packed. There is a different arrangement for holding the minor weight, which the engraver has failed in representing so well as the rest.

Plate 9 shows also a variety of milled screw-heads, each of which has of course a purpose; but as neither of them, except one by which the lower weight is turned round, has any part in the observations such as they are described above, but only in ultimate manipulations which it is unnecessary to dwell upon here, they may be regarded as ornaments. It will be noticed that the collimator is removed, and one of the side supports is supposed broken off, to discover the minor weight; which last, with its mirror and magnet bar, is seen turned through 30° or 40° into an oblique position. At the same level and outside the chamber are seen arms, one of which resembles a cross. These are the guides for two magnets which have been removed. Their intended purpose is mentioned by Broun in his description.

The pillar alongside the shaft is a case for a thermometer, the bulb of which is within the chamber.

"On the Coefficients of Expansion of the Di-iodide of Lead, PbI_2, and of an Alloy of Iodide of Lead with Iodide of Silver, $PbI_2.AgI$." By G. F. Rodwell, F.R.A.S., F.C.S., Science Master in Marlborough College. Communicated by Professor A. W. Williamson, For. Sec. R.S. Received March 10. Read March 31, 1881.

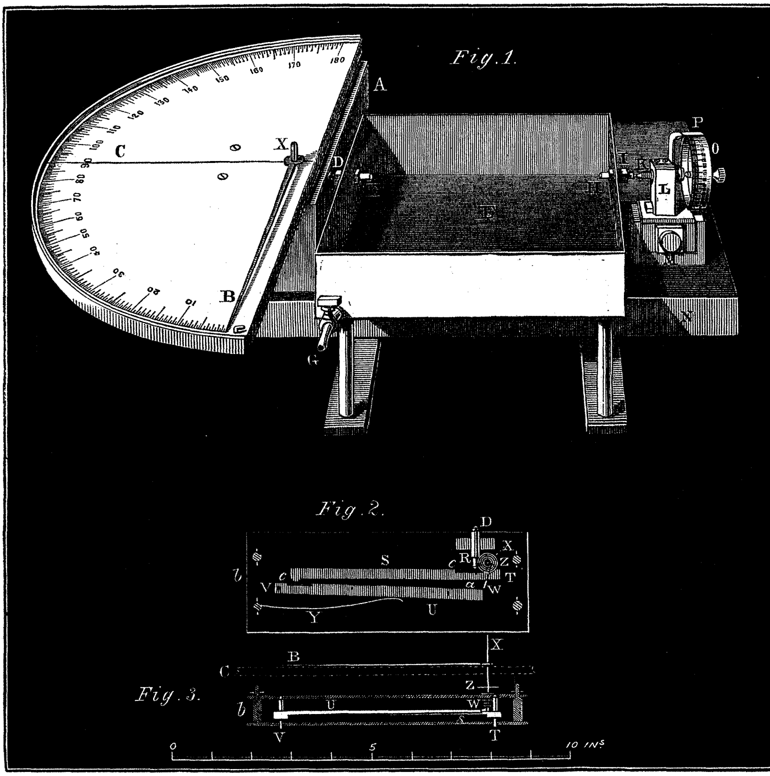
In former communications which I have had the honour of submitting to the Royal Society, I have given determinations of the coefficients of expansion by heat of the chloride and bromide of silver and the iodide of mercury between 0° C. and the fusing point; also determinations of the coefficients of expansion and contraction of the iodide of silver, and of certain chlorobromiodides of silver. (" Proc. Roy. Soc.," vol. 25, pp. 280–303, and vol. 28, p. 284.)

The iodide of lead, and an alloy of iodide of lead with iodide of silver, were thought to be very suitable substances for a continuation of these experiments. The following pages describe the results obtained.

The experimental method was precisely similar to that before described, but the expansion apparatus was rendered more delicate by several notable changes suggested during the course of the former experiments. It is unnecessary to describe this apparatus again (for description *vide* " Proc. Roy. Soc.," vol. 25, p. 281–2), but it may be remembered that a homogeneous rod of the substance under examination is connected with a series of levers which multiply 5,382 times, while the value of the movements is estimated by a micrometer screw reading to $\frac{1}{50000}$ of an inch. The following alterations were made mainly with a view of reducing the resistance by diminishing friction, and thus adding to the sensibility of the apparatus :—

1. The wooden base N (fig. 1) was replaced by a massive stone

block, to which the box containing the levers and the upright carrying the micrometer head were firmly bolted.



This block with figs. 1, 2, 3 is a reprint from "Proceedings," vol. 25, p. 280-282, where all are described.

2. The levers S, U (fig. 2) were reduced in weight.

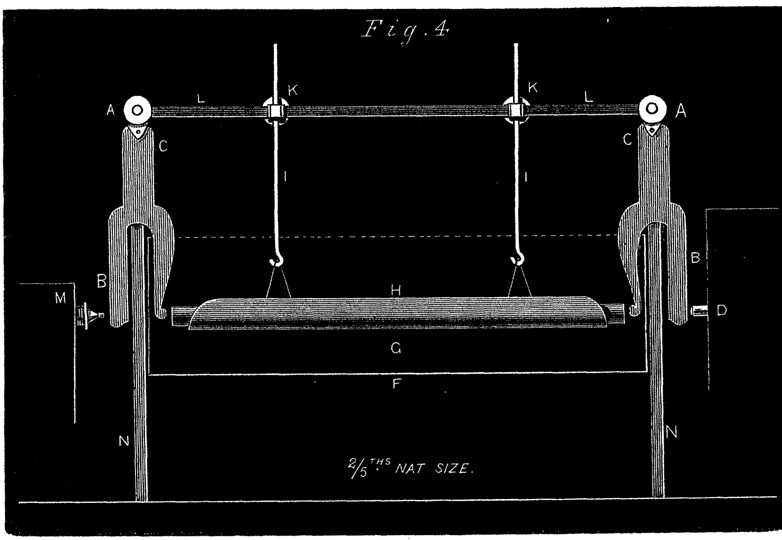
3. The spring Y (fig. 2) was removed, as it was found that the recoil of the helical spring Z was quite sufficient to bring the index back to zero, and the presence of Y served only to increase the resistance and general strain.

4. The vertical axis X (figs. 1 and 3) was no longer allowed to work in the upper confining plate of the framework *b*, but it was caused to turn lightly on a bent arm above, while below it rested upon a slightly hollowed ruby.

5. The steel chain W communicating motion from the lever U to the vertical axis X, which carries the index, was shortened and caused to wind upon the barrel in such a manner that when unwound to the

extent of half a single coil, it moved the index through its entire range, viz., from 0° to 180° of arc. By this means any possibility of the chain doubling upon itself was obviated.

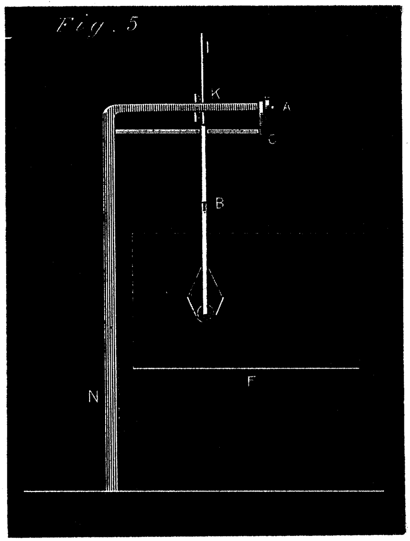
6. But perhaps the most important changes were the removal of stuffing boxes I and the rods H from the trough F, and the substitution of levers working over the rim of the trough; and the suspension of the rod of substance under examination in a cradle between the levers. This was effected in the following manner:—



Section through the trough longitudinally, showing the mode of suspension of the bar, and the position of the levers.

A horizontal bar LL (fig. 4) was supported by rods N, N, strengthened by cross bars (not shown) let into the stone base of the instrument; it carried Y-shaped brass levers B, B, moving about axes at C, C (figs. 4 and 5), attached at the points A, A. F is the trough in which hot ceresine is used for heating the bar under examination, H, supported by the cradle G. Two rods I, I, which slide in holes K, K, and are capable of being held at any height by screws, support the cradle G. D is the rod (figs. 1 and 2) which bears upon the lever S, and M the point of the micrometer screw.

The apparatus was standardised at frequent intervals by the use of a rod of fine homogeneous silver. Ceresine boiling at 430° C. was used to heat the rods in F, and it was heated to any desired temperature by means of a Bunsen burner placed beneath, and near the centre of the trough.



End section of the trough, showing one of the levers, and the bar which carries it.

Iodide of Lead.—Pure iodide of lead was cast into rods one-third of an inch in diameter and 6 inches long. The ends were made plane by a fine steel saw, and they were furnished with copper caps. Great difficulty was experienced in casting the rods, owing to the brittleness of the iodide. Slightly greased tubes of very thin German glass were used as the moulds, and as the rods would rarely slip out of the tubes the glass had usually to be chipped away along the whole length of the rod by the point of a knife. The iodide underwent the same changes of colour as were observed in the iodide of silver; that is to say, it fused to a bromine-red liquid, which, when solidified, became red-brown, and, while cooling, brick-red, reddish-yellow, and, when completely cool, orange-yellow. Harsh noises, like those produced by bending tin, were heard during the cooling of the mass, and the fracture was highly crystalline.

Differences of opinion appear to exist as to the effect of fusing iodide of lead in the air. In the same volume of a standard work I find two exactly contrary opinions: for it is stated, on the one hand, that the iodide if fused in contact with air gives off a part of its iodine, becoming oxyiodide of lead; while elsewhere the iodide is classed among those which may be fused in an open vessel without change.

In order to set this matter at rest, 56·1690 grms. of iodide were fused in a covered porcelain crucible. The fusion was continued

for eight minutes, during which the cover was three times momentarily removed. Violet fumes of iodine escaped on each occasion, but on weighing the loss was found to amount to only

·11036 per cent.

Again, the mass was kept fused for four minutes, and the crucible cover was twice removed, but the loss had only increased to

·1584 per cent.

After a third fusion the total loss only amounted to

·1718 per cent.

Hence it is manifest that iodide of lead may safely be fused out of contact with air, with scarcely appreciable loss. When, however, the crucible cover was permanently removed, the iodide rapidly decomposed.

When the iodide was heated in a current of carbonic anhydride, it sublimed unchanged in crystals; while if it was heated in a current of dry oxygen it rapidly decomposed, fine crystals of iodine collecting in the fore part of the tube.

The specific gravity of iodide of lead, in common with the iodides of copper, silver, and potassium, is less than the mean specific gravity of its constituents. Karsten found it to be 6·0282, Boullay 6·11, and my own determinations gave 6·12. The calculated specific gravity is 6·629.

The fusing point as determined by Mr. Carnelley is 383° C.

The coefficient of cubical expansion for 1° C. was found to be

·00007614

for temperatures between 0° C. and 205° C. It increased to

·00008317

between 205° C. and 253° C.

Between 253° C. and 265° C. the mass expanded rapidly, with a coefficient nearly eight times greater than the previous, viz.:—

·0006378.

After the subsidence of this rapid expansion it no longer retained the original coefficient, but assumed one of more than double the amount, viz.:—

·000180.

At temperatures some distance from the melting point the rod began to bend, and it became necessary to assume that this last coefficient continues to the melting point. The expansion in passing from the solid to the liquid condition was determined by the method described in my previous paper.

It will be observed that the iodide of lead, as in the case of the iodide of mercury ("Proc. Roy. Soc.," vol. 28, p. 284), has three coefficients of expansion, viz. :—(*a*) a coefficient somewhat less than that of chloride of silver up to 253° C.; (*b*) a coefficient during 12° C., nearly eight times greater than the preceding; and (*c*) finally a coefficient somewhat more than twice as great as that between 0° and 253° C., at temperatures above 265° C. Undoubtedly the iodide of lead, as in the case of the iodide of mercury, undergoes a molecular change while rapidly expanding between 253° and 265° C., and before assuming the higher coefficient. This is supported by the fact that the highly brittle and crystalline rod showed itself capable of bending after having undergone the rapid expansion. It will be remembered that the iodide of silver, which is very crystalline and brittle below 145° C., becomes amorphous and plastic above that temperature. The familiar example of sulphur will also recur to the mind.

If we suppose a mass of iodide of lead to be heated from 0° C. to the melting point (383° C.) the following will be the volumes at the respective temperatures.

Volume at	0° C.	=1·000000.
,,	205°	=1·015608.
,,	253°	=1·019595.
,,	265°	=1·027248.
,,	383° (solid)	=1·048488.
,,	383° (liquid)	=1·078080.

The curve is shown in Table A.

The specific gravity of the iodide in the molten condition is 5·6247.

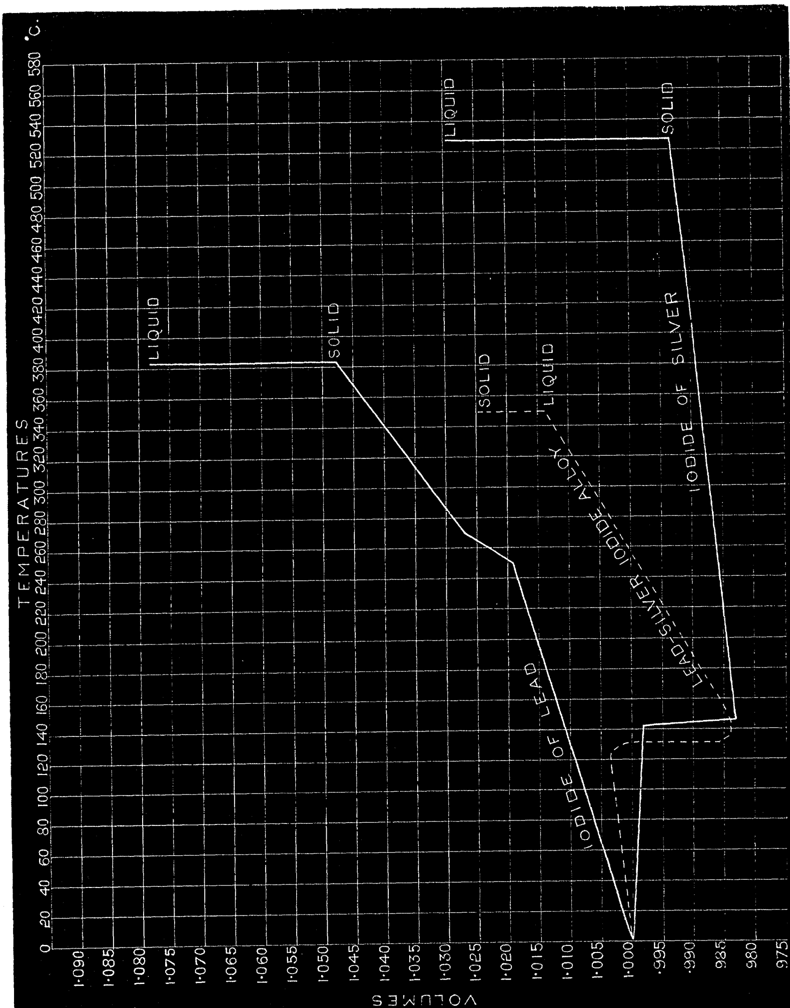
The fact that a substance may possess two or three different coefficients of expansion has apparently only been observed hitherto in the case of such substances as fusible alloy, because in determining the coefficients of solid bodies temperatures exceeding 100° C. have rarely been employed. Paraffine or ceresine used as a heating medium will allow the determination of coefficients to a temperature of 300° C., and, undoubtedly, many bodies when thus examined would be found to present anomalies similar to those remarked in the case of the iodides of lead and mercury.

The Lead-Silver Iodide Alloy.

Bearing in mind the peculiar nature of the coefficients of certain alloys of iodide of silver with the chloride and bromide ("Proc. Roy. Soc." vol. 25, p. 292), it was thought to be advisable to determine the coefficients of an alloy of iodide of lead with iodide of silver.

These bodies were accordingly fused together in the proportion of one molecule of each, viz., $PbI_2.AgI$. This contains in 100 parts

Table A.—Table showing the Relationship between the Temperature and Volume of Iodide of Lead, Iodide of Silver, and of the Lead-Silver Iodide Alloy, $PbI_2.AgI$.



Iodide of lead......	66·206	Lead............	29·7449
Iodide of silver	33·794	Silver.	15·5642
		Iodine...........	54·6909
	100·000		100·0000

The substances were fused together in a porcelain crucible, and cast in thin glass tubes 9 inches long by one-third of an inch in diameter. The molten mass underwent the same changes of colour in cooling as either one of its constituents, and ultimately became a dull orange-coloured compact mass. Although composed of two substances which are highly crystalline and brittle, the alloy was found to be hard and tenacious. Although the constituents are coarsely crystalline in structure, the alloy is finely granular. During the cooling of the mass it expanded with sufficient force to break the glass tube. Harsh noises were emitted during cooling, and the whole mass was sometimes jerked from its position; while, if held in the hand, it was felt to be agitated by strong tremors.

Mr. T. Carnelley has determined for me the melting point of the alloy, which he finds to be 350° C.

The specific gravity is 5·923.

By repeated digestion with large volumes of boiling water the alloy is decomposed, the iodide of lead being dissolved, while the iodide of silver remains as a dull green powder.

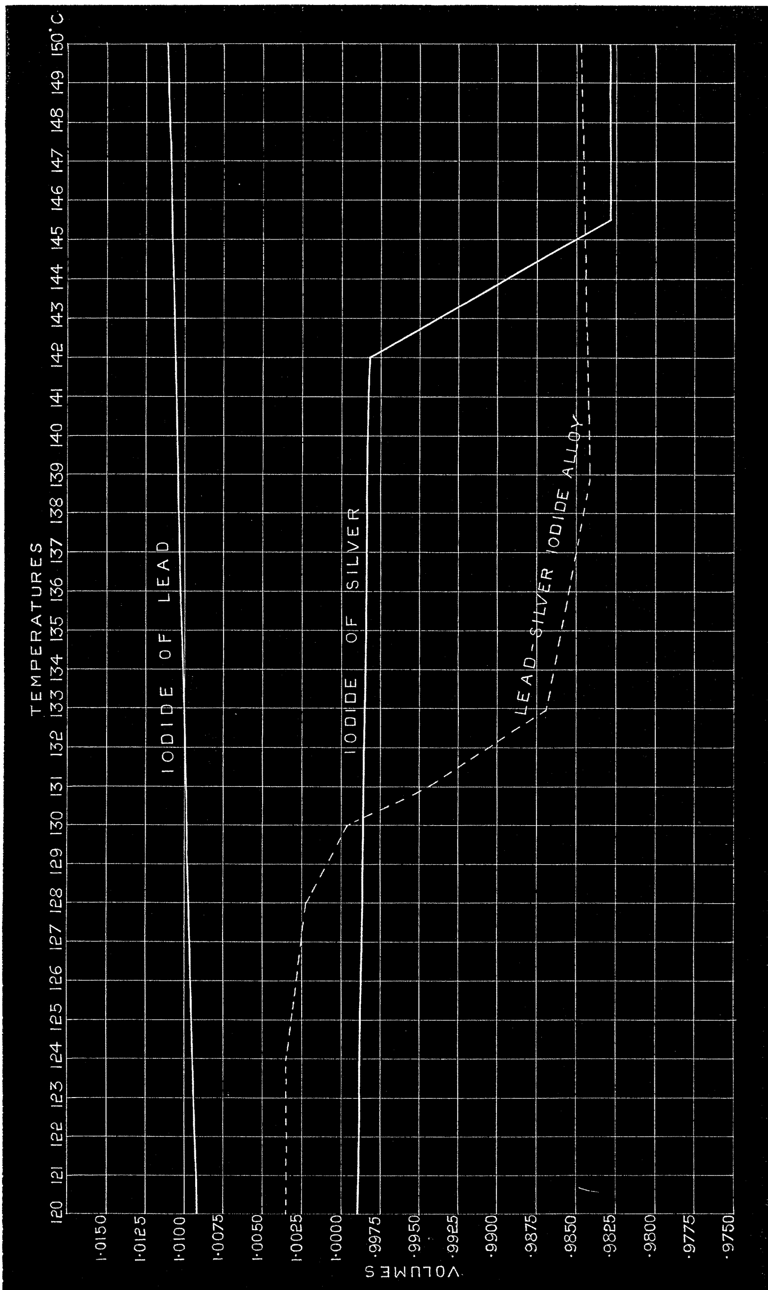
On examination in the expansion apparatus the alloy was found to undergo slow expansion to a temperature of 118° C., then, for 6° C., it simply absorbed heat without either contracting or expanding. At 124° C. contraction commenced, and continued at unequal rates till a temperature of 139° C. was attained. Then, again, the mass underwent neither contraction nor expansion during heating through 5° C., and then it commenced to expand somewhat rapidly. The most rapid contraction on heating took place between 130° and 133° C. Thus, in all, for the temperatures during which the mass contracted, the index moved through fifteen revolutions of 180° to 0° of arc, and these were related to the temperatures in the following manner:—

1 revolution of index	took place	during heating	from	124—128° C.
2	,,	,,	,,	128—130° C.
4	,,	,,	,,	130—131° C.
6	,,	,,	,,	131—133° C.
2	,,	,,	,,	133—139° C.

The details of these contractions are shown in Table B.

The heating, especially at these temperatures, was excessively slow, and so moderated that a complete observation of the behaviour of the substance in the expansion apparatus lasted from three to four hours. Above 144° C. the alloy expanded with a coefficient about three times greater than that which it possessed between 0° and 118° C.

Table B.—Details of the Contraction by Heat of Iodide of Silver, and of the Lead-Silver Iodide Alloy.



Coefficients of Cubical Expansion and Contraction of the Alloy for 1° *C.*

Between	0°	and	118° C. =	+·0000306
"	124	"	128° C. =	−·0003240
"	128	"	130° C. =	−·0012990
"	130	"	131° C. =	−·0017330
"	131	"	133° C. =	−·0039000
"	133	"	139° C. =	−·0004329
"	144	"	350° C. =	+·0001150

Plus has been placed before the coefficients of expansion on heating; *minus* before the coefficients of contraction. The expansion in passing from the solid to the liquid condition was determined as before.

The coefficient between 144° C. and the fusing point increased rapidly with the temperature.

If we take the volume at 0° C. as unity, we have the following volumes corresponding to the temperatures given:—

Volume at	0° C.	= 1·000000
"	118	1·003610
"	124	1·003610
"	128	1·002314
"	130	·999716
"	131	·994517
"	133	·986717
"	139	·984120
"	144	·984120
"	150	·984810
"	300	1·006500
"	350 (solid)	1·013790
"	350 (liquid)	1·024370

In regard to this alloy the following points may be noted:—

1. It possesses a similar density at three different temperatures. Thus, it is obvious that the density is the same at 0° C., at just below 130° C., and at 282° C.

2. Although the alloy contains only 33·794 per cent. of iodide of silver, it contracts as considerably *during heating* as the iodide itself.

3. While the iodide of silver commences its contraction at 142° C., and finishes it at 145°·5, the alloy commences to contract 18° C. lower (viz., at 124° C.) and finishes 6°·5 C. lower (viz., at 139° F.).

4. The chlorobromiodides of silver also began to contract on heating (an effect which, of course, we must attribute solely to the presence of iodide of silver) at 124° C., but they finished at 133° C.

5. The harsh sounds emitted by the alloy during cooling, and the tremors simultaneously propagated through the mass, prove that violent molecular agitation is going on at such time as the iodide of

silver is passing from the amorphous plastic condition to the brittle crystalline condition, within the mass of the iodide of lead.

6. The fusing point of the alloy is 177° C. lower than that of the iodide of silver, which constitutes one-third of its weight, and 33° C. lower than that of the iodide of lead, which constitutes two-thirds of its weight.

7. If the lowering of the fusing point (also markedly apparent in the case of the chlorobromiodides of silver) is due to the fact that similar particles of matter attract each other more powerfully than dissimilar, and hence, when the particles of two bodies are mutually diffused, the attraction becomes less, and the molecular motion is consequently more readily assimilated; the same cause may serve to explain the commencement of the phase of contraction on heating the alloy at a temperature 18° C. lower than the substance to which it owes this property.

8. It is interesting to compare one of the chlorobromiodides of silver with the lead-silver iodide alloy. For this purpose we will take the chlorobromiodide which contains the nearest approach to the same quantity of iodide of silver as the alloy. The second of the chlorobromiodides before described ("Proc. Roy. Soc.," vol. 25, p. 295) contains 41·484 per cent. of iodide of silver, and 58·5160 per cent. of the chloride and bromide of silver, which latter, from the heat point of view, may be regarded as the same substance, because their coefficients of expansion are practically the same. It may be noted (*vide* below) that while the expansion of the bromide (which is slightly greater than that of the chloride) scarcely exceeds that of the iodide of lead, and while, moreover, the chlorobromiodide contains 8 per cent. more iodide of silver than the lead-silver iodide alloy, the amount of *contraction* by heat of the latter is *more than twenty times greater* than that of the former, although we must believe this effect to be solely due to the iodide of silver in each case.

Comparison of the Coefficients of the Iodide of Lead and the Bromide of Silver, used in conjunction with Iodide of Silver in the formation of the two Alloys given below.

	Iodide of lead.	Bromide of silver.
Melting point	383° C.	427° C.
Volume at 0° C.	1·000000	1·000000
,, 205	1·015608	1·021945
,, 253	1·019594	1·027369
,, 265	1·027248	1·028725
,, 383 (solid)	1·048488	1·042531
,, 383 (liquid)	1·078080	
,, 427 (solid)		1·047855
,, 427 (liquid)		1·107225

Comparison of the Coefficients of the Lead-silver Iodide Alloy with those of a Chlorobromiodide of Silver, and of Iodide of Silver.

	Lead-silver iodide alloy, containing 33·794 per cent. of iodide of silver.	Chlorobromiodide of silver, containing 41·484 per cent. of iodide of silver.	Iodide of silver.
Composition	PbI_2AgI	AgI,AgBr,AgCl.	AgI.
Volume at 0° C.	1·000000	1·000000	1·000000
„ 118	1·0036108		
„ 124	1·0036108	1·012037	·998765
„ 128	1·002314		
„ 130	·999716		
„ 131	·994517		
„ 133	·986717	1·006637	·998608
„ 139	·984120	.. ..	·998503
„ 142	.. ..	.. ..	·998450
„ 144	·984120		
„ 144·5	.. ..	.. ..	·982700
„ 150	·984810	.. ..	·982828
„ 300	1·002060	1·039239	·987094
Volume of solid at melting point	1·013790	1·046646	·993550
„ liquid at solidification point	1·024370	1·097486	1·029450
Melting point	350° C.	331° C.	527° C.

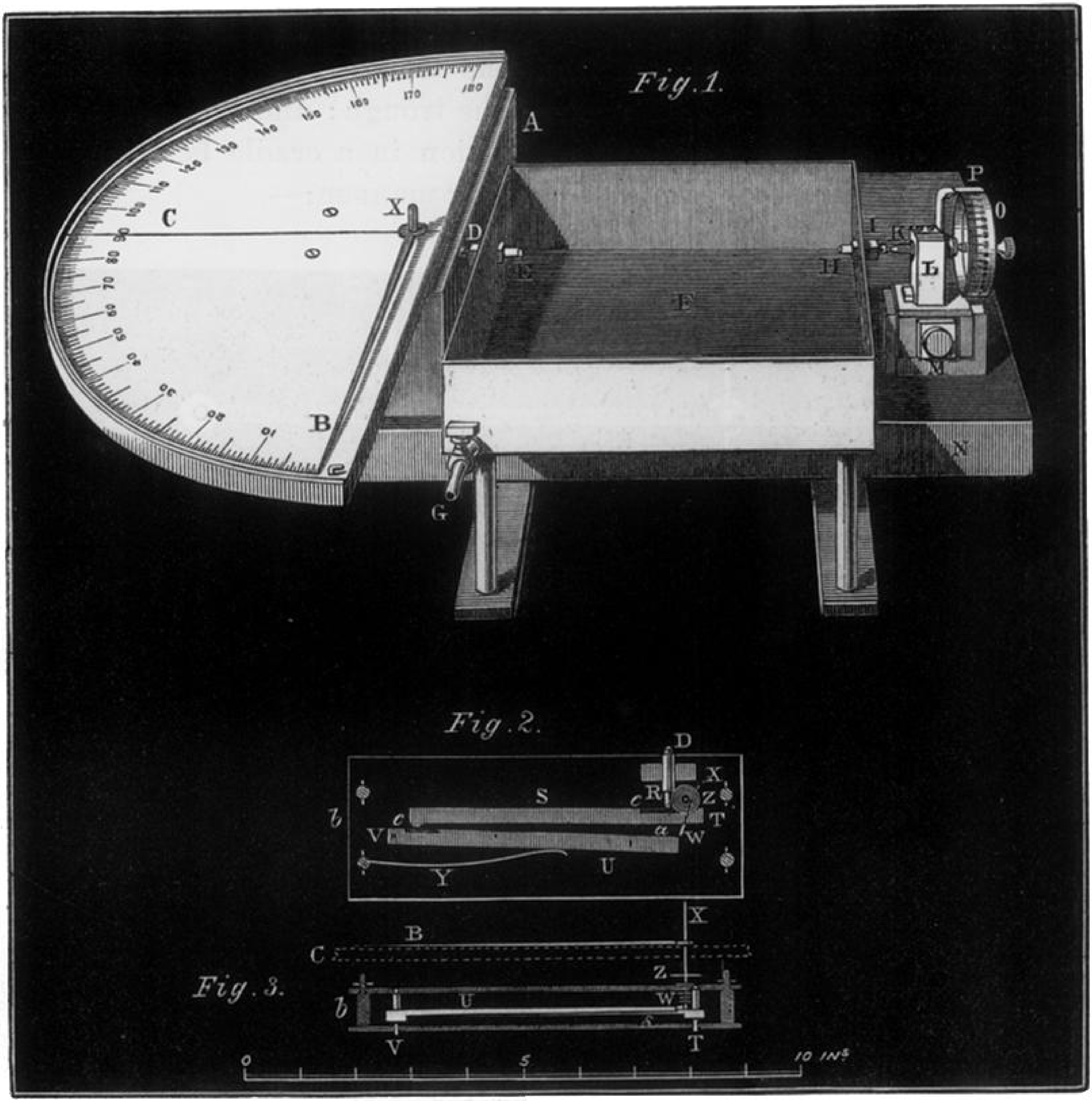
The accompanying tables show the curves of contraction and expansion of the lead-silver iodide alloy, and of its constituents. In Table B the scale has been enlarged in order to show the details of the contraction of the alloy on being heated from 124° C. to 139° C.

(Addendum. Received April 8, 1881.)

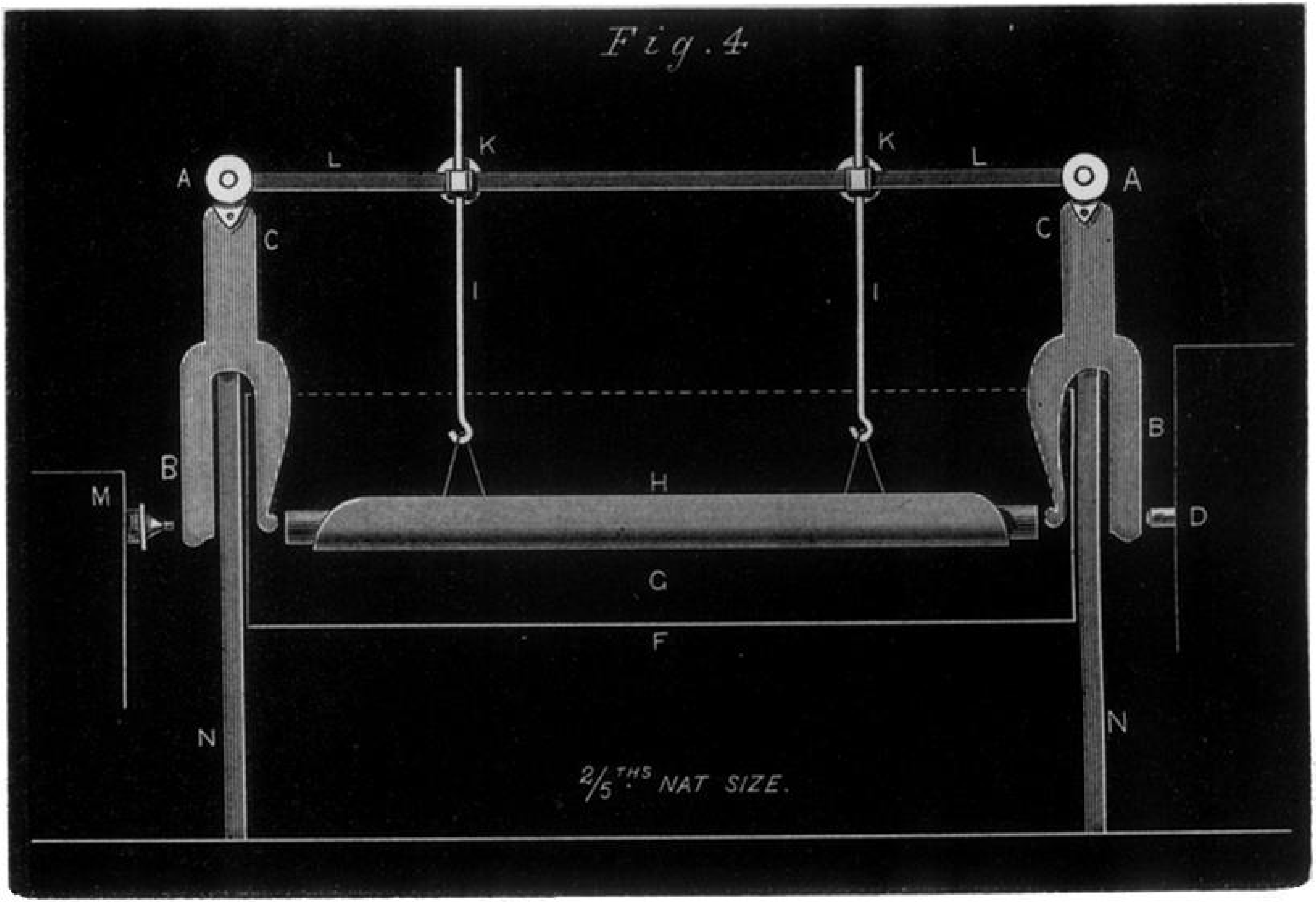
Other alloys of iodide of lead with iodide of silver have since been made, having the following composition :—

(1.)	$2AgI.PbI_2$,	containing	50·517	per cent.	of iodide of silver.
(2.)	$3AgI.2PbI_2$	,,	43·360	,,	,,
(3.)	$4AgI.3PbI_2$	,,	40·497	,,	,,
(4.)	$5AgI.4PbI_2$	,,	38·950	,,	,,
(5.)	$10AgI.9PbI_2$	,,	36·190	,,	,,

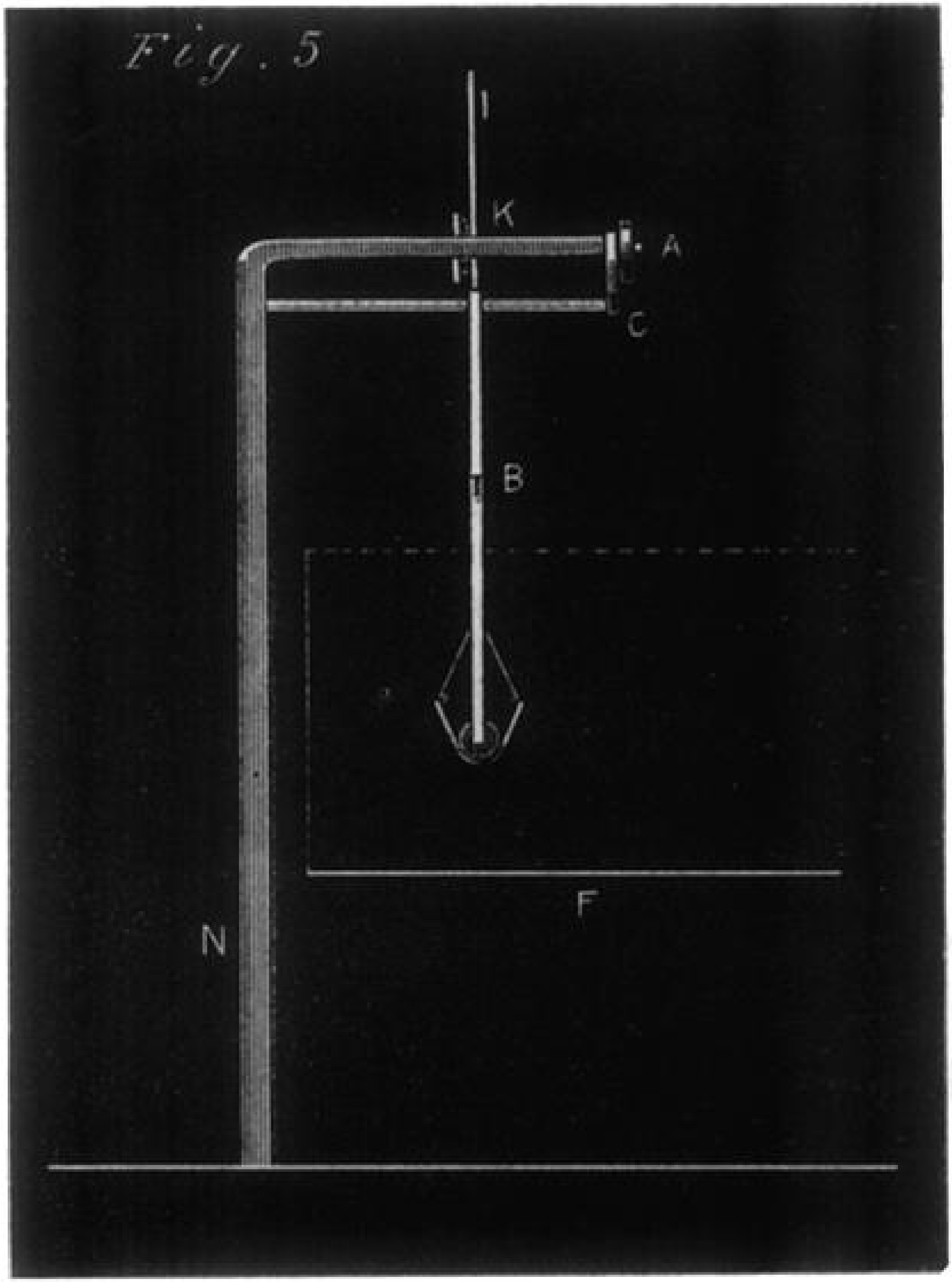
These all possessed the same general appearance as the alloy $AgI.PbI_2$ described above, which contains 33·794 per cent. of iodide of silver. But with the exception of No. 5 they were all so brittle that they could not be cast into rods suitable for use with the expansion apparatus. During cooling large rifts appeared in the rod at right angles to its length, at the time when the iodide of silver commenced to expand. In the case of No. 1 the rod was violently broken during its cooling by the expanding iodide of silver; even when slowly annealed in hot paraffine. It may be noted that no such effect was produced in the case of the chlorobromiodides of silver, having the composition respectively: $Ag_2I_2.AgBr.AgCl$; $Ag_3I_3.AgBr.AgCl$; $Ag_4I_4.AgBr.AgCl$; and containing in each case a larger percentage of iodide of silver (viz., 58·6404; 68·0171; and 73·9285) than the silver-lead iodide alloy No. 1. The chlorobromiodides, although, of course, their brittleness increased with the percentage of iodide of silver, formed less brittle rods than the iodide of silver, and than the first of the silver-lead iodide alloys, although the latter contains 23 per cent. less iodide of silver than the chlorobromiodide $Ag_4I_4.AgBr.AgCl$.



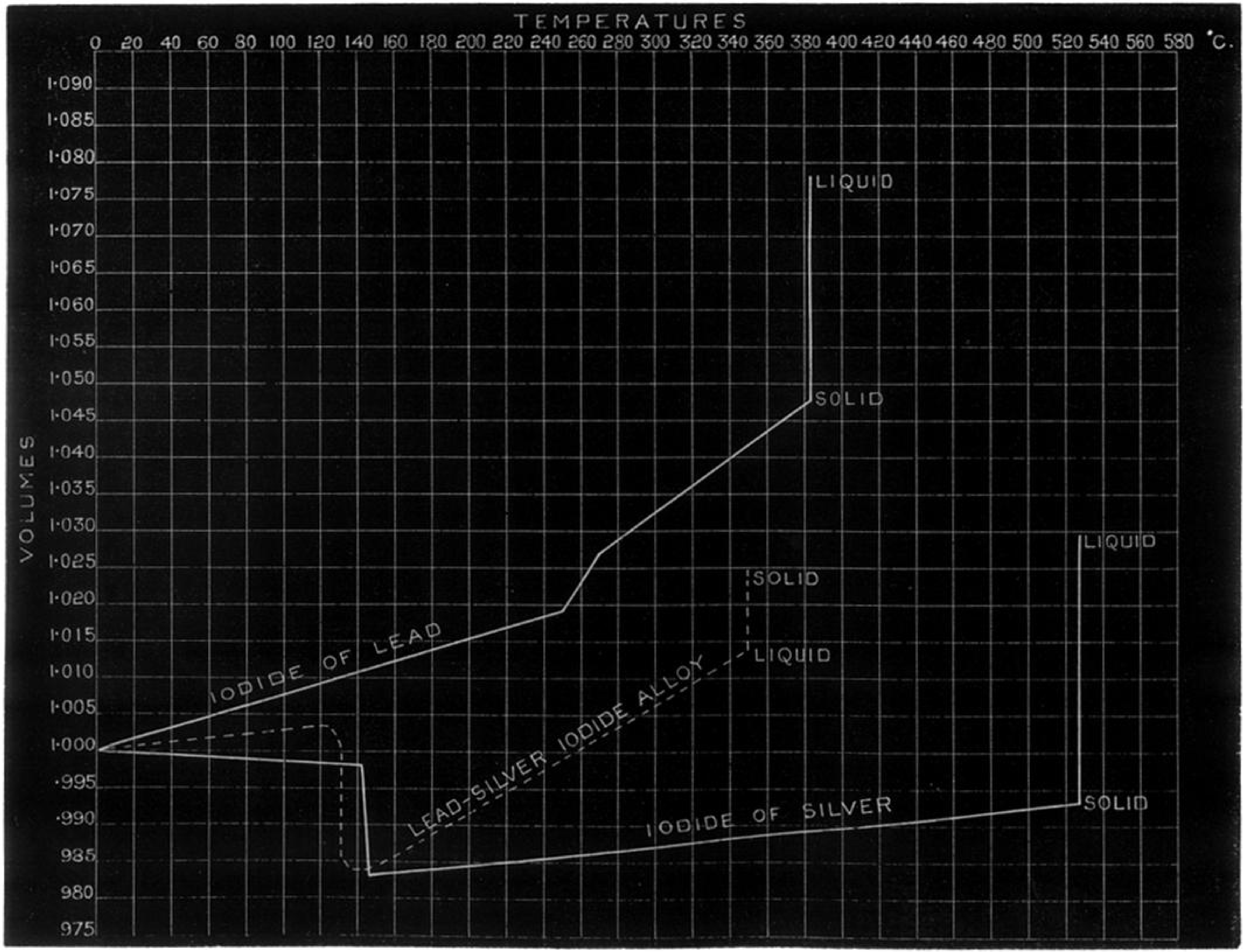
This block with figs. 1, 2, 3 is a reprint from "Proceedings," vol. 25, p. 280-282, where all are described.



Section through the trough longitudinally, showing the mode of suspension of the bar, and the position of the levers.



End section of the trough, showing one of the levers, and the bar which carries it.


TEMPERATURES
0 20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 500 520 540 560 580 °C.
VOLUMES
1·090
1·085
1·080
1·075
1·070
1·065
1·060
1·055
1·050
1·045
1·040
1·035
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1·010
1·005
1·000
·995
·990
985
980
975
LIQUID
SOLID
LIQUID
SOLID
LIQUID
SOLID
IODIDE OF LEAD
LEAD-SILVER IODIDE ALLOY
IODIDE OF SILVER

Table B.—Details of the Contraction by Heat of Iodide of Silver, and of the Lead-Silver Iodide Alloy.