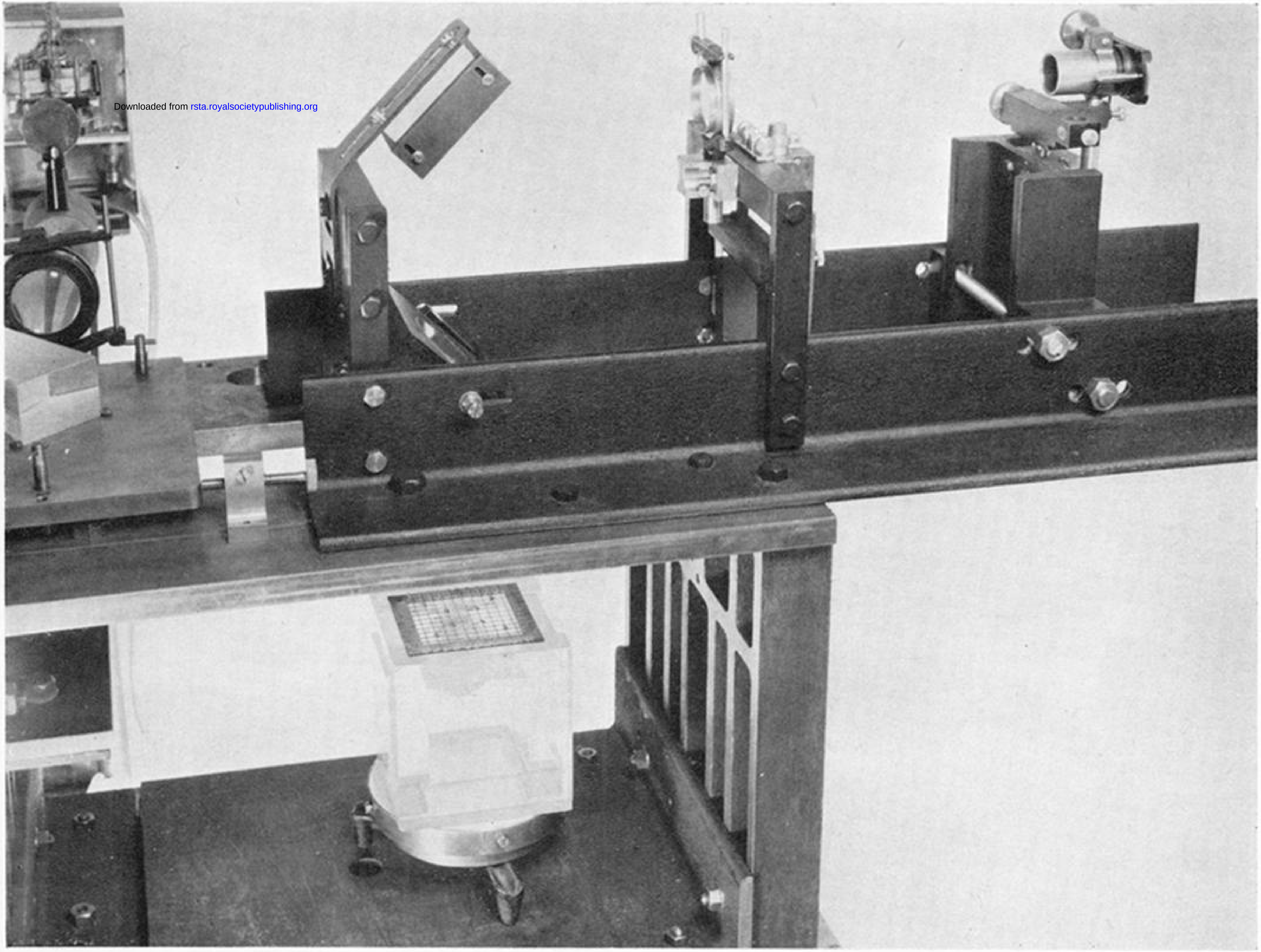


FIGURE 1. Photograph of the hollow cube of fused silica (before attachment of stainless-steel fitting).



IGURE 5. Cube in interferometer for observation of three-beam interference fringes, showing graticule on cube. For clarity the cube has been removed from its vacuum vessel.

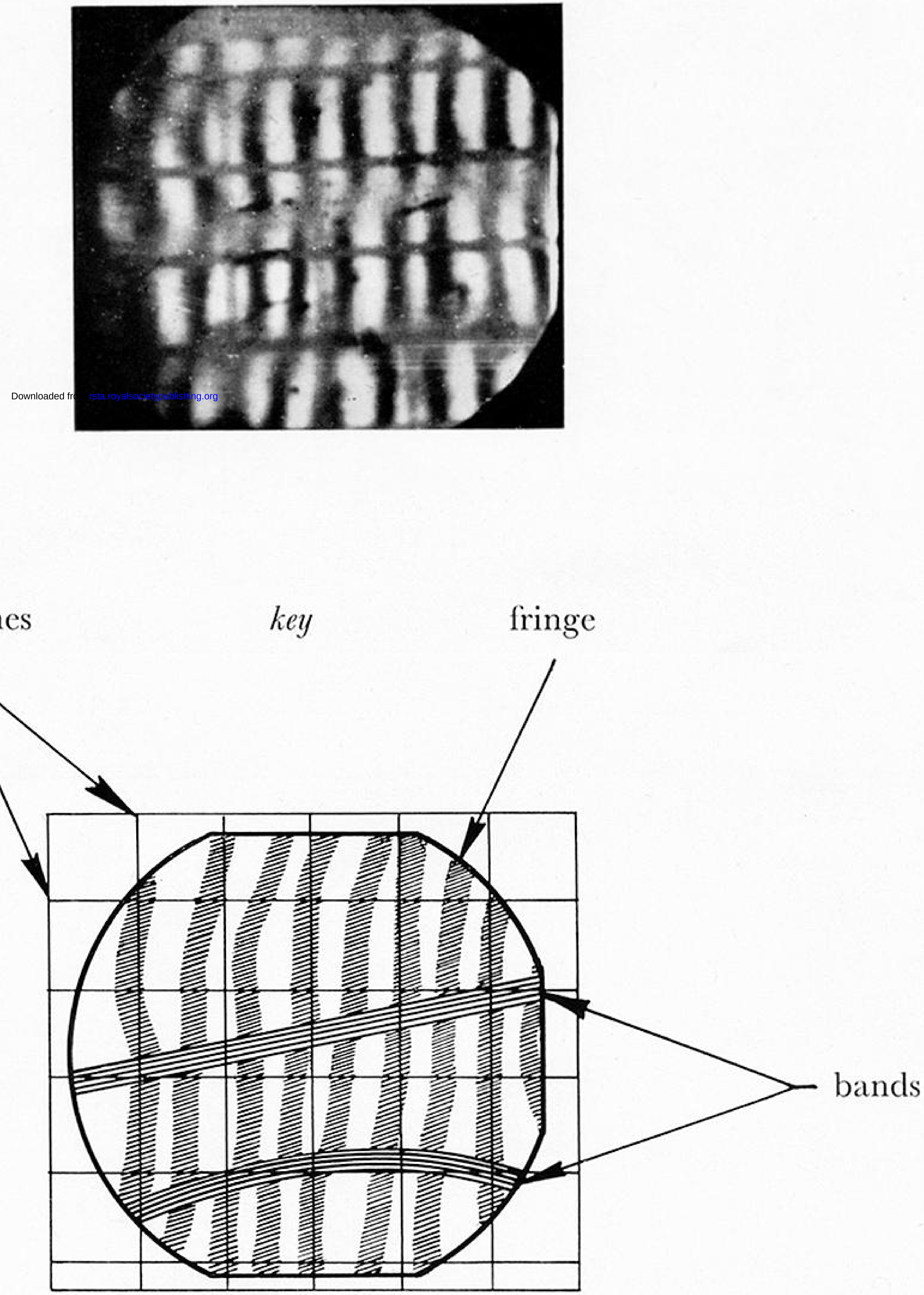


FIGURE 6. Appearance of three-beam fringes.