

XXVI. *On the Effects of Heat on certain Haloid Compounds of Silver, Mercury, Lead, and Copper.*

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## 1. INTRODUCTION.

THE researches described in the following pages, which were commenced in 1874, were suggested by observations made by Professor CLERK MAXWELL and M. FIZEAU. The former ('Theory of Heat,' p. 8), in discussing the effects of heat upon matter, writes: "The body generally expands (the only exception among solid bodies, as far as I am aware, is iodide of silver, which has been found to contract as the tempera-

\* The author has been engaged at intervals during the last five years on an investigation of the effect of heat in producing expansion and contraction in iodide of silver and some other allied iodides and their alloys. A series of papers on the subject, written as the results were successively got out, have been published in the Proceedings of the Royal Society.

The paper which forms the last of the series, and which contains the results obtained with an extended series of alloys, by the methods which were ultimately adopted as the best, was read before the Royal Society on December 8, 1881, and an abstract only of it has appeared in the Proceedings. The present memoir is made up of the paper in question, preceded by a general account of the whole investigation.

ture rises)." The latter ('Nouvelles observations relatives à l'Iodure d'Argent'), remarks: "Ce corps, en effet, paraît offrir l'exemple d'une inversion complète des phénomènes ordinaires de la dilatation par la chaleur, car son volume diminue très-certainement pendant l'échauffement, et augmente pendant le refroidissement."

It was thought that results of interest might be obtained as to the molecular constitution of this anomalous body, by examining the effects of heat upon it at higher temperatures than those employed by FIZEAU (which in no case exceeded 100° C.); also by forming compounds, or alloys, with it, and other bodies, and determining the effect of its presence upon the coefficients of expansion and the physical structure of such bodies.

In this connexion we must remember that the phenomena exhibited by the iodide of silver on heating, are approximated to the anomalous behaviour of ice, bismuth, and some other substances, which at the moment of fusion, and for a few degrees above that point, exhibit contraction.

Moreover, certain crystals contract in the direction of one of their axes on heating; while garnets and some other minerals undergo an increase of specific gravity on being strongly heated, and slowly recover their original density. ERMAN asserts that the alloy of 2 parts bismuth, 1 part lead, and 1 part tin, which fuses at 94° C., expands when heated from 0° to 44° C., but on further heating contracts so that at 56° C. the density is the same as at 0°, and at 69° greater than at 0°. At a higher temperature expansion again sets in, and at 87.5 the alloy has again the same density as at 0°, while the density just before fusion is the same as that at 44° C. A number of metallic alloys of somewhat similar constitution, also possess anomalous coefficients.\*

## 2. METHOD OF RESEARCH, AND THE APPARATUS EMPLOYED.

The first series of experiments were made with a view of determining the volume occupied by iodide of silver at different temperatures between 0° and 300° C. Preliminary experiments showed the nature of the changes to be examined. A mass of iodide of silver fused in a glass tube contracted while cooling so that it could be withdrawn from the tube, but on returning it to the tube and permitting it to cool further, it was seen to suddenly change in colour and structure, and simultaneously to expand, and violently break the tube.

Again, a thin spherical flask, which contained 10 cubic centims., was fitted with a long capillary tube attached to an accurately ground stopper. Iodide of silver was placed in the flask, which was then filled with mercury, and the capillary tube attached, forming in fact a large thermometer, the bulb of which contained, in addition to the mercury, a quantity of iodide of silver. On heating such an arrangement the mercury was observed to expand, until the contraction of the iodide exceeded the expansion of the mercury, when on further heating, the column of mercury descended in the tube.

\* See a paper "On the Expansion and Specific Heat of Fusible Alloys," by W. SPRING, *Ann. Chim. Phys.*, [5], vii., 178-228.

On cooling, the mercury rose in the tube, until the contraction of the mercury exceeded the expansion of the iodide.

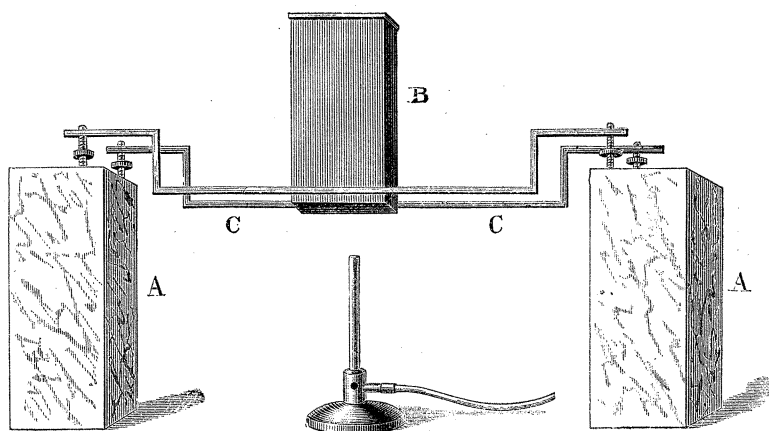
Thus it was obvious that some method of examination must be adopted, which should be equally applicable to the indication, and measurement, of either expansion or contraction.

Three experimental methods were tried. The last ( $\gamma$ ) was finally adopted.

*a. Method of the specific gravity flask.*—Professor GUTHRIE suggested to me that a convenient mode of determining the contraction of the iodide might be to fill a specific gravity flask with mercury, and to determine the amounts of mercury driven through the capillary tube of the stopper for every ten or twenty degrees increase of temperature; then to place in the flask a known weight of fused iodide of silver, together with a known weight of mercury, and to repeat the determinations for similar ranges. 440 grms. of mercury were thus heated, and weighings were made at intervals of  $10^{\circ}$  C.; afterwards 38.3680 grms. of iodide of silver were introduced, and the heating maintained through similar ranges; but it was found that as the temperature approached  $70^{\circ}$  C. the iodide of silver was slightly decomposed by the hot mercury, green protoxide of mercury,  $\text{HgI}$ , being formed. Thus this method had to be abandoned.

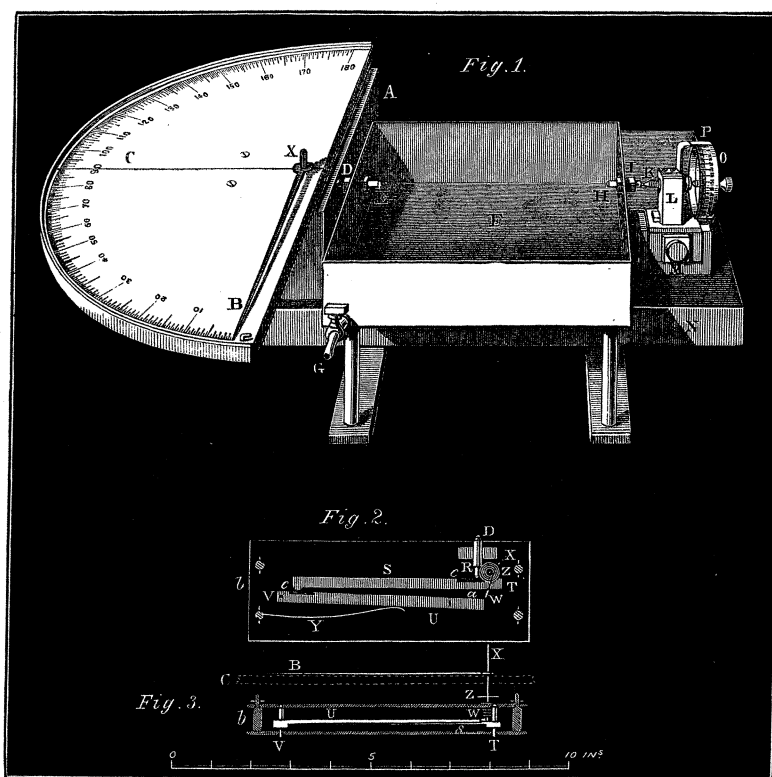
*$\beta$ . Method of the microscope.*—It was thought that rods of the iodide might be placed in a vertical bath of paraffine, and examined in the field of a microscope fitted with a micrometer eyepiece, during heating through various ranges of temperatures. The following apparatus was constructed for this purpose:—Two blocks of white marble (A, A, fig. A), 8 inches high by 4 inches by 3 inches, were placed 15 inches

Fig. A.



apart. Between them the paraffine bath B of copper was supported on massive iron bars C, C, terminated by levelling screws which rested on the marble blocks. The length of the bend in the iron bars, and the height of the brass levelling screws between the marble and the iron bars were so arranged that the upward expansion of the one compensated the downward expansion of the other. The bath contained ceresine capable of being heated to  $340^{\circ}$  C. A frame fitted into the bath containing

supports for the rod of iodide of silver, and a system of vanes for agitating the liquid during heating. The rod of iodide was cast, sawn plane at the ends, smoothed by sand-paper, and furnished at one end with a cross wire arrangement for viewing in the field of the microscope. A cover fitted upon B through which a thermometer passed, also the head of the cross wire arrangement. The microscope was horizontally attached to a massive iron pillar, which was fixed in a block of white marble. Of course numerous precautions were taken to avoid the acquisition of heat by any portion of the microscope or stand, and every attempt was made to eliminate errors. But the method was unsatisfactory and had to be abandoned. Walking on the floor, resting an arm on the table, and other inevitable disturbing causes, produced tremors of such magnitude that all accurate observation came to an end.



*γ. Method of the expansion apparatus.*—I finally decided to attempt to enormously multiply a small motion by means of a system of levers; to cause bars of the iodide of silver, or other substance under examination, to act upon these levers while being heated through various known ranges of temperature; and to measure the movements by means of a micrometer-screw. This plan was adopted for all the determinations hereinafter given.

The following apparatus was devised in order to carry out the idea. The box A, fig. 1 (drawn to scale), contains the levers, shown in plan and section in figs. 2 and 3; B is an index moving through  $180^\circ$  of arc over the graduated half-circle C. B is attached to the axis X, which is in connexion with the second lever U. D is a

sliding bar, one end of which bears upon the first lever, while the other is in contact with a short rod of glass E, which moves freely, but water-tight, in a metal stuffing-box. The rod of glass thus enters a brass trough F, which can be filled with water or melted paraffine, and heated by means of a BUNSEN'S burner. The water or paraffine is allowed to run off at the end of an experiment by the tap G. H is a rod of glass similar to E, which moves freely, but water-tight, in the metal stuffing-box I. Between E and H is placed the rod of substance, the expansion or contraction of which, we desire to determine. The end of H external to the trough F rests against the end of the micrometer-screw K, which is tipped with agate, and which moves steadily in the support L firmly clamped to the iron bar M, which is screwed to the base of the instrument N. The head of the micrometer-screw, O, is graduated into 250 divisions, and is figured to 500; the graduations are read off against the cross arm P. A plan of the levers is shown in fig. 2, where D (the end of which is seen in fig. 1) is the movable bar, sliding in a socket R and bearing against the first lever S, which is pivoted at T. The lever S bears against a second lever U, pivoted at V. From the opposite extremity of U a very fine steel chain W, such as is employed in watches, passes to a vertical axis X, which carries the needle B. The needle is brought back to zero by the pressure of the spring Y against the lever U, and also by a fine steel mainspring Z, which is fixed to the vertical axis X.  $\alpha$  is a small pin to stop the lever U as soon as the needle has passed the zero-point by a few degrees. The levers are shown in section in fig. 3; the lettering is the same throughout. The framework *b* is of brass, as are also the levers; the pivots are of steel. Pieces of glass, *c c*, are let into the levers at the bearing points to diminish the friction.

The micrometer has threads  $\frac{1}{100}$ th of an inch apart: hence one complete revolution of the micrometer-head is equal to  $\frac{1}{100}$ th of an inch, and a movement of the head through one division is equal to  $\frac{1}{25000}$ th of an inch; but it is quite easy to read to half a division, and hence to  $\frac{1}{50000}$ th of an inch. The rods inserted between the micrometer and the lever are 6 inches long, and from  $\frac{1}{4}$  inch to  $\frac{1}{8}$  inch in diameter; they rested in the earlier experiments on light glass rollers placed in the trough F. A rod of the substance to be examined is inserted between E and H; perfect continuity of the parts is established, and the micrometer-head is turned until the needle stands at zero; the reading on the micrometer is registered, and the head is then turned until the index B has passed to  $180^\circ$  of arc; by again reading the micrometer, the relation between the micrometric divisions and the divisions on the scale of C is established.

By this means it was found that a movement of .0035 inch in the micrometer moves the index through  $180^\circ$  of arc. Now since the index is 6 inches long, in moving through half a circle its extremity passes over 18.84 inches, and this motion is produced by a movement of .0035 inch; hence the levers multiply any motion communicated to them 5382 times. The precise value of this index-scale having been ascertained, the determination of the expansion of a body by heat becomes an easy matter, provided that we are careful to secure perfect rigidity in all the fixed parts of the apparatus (by no means an easy task), and are further careful to prevent the

conduction of heat from the short glass rods (E and H) to the interior of the apparatus. The coefficient of expansion of E and H must also be ascertained, and allowed for in all determinations. If, on the other hand, we wish to determine the contraction of a body, the index is pushed up to  $180^\circ$  of arc by means of the micrometer-screw, and is pushed back to zero as the bar contracts by the spring Y and the helical mainspring Z. The precise value of the return movement must be, of course, ascertained by means of the micrometer-head. It is obvious that in moving from  $0^\circ$  to  $180^\circ$  of arc the spring Y acts *against* the motion of the expanding body; while in moving from  $180^\circ$  to  $0^\circ$  it moves *with* the motion of the contracting body. All the earlier determinations were made with the apparatus in this form.

Subsequently, and for the later determinations, the following changes were made mainly with a view of reducing the resistance by diminishing friction:—

1. The wooden base N was replaced by a massive stone block, to which the box containing the levers, and the upright carrying the micrometer-head were firmly bolted.

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 in 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  $0^\circ$  to  $180^\circ$  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 the 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:—

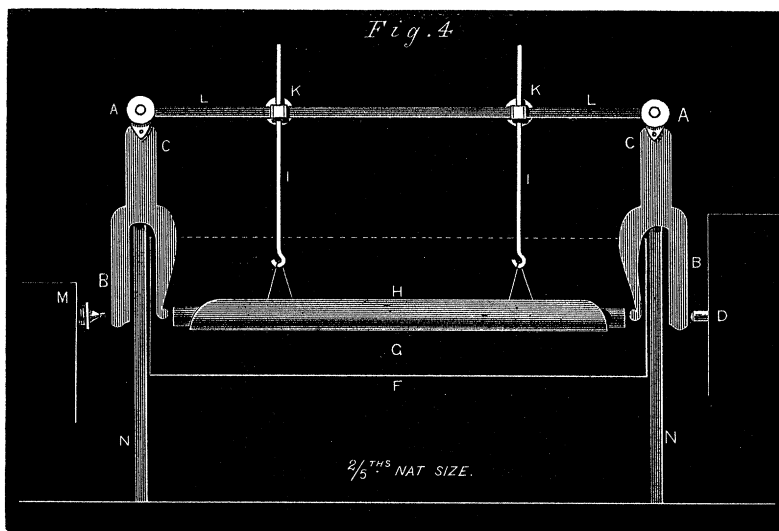
A horizontal bar L, L (fig. 4) was supported by rods N, N, strengthened by cross bars (not shown) let into the stone base of the instrument; it carried Y-shaped brass levers B, B, moving about axes at C, C (figs. 4 and 5), attached at the points A, A. F is the trough in which hot ceresine is used for heating the bar under examination, H, which is 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.

A bar of fine homogeneous silver was used in order to test the delicacy of the apparatus. It was placed between the levers B, B, and cold water was poured into the trough. The temperature was indicated by two thermometers reading well together, placed near the opposite extremities of the silver bar, and the needle was

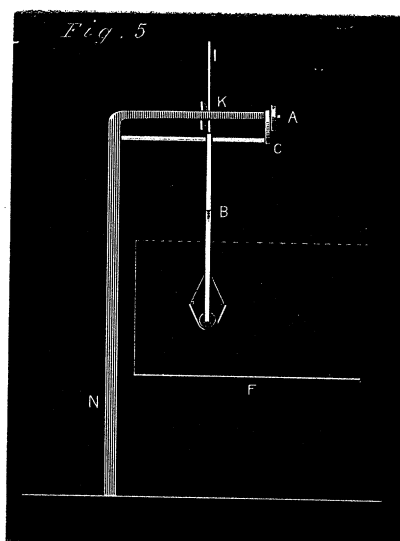
brought to zero. The water was then heated, being constantly stirred to produce uniformity of temperature throughout the whole mass, until the needle had been forced round to  $180^\circ$  of arc. The number of degrees of heat being read off, showed the heat necessary to produce a certain known expansion, and from this the coefficient of expansion was easily ascertained. Five results gave  $10^\circ$  C.,  $10^\circ$ ,  $10^\circ$ ,  $10^\circ$ ,  $9^\circ.5$ . The coefficient deduced from the mean of the determinations was for  $1^\circ$  C.

·0000193083.

Now LAVOISIER gives it as ·00001910; DANIELL ·00001951; FIZEAU (determined by the same method as that which he applied to the iodide, chloride, and bromide of



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.

silver) gives  $\cdot 00001921$ ; and more recently MATTHIESSEN (Phil. Trans., 1866) found it to be  $\cdot 000019436$ .

Rods of other metals gave the following results:—

	Expansion-apparatus.	Various observers.
Iron. . . . .	$\cdot 000011025$	$\left\{ \begin{array}{l} \cdot 00001182 \\ \cdot 00001194 \end{array} \right.$
Copper. . . . .	$\cdot 0000174433$	$\left\{ \begin{array}{l} \cdot 00001666 \\ \cdot 00001678 \\ \cdot 00001722 \end{array} \right.$
Lead . . . . .	$\cdot 0000302121$	$\cdot 00002924$
Zinc . . . . .	$\cdot 0000288761$	$\cdot 00002918$

It is thus evident that the apparatus is capable of considerable accuracy, especially when we remember that we are dealing with rods of substance only 6 inches in length. I venture to think that such an apparatus would prove a useful adjunct to a Physical Laboratory; for it would not only afford a means of determining coefficients of expansion with rapidity and accuracy, but it might be used for determining thicknesses in thousandths and ten-thousandths of an inch. For if the substance were introduced between the agate face of the micrometer-screw and the lever B, and if the index were then driven round to a certain point (say  $20^\circ$  of arc), and so with the other substances tested, an exact uniformity of pressure of the face of the screw on the substance would be secured, and minute thicknesses might thus be measured with accuracy.

In constructing such an apparatus, extreme rigidity of the fixed parts is a main necessity; the base should be of thick marble, and the micrometer-screw support should be deeply let into it and firmly secured. Massive supports, apparently fixed with the utmost firmness, sometimes yield with surprising readiness to the extent of  $\frac{1}{500}$ th of an inch. The elasticity of the metal often causes great inconveniences. The levers must be firm and strong, but not unnecessarily heavy; they should work very smoothly. Agate should be let into the brass at the points of contact. Care should be taken to avoid any transference of heat from the hot trough to other parts of the apparatus. By the use of a paraffine of high boiling-point, the temperature of a bar submitted to heat in the trough (F) can be raised to  $340^\circ$  C. Under such circumstances great care is requisite to prevent heat from being radiated or otherwise communicated to other parts of the apparatus.

*Means employed to determine the expansion in passing from the solid to the liquid condition.*

The determination of the amount of expansion which the various bodies examined undergo in passing from the solid to the liquid condition was effected in the following manner:—A conical tube of platinum weighing 44·844 grms. was carefully filled with mercury at a known temperature. It contained 105·43 grms. of mercury. It was



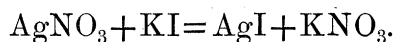
then filled with the substance under examination at its melting-point; the substance was allowed to solidify, and the whole was weighed. The cavity due to the contraction of the mass in solidifying was then filled with mercury to the level of the mouth of the conical tube, and the mercury was weighed. Then, knowing the capacity of the tube, the specific gravity of mercury, and of the substance under examination, the temperature of the fusing-point, and the coefficient of expansion of the platinum cone, we have all the data requisite for the determination. A glass tube was sometimes employed. The real difficulty is the determination of temperatures above the boiling-point of mercury; and until a trustworthy method of general application has been devised, such determinations must be regarded as approximations. The expressions "below a red heat," "a dull red heat," &c., are still common in text-books and in memoirs; but the very definitions of what is meant by a "dull red heat" vary, as also do the temperatures assigned to it by different writers. The method of Mr. CARNELLEY (Jour. Chem. Soc., 1876) appears to be the most accurate yet devised.

### 3. IODIDE OF SILVER, AgI.

Experiments were made in order to determine certain general physical properties of iodide of silver before placing it in the expansion apparatus.

It was prepared:—

( $\alpha$ ) By precipitation according to the equation



A dilute solution of pure iodide of potassium was added to a dilute solution of nitrate of silver. The precipitated iodide was thoroughly washed with boiling distilled water, slowly dried, fused rapidly in a porcelain crucible, and cast into cylindrical rods in warm thin tubes of well-annealed glass.

( $\beta$ ) By dissolving pure silver (for which my thanks are due to Professor CHANDLER ROBERTS) in strong hydriodic acid, evaporating to dryness, and fusing.

( $\gamma$ ) By exposing silver leaf to the spontaneous evaporation of iodine.

The iodide prepared by precipitation was commonly used for all the purposes described in the following pages, with the exception of the experiments relating to the effect of light upon the iodide.

*General physical properties.*—The molten iodide which forms a mobile bromine-red liquid, solidifies at 527° C. to a perfectly transparent, very flexible, claret-coloured solid; as it cools it becomes lighter in colour, and the colour of amber, and as 163° C. is approached it becomes pale yellow. All this time it has been slowly contracting on cooling. At 163° C. the contraction ceases, and the mass neither expands nor contracts till the temperature has fallen to 156°·5 C., when expansion commences, slowly at first, but becoming very rapid between 151°·3 C. and 148° C. The body simultaneously changes from a plastic transparent, amorphous state, to that of a crystalline, opaque,

pale green, solid. The more rapid expansion on cooling ceases at  $142^{\circ}$  C., and as it continues to cool an extremely slight expansion continues, until, according to FIZEAU'S calculation, it attains a minimum density and maximum volume at  $-60^{\circ}$  C.

It is well known that plastic sulphur in becoming yellow, opaque, and crystalline, gives out a good deal of heat. Transparent plastic iodide of silver was also found to give out heat in changing from the amorphous to the crystalline condition.

The iodide of silver obviously possesses at least two allotropic modifications: the one plastic, amorphous, and transparent above  $156^{\circ}\cdot5$  C.; the other brittle, crystalline, and opaque below  $142^{\circ}$  C. If it be melted and poured into cold water a very brittle, yellow, opaque mass is the result.

Successive fusions appeared to make the iodide more brittle, but did not affect the specific gravity materially. Thus a specimen which had been fused many times had a specific gravity of 5.675, while another specimen after a single fusion gave 5.66. A specimen prepared by the solution of silver in hydriodic acid was found to have a specific gravity of 5.812. Several specimens of precipitated iodide, fused, gave 5.681. DEVILLE found 5.687, and in the case of the unfused precipitated iodide 5.807. DAMOUR found the native crystals to have a specific gravity of 5.667.

When a mass of iodide passes from the amorphous into the crystalline condition, the molecular commotion is so considerable that portions of the mass are sometimes jerked off from the ends of the bar, and large fissures a millimetre broad and several centimetres in length appear in the rod. Within these, crystals are sometimes seen projecting from the sides or the fissure. Under the microscope they present the appearance shown in fig. 6.

Fig. 6.



The expanding force is considerable. Attempts to burst an iron bottle did not succeed, but a thick porcelain tube was violently broken.

An attempt to determine with accuracy the relative conductivities, for heat, of iodide, bromide, and chloride of silver was not successful; but the result showed that the bromide conducts somewhat better than the chloride, and more than twice as well as the iodide.

We have seen above that iodide of silver passes at between  $156^{\circ}5$  C. and  $142^{\circ}$  C. from the transparent amorphous variety to the opaque crystalline state. WERNICKE (Pogg. Ann., cxliii., p. 560) mentions that prisms of fused iodide when cooled to  $138^{\circ}$  C. exhibit a sudden alteration of colour and transparency; and he considers that at a high temperature "part of the iodine is separated from its combination with the silver, and is absorbed by the remaining substance in the liquid state, for the spectrum, like that of solid and liquid iodine, contains no blue or violet light. In the normal state, below  $138^{\circ}$  C., silver iodide gives a spectrum less bright but twice as long, and particularly developed in the blue-violet portion." The supposed redistribution of the iodine at a high temperature was not borne out by any of our results.

Many experiments were made in order to decide between the very contradictory statements in regard to the action of light upon the iodide of silver, with the general result that the pure iodide is quite unaffected. Even when the iodide was precipitated in a cell at the apex of rays of the electric light concentrated by a large lens, it did not darken.

*Determination of the coefficients of expansion and contraction.*—FIZEAU "by a method depending on the accuracy with which extremely minute movements can be appreciated, by observing the changes they produce in a system of NEWTON'S rings," determined the coefficient of cubic contraction of iodide of silver between  $-10^{\circ}$  C. and  $+70^{\circ}$  C., and found it to be  $\cdot 00000417$  for  $1^{\circ}$  C. This possession of what FIZEAU terms a "negative coefficient of expansion" is the more remarkable when we remember that the chlorides, bromides, and iodides of potassium, sodium, and ammonium, and the chloride and bromide of silver, expand considerably when heated, more so, indeed, than the most expansible metals, such as lead, tin, and zinc. The contraction of the iodide of silver is, according to FIZEAU, quite regular between  $-10^{\circ}$  C. ( $14^{\circ}$  F.) and  $+70^{\circ}$  C. ( $158^{\circ}$  F.); and he calculates that the contraction is equal to about  $\frac{1}{7000}$  of its volume at  $0^{\circ}$  C. for  $100^{\circ}$  C., or, again, equal to one-sixth the expansion of platinum for  $100^{\circ}$  C. He also found that a large hexagonal crystal exhibited a very considerable contraction in the direction of the axis of symmetry, while a slight expansion was produced in a direction normal to the axis of the crystal.\* The contraction was observed in the case both of the crystal, a confused crystalline mass, and an amorphous mass produced by strongly compressing the precipitated iodide until it became a hard mass capable of receiving a fine polish, and possessing a specific gravity of  $5\cdot 569$ . FIZEAU considers

\* "Sur le propriété qui possède l'iodure d'argent de se contracter par la chaleur et de se dilater par le froid." Comptes Rendus, 1867. (Tom. lxiv. p. 314.)

that the iodide possesses its maximum of volume or minimum of density at a temperature of  $-60^{\circ}$  C. ( $-76^{\circ}$  F.).

M. FIZEAU'S determination was adopted for the range of temperature between  $-10^{\circ}$  C. and  $+70^{\circ}$  C.

For higher temperatures the iodide was examined in the expansion apparatus (p. 1128). Careful castings were made of the iodide in tubes of thin warm glass, 9 inches long by 0.3 inch diameter. The ends were sawn plane and carefully worked on fine sand-paper so as to produce a rod 6 inches in length. Copper caps were fitted on the ends of the bar, and it was supported in the cradle G (fig. 4) of the apparatus. By turning the micrometer-screw the index was forced up to  $135^{\circ}$  of arc. Water was used for heating the bars up to  $90^{\circ}$  C., and ceresine for higher temperatures. On heating the bar the index began to retreat very slowly, showing contraction, and this continued until a temperature of  $142^{\circ}$  C. was attained, when the contraction became more rapid; between  $148^{\circ}$  C. and  $151^{\circ}3$  C. it was very rapid; at  $156^{\circ}5$  C. it ceased altogether, and the needle was motionless, showing that although heat was being absorbed neither contraction nor expansion was taking place; and at  $163^{\circ}$  C. expansion commenced and continued to the melting point.

The contraction, as stated, commenced at  $142^{\circ}$  C. and terminated at  $156^{\circ}5$  C.; but it mainly took place between  $148^{\circ}$  C. and  $151^{\circ}3$  C. Thus in all for the  $14^{\circ}5$  C., during which the mass contracted, the index retreated through 18 revolutions of  $135^{\circ}$  to  $0^{\circ}$  of arc of the instrument, and these were related to the temperatures in the following manner:—

	1	revolution of the index took place during heating from $142^{\circ}$	to $148^{\circ}$ C.
14	„	„	„ $148^{\circ}$ „ $151^{\circ}3$ C.
2	„	„	„ $151^{\circ}3$ „ $153^{\circ}$ C.
1	„	„	„ $153^{\circ}$ „ $156^{\circ}5$ C.

#### COEFFICIENTS of cubical contraction and expansion for $1^{\circ}$ C.

Between	$0^{\circ}$	and	$70^{\circ}$ C.	=	$-00000417$
„	$70^{\circ}$	„	$142^{\circ}$ C.	=	$-00001749$
„	$142^{\circ}$	„	$148^{\circ}$ C.	=	$-00016363$
„	$148^{\circ}$	„	$151^{\circ}3$ C.	=	$-00420000$
„	$151^{\circ}3$	„	$153^{\circ}$ C.	=	$-00120000$
„	$153^{\circ}$	„	$156^{\circ}5$ C.	=	$-00030000$
„	$156^{\circ}5$	„	$163^{\circ}$ C.	=	$00000000$
„	$163^{\circ}$	„	$527^{\circ}$ C.	=	$+00006921$

*Plus* has been placed before the coefficient of expansion on heating, *minus* before the coefficients of contraction. The increase of volume in passing from the solid to the liquid state was determined by the method described on p. 1132.

If we take the volume at  $0^{\circ}$  C. as unity, the following volumes correspond to the temperatures given between  $0^{\circ}$  and the melting point:—

Volume at	0 °C.	. . . . .	= 1.000000	} Phase of contraction on heating. Expansion on cooling.
"	124	. . . . .	= .998765	
"	133	. . . . .	= .998608	
"	142	. . . . .	= .998450	
"	148	. . . . .	= .997469	
"	151.3	. . . . .	= .983609	
"	153	. . . . .	= .981560	
"	156.5	. . . . .	= .980510	
"	163	. . . . .	= .980510	
"	200	. . . . .	= .982377	
"	300	. . . . .	= .989298	
"	400	. . . . .	= .996219	
"	500	. . . . .	= 1.003140	
"	527 (solid)	. . . . .	= 1.005008	
"	527 (liquid)	. . . . .	= 1.040908	

Obviously the iodide possesses two points of similar density at different temperatures. Thus the density at 124° C. is the same as that at about 430° C.

If 5.675 be the specific gravity at 0° C., the specific gravity at the maximum density will be 5.771; at the minimum density 5.673, and in the molten condition at 527° C., the specific gravity will be 5.522.

#### 4. BROMIDE OF SILVER.

Precipitated bromide of silver was fused, and cast in warm glass tubes. The mass when warm was found to be somewhat tenacious; the surface of the fused rod was smooth and brilliant, the fracture crystalline. Repeated fusion seemed to render the substance more crystalline. Although crystalline, the bromide was very compact, and altogether unlike the crystalline condition of the iodide; the rod contracted a good deal in cooling, and easily came out of the tube in which it was fused. Rods 6 inches long by .3 inch diameter had their ends levelled by means of a fine steel saw, and were placed in the expansion-apparatus, and tested as described in the case of the iodide of silver bars. The coefficient of cubical expansion for 1° C. was found to be

$$.00010500.$$

FIZEAU by his optical method found the coefficient to be .000104061. The coefficient increases with the temperature, at least to the extent of .000004 for each 100° C. increase of range. The expansion is very considerable in passing from the solid to the liquid condition.

The volumes corresponding to different temperatures and certain physical properties are tabulated with those of the chloride of silver (see p. 1138).

The bromide fuses to a reddish-brown liquid, not unlike bromine, and it solidifies to a bright yellow transparent solid when seen in thin layers. In thick layers it appears to be brownish-yellow. It is brittle even before it is quite cold. During the process

of cooling loud cracking noises, like the cracking of a piece of porcelain or thick glass, are produced. The solidified solid produces a metallic ring when struck; but this is less marked than in the case of the chloride of silver.

5. CHLORIDE OF SILVER.

Precipitated chloride of silver was fused and cast in warm glass tubes. It had been very carefully prepared in the dark, and the fused mass in thin layers was colourless and quite transparent. When warm, a rod of the chloride was very flexible, and to some extent malleable; when cold, the bar did not bend without fracture, and repeated fusings seemed to render it more liable to fracture. The rod contracted a good deal on cooling, and easily came out of the tube in which it was cast. Rods of 6 inches long by .3 inch in diameter had their ends levelled by means of a fine steel saw, and were placed in the expansion-apparatus, and tested as described in the case of the iodide of silver bars. The coefficient of cubical expansion for 1° C. was found to be

$$.000095454.$$

FIZEAU by his optical method found the coefficient to be .000098814. The coefficient increases with the temperature, at least to the extent of .000003 for each 100° C. increase of range. The expansion is considerable in passing from the solid to the liquid condition.

The volumes corresponding to the different temperatures and certain physical properties are tabulated below with those of the bromide of silver.

The chloride fuses to a dull light-red liquid, and becomes faintly yellow when solidified; in thin layers, colourless and quite transparent. When cold, it forms a pale greenish-yellow solid, also transparent in thin layers. No sounds were emitted during cooling. In thin layers the chloride is very flexible when cold; and thick rods of it are flexible while hot. It has a decided metallic ring if struck when cold.

	Ch'l'oride of silver.	Bromide of silver.
Fusing point . . . . .	451° C.	427° C.
Specific gravity at 0° C. . . . .	5.505	6.245
"    "    fusing point. . . . .	4.919	5.595
Volume at -60° C. . . . .	1.000000	1.000000
"    -10° C. . . . .		
"    0° C. . . . .	1.005547	1.006060
"    70° C. . . . .		
"    100° C. . . . .	1.015092	1.016560
"    142° C. . . . .		
"    200° C. . . . .	1.024937	1.027460
"    300° C. . . . .	1.035082	1.038760
"    400° C. . . . .	1.045227	1.050460
"    fusing point (solid) . . . . .	1.050319	1.053470
"    "    "    (liquid) . . . . .	1.116427	1.122840
Physical structure, &c., of fused mass .	Crystalline fracture; thin layers transparent and flexible; thick rods very flexible when hot.	Crystalline and brittle.

6. CHLOROBROMIODIDES OF SILVER, HAVING THE COMPOSITION :—AgI, Ag<sub>2</sub>Br<sub>2</sub>, Ag<sub>2</sub>Cl<sub>2</sub>; AgI, AgBr, AgCl; Ag<sub>2</sub>I<sub>2</sub>, AgBr, AgCl; Ag<sub>3</sub>I<sub>3</sub>, AgBr, AgCl; Ag<sub>4</sub>I<sub>4</sub>, AgBr, AgCl.

Compounds of silver with iodine, bromine, and chlorine are found in nature: *embolite* (ἐμβόλιον) is a chlorobromide of silver, and minerals having respectively the composition Ag<sub>3</sub>BrCl<sub>2</sub>, Ag<sub>5</sub>Br<sub>2</sub>Cl<sub>3</sub>, Ag<sub>4</sub>Br<sub>3</sub>Cl, Ag<sub>9</sub>Br<sub>4</sub>Cl<sub>5</sub>, and Ag<sub>4</sub>BrCl<sub>3</sub>, have been analysed by DOMEYKO, FIELD, MÜLLER, RICHTER and others. They occur chiefly in Chili, and constitute the principal ores of the silver mines of Chañarcillo. They possess specific gravities which vary from 5·75 to 6·2, and according to DANA the colour is "greyish-green, and asparagus-green to pistachio or yellowish-green, and yellow; often dark, becoming darker externally on exposure." Von LASAULX has described in the 'Jahresberichte für Mineralogie,' for 1878, a new silver haloid mineral having the composition Ag<sub>3</sub>Br<sub>2</sub>, Ag<sub>2</sub>Cl<sub>2</sub>, AgI which he cites as the first instance of the three haloid salts occurring crystallized together in nature. Two years previously I had prepared, for the purposes of this enquiry, a substance having the same composition, and its properties were described in Proc. Roy. Soc., No. 174, 1876. It was found by Von LASAULX, associated with BEAUDANTITE, in a mine in the district of Ems, Nassau, in the form of small yellow, or olive-green octohedra, never exceeding 3 millims. in size.

Five compounds of the halogens with silver were prepared, the first having the composition AgI, Ag<sub>2</sub>Br<sub>2</sub>, Ag<sub>2</sub>Cl<sub>2</sub>, and the others increasing by one molecule of AgI to Ag<sub>4</sub>I<sub>4</sub>, AgBr, AgCl. The substances were fused together in a porcelain crucible, and cast in glass tubes. They were examined in the expansion apparatus in the usual manner. The coefficients and more prominent physical characteristics are given in the following table. Generally speaking, of all the compounds it may be said that they fused to a bromine-red transparent liquid, becoming successively brick-red, dull orange, and yellow or yellowish-brown on cooling. They furnished bright yellow powders, turning green on exposure to light.

CHLOROBROMIDES of Silver.

	1. AgI, Ag <sub>2</sub> Br <sub>2</sub> , Ag <sub>2</sub> Cl <sub>2</sub> *	2. AgI, AgBr, AgCl.	3. Ag <sub>2</sub> I <sub>2</sub> , AgBr, AgCl.	4. Ag <sub>3</sub> I <sub>3</sub> , AgBr, AgCl.	5. Ag <sub>4</sub> I <sub>4</sub> , AgBr, AgCl.
Fusing point . . . . .	383° C.	331° C.	326° C.	354° C.	380° C.
Specific gravity at 0° C. . . . .	6.152	6.1197	6.503	5.9717	5.907
" " fusing point . . . . .	5.5118	5.5673	5.6971	5.6430	5.680
" " 0° C. calculated . . . . .					
on the assumption that no change of volume occurs. . . . .	5.836	5.8010	5.762	5.741	5.725
Volume at 0° C. . . . .	1.000000	1.000000	1.000000	1.000000	1.000000
" 124° C. . . . .	1.015331*	1.012037	1.010301	1.007440	1.006696
" 133° C. . . . .	1.015037	1.006637	.993201	.984041	.979696
" of solid at fusing point . . . . .	1.054986	1.046646	1.032283	1.009612	1.006372
" liquid at solidification point . . . . .	1.112376	1.097486	1.059998	1.057645	1.040513
Certain physical properties . . . . .	Crystalline fracture; brittle both when hot and cold. Resembled bromide of silver.	Compact, hard, homogeneous; semi-crystalline fracture, very tenacious when cold; bends slightly at 250° C., but breaks easily.	Compact, hard, homogeneous, very tenacious when cold; at 250° C. flexible through an angle of 40° without breaking.	Brittle when cold; at 250° C. flexible enough to be bent through a right angle.	Crystalline fracture, more brittle when cold than any of the preceding, except No. 1. Very flexible at 250° C., and capable of being twisted without fracture.
Composition in 100 parts :—					
Iodide of silver . . . . .	26.1692	41.484	58.6404	68.0178	73.9285
Bromide of silver . . . . .	41.8708	33.186	23.4557	18.1379	14.7856
Chloride " . . . . .	31.9600	25.330	17.9039	13.8450	11.2859

\* In the case of No. 1, the temperatures at which contraction began and finished respectively were 125.5° and 131.5°, not, as in the case of the others, 124° and 133° C.



Several facts require to be noted in regard to these compounds.

(1) No. 1, containing 26 per cent. of AgI is almost unaffected by it, and closely resembles bromide of silver, save that a very slight contraction occurs on heating between  $125^{\circ}5$  and  $131^{\circ}5$  C., and the orange coloured powder produced by pulverisation turns green on exposure to light. In No. 3, which contains a little more than half its weight of iodide of silver, we find the greatest divergence in every respect from the properties of its constituents, although the influence of the AgI is very marked both in the plasticity of the substance above  $250^{\circ}$  C., and in the considerable contraction which takes place between  $124^{\circ}$  C. and  $133^{\circ}$  C. It possesses the lowest melting point (viz. :  $326^{\circ}$  C., which is  $101^{\circ}$  C. lower than that of AgBr, which constitutes nearly one-fourth of its weight, and  $201^{\circ}$  C. lower than that of AgI, which constitutes more than half its weight), and the highest specific gravity. In No. 5, the influence of the AgI is most marked, but the melting point is still  $147^{\circ}$  C. lower than that of the AgI, which constitutes nearly three-fourths of its weight.

(2) We may note that the fusing points diminish from 1 to 3, and increase from 3 to 5; while the specific gravities diminish on both sides of No. 3.

(3) While iodide of silver commences its considerable contraction consequent upon change of state at  $142^{\circ}$  C., and finishes it at  $156^{\circ}5$  C. (mainly, however, between  $148^{\circ}$  and  $151^{\circ}3$  C.), the chlorobromiodides all commence their contraction at  $124^{\circ}$  C., viz. :  $18^{\circ}$  C. lower, and finish at  $133^{\circ}$  C., or  $23^{\circ}5$  C. lower. The lead-silver iodide (p. 1149) practically does the same thing. This matter is alluded to in greater detail in the general discussion of results (pp. 1162, 1163).

(4) It is a curious fact that until the percentage of iodide of silver in the compounds becomes considerable, its chief influence is exerted between a narrow range of temperature; and more than this, so soon as the contraction is over the mass undergoes far more rapid expansion than any of its constituents when heated through the same range of temperature. The condition is obviously one of great complexity. Take the case, for example, of the chlorobromiodide No. 3. Between  $0^{\circ}$  C. and  $124^{\circ}$  C. any mass of 100 molecules consists of 58 which are undergoing slight contraction on heating, while 42 are undergoing rapid expansion. Then between  $124^{\circ}$  C. and  $133^{\circ}$  C. 58 molecules are rapidly contracting; heat is disappearing in internal work and is changing the crystalline into the amorphous iodide, *i.e.*, converting an opaque, brittle, highly crystalline body into a transparent, plastic, denser body; while the 42 molecules of chloride and bromide are still expanding. Finally, from  $133^{\circ}$  C. to the fusing point, all the molecules are expanding, 42 of them quickly, and 58 of them slowly.

## 7. DI-IODIDE OF MERCURY, $HgI_2$ .

This substance is dimorphous. In the amorphous condition it presents the appearance of a brilliant scarlet powder, which, if heated, fuses at  $200^{\circ}$  C. and volatilises just above the fusing point to a vapour more than twice as dense as that of mercury.

The vapour condenses to rhombic prismatic crystals, which frequently become scarlet while cooling, but which, if they still remain yellow when cold, instantly become scarlet if rubbed or otherwise mechanically agitated.

On heating a mass of the crimson amorphous iodide it turns yellow at  $126^{\circ}$  C., and just before the melting point is attained, the yellow changes to a deep red-brown. The liquid resulting from the fusion has the appearance of liquid iodide of silver—that is to say, it has the exact colour of bromine. The liquid when cooled solidifies to a red-brown solid, which speedily becomes yellow, and at  $126^{\circ}$  C. it changes to the crimson octohedral variety. Distinct cracking sounds, due to inter-molecular movements, were heard during the continuance of the change. Heat is absorbed when the red iodide changes to yellow, and is given out when the yellow iodide changes to the red.

A bar of the iodide was placed in the expansion apparatus, melted paraffine was poured upon it, and when the index had become steady a gentle heat was applied to the paraffine. The index showed a regular and slow expansion until a temperature of  $126^{\circ}$  C. was reached, when the bar began to change from the octohedral to the prismatic condition, and without further rise of temperature rapid expansion took place. The temperature was kept constant until the change was complete, and was then slowly raised. A regular expansion now took place under a higher coefficient than before the molecular change, and this continued until the melting point was attained.

The coefficient of cubical expansion for  $1^{\circ}$  C. from  $0^{\circ}$  C. to the point of change— $126^{\circ}$  C.—was found to be—

$$\cdot 0000344706.$$

At  $126^{\circ}$  C., during the change from the red octohedral to the yellow prismatic condition, the body increased in bulk to the extent of—

$$\cdot 00720407.$$

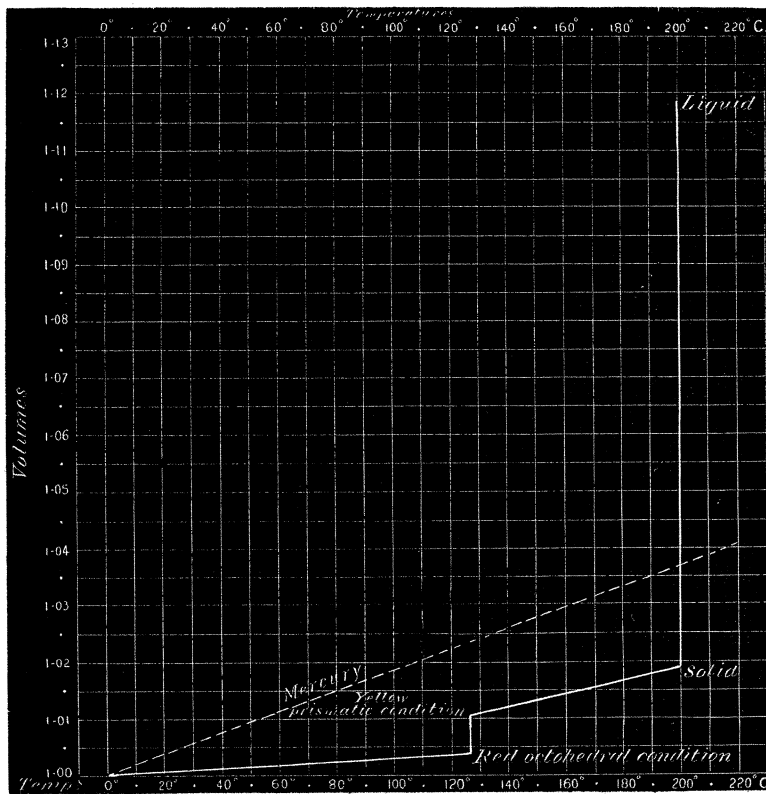
The coefficient of cubical expansion for  $1^{\circ}$  C. from  $126^{\circ}$  C., after the change to the melting point,  $200^{\circ}$  C., was—

$$\cdot 0001002953.$$

Thus, if we suppose a molten mass of the iodide of mercury to be cooling down from  $200^{\circ}$  C. to  $0^{\circ}$  C., the following would be the volumes under the conditions indicated:—

Volume at $200^{\circ}$ C. of the liquid mass . . . . .	=1.1191147
„ „ „ solid mass . . . . .	=1.0190453
„ $126^{\circ}$ C. (yellow prismatic condition). . . . .	=1.0115378
„ „ (red octohedral condition) . . . . .	=1.0043337
„ $0^{\circ}$ C. . . . .	=1.0000000

The changes are shown at one view in the accompanying curve table, in which the expansion of mercury is given for comparison.



According to SCHIFF the specific gravity of the octohedral iodide is 5.91, while KARSTEN makes it 6.209, and BOULLAY 6.320.

Two distinct specimens with which we worked gave respectively—

- (1) 6.3004
- (2) 6.2941.

The specific gravity of the fused iodide was found by the method before described to be—

5.2865.

Thus the specific gravities corresponding to the five marked conditions shown in the curve table are as follows:—

Specific gravity at	0° C.	. . . . .	=6.297
"	"	126° C. (octohedral condition) . . . . .	=6.276
"	"	" (prismatic condition) . . . . .	=6.225
"	"	200° C. solid . . . . .	=6.179
"	"	" liquid . . . . .	=5.286

In the above experiments on the di-iodide of mercury I have to acknowledge the assistance of Mr. H. M. ELDER, at that time a pupil in Marlborough College.

8. DI-IODIDE OF LEAD,  $\text{PbI}_2$ .

Pure iodide of lead was cast into rods one-third of an inch in diameter and 6 inches in length. The ends were made plane by a fine steel saw, and they were furnished with copper caps. 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 exist as to the effect of fusing iodide of lead in the air. Experiments showed that it may be fused out of contact with air, with scarcely appreciable loss. When, however, it was fused in contact with air, rapid decomposition ensued.

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  $383^\circ \text{C}$ .

The coefficient of cubical expansion for  $1^\circ \text{C}$ . was found to be

$$.00007614$$

for temperatures between  $0^\circ \text{C}$ . and  $205^\circ \text{C}$ . It increased to

$$.00008317$$

between  $205^\circ \text{C}$ . and  $253^\circ \text{C}$ .

Between  $253^\circ \text{C}$ . and  $265^\circ \text{C}$ . 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 previously described.

It will be observed that the iodide of lead, as in the case of the iodide of mercury (*vide* p. 1142), has three coefficients of expansion, viz.:—(a) a coefficient somewhat less than that of chloride of silver up to  $253^\circ \text{C}$ .; (b) a coefficient during  $12^\circ \text{C}$ ., nearly

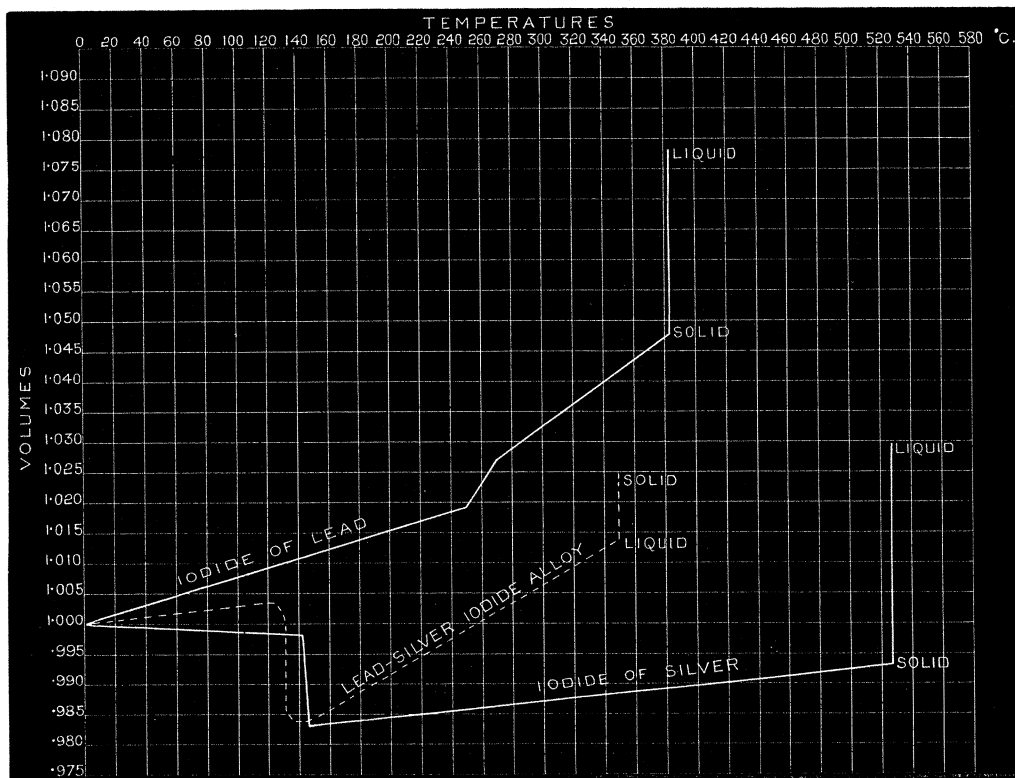
eight times greater than the preceding; and (c) finally a coefficient somewhat more than twice as great as that between 0° and 253° C., at temperatures above 265° C. Undoubtedly the iodide of lead, as in the case of the iodide of mercury, undergoes a molecular change, while rapidly expanding between 253° C. 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.

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<sub>2</sub>.AgI.



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 if used as a heating medium will allow the determination of coefficients to a temperature of 340° C., and, undoubtedly, many bodies if thus examined would be found to present anomalies similar to those remarked in the case of the iodides of lead and mercury.

### 9. THE LEAD-SILVER IODIDE.

Bearing in mind the peculiar nature of the coefficients of the chlorobromiodides of silver (*vide* p. 1140), it was thought to be advisable to determine the coefficients of a lead-silver iodide.

These bodies were accordingly fused together in the proportion of one molecule of each, viz.:  $\text{PbI}_2, \text{AgI}$ . This contains in 100 parts

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

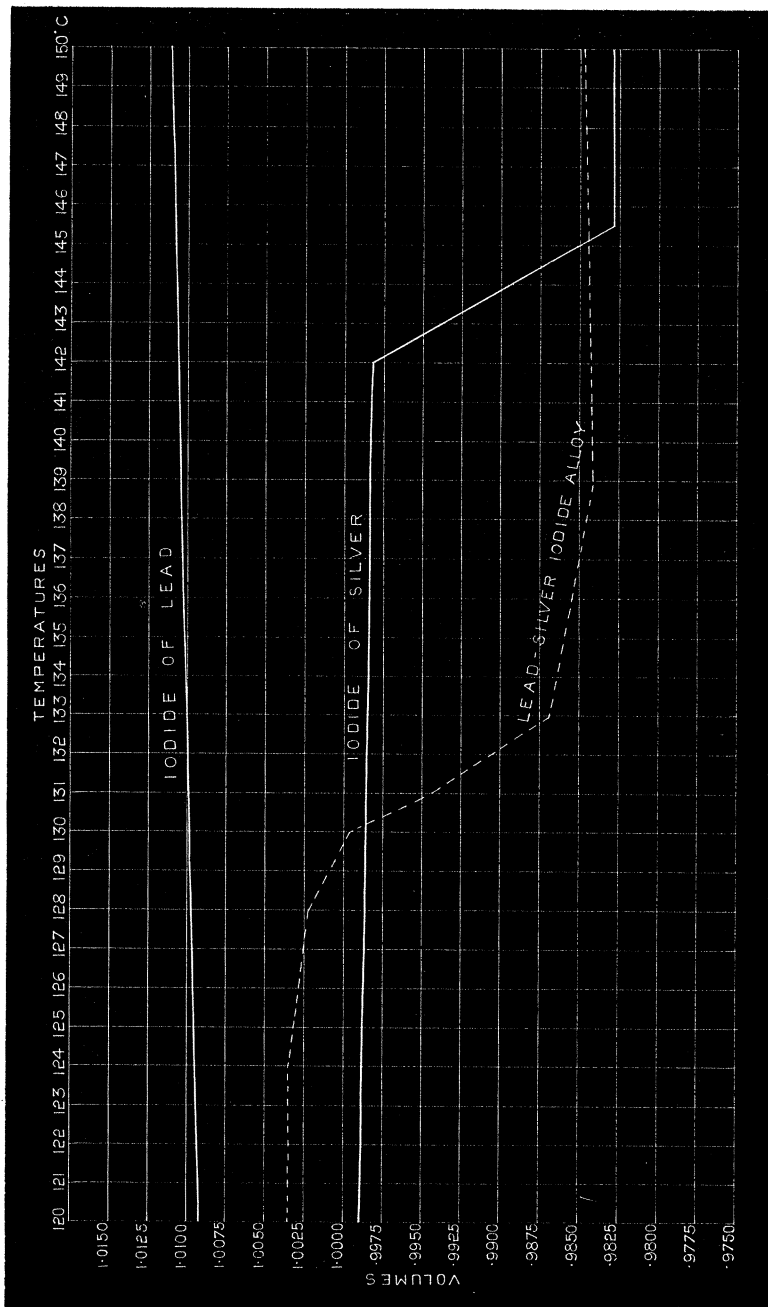
Mr. T. CARNELLEY has determined for me the melting point of the alloy, which he finds to be 350° C.

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

TABLE B.—Details of the contraction by heat of iodide of silver, and of the lead-silver iodide alloy.



at unequal rates till a temperature of  $139^{\circ}$  C. was attained. Again, the mass underwent neither contraction nor expansion during heating through  $5^{\circ}$  C., and then it commenced to expand somewhat rapidly. The most rapid contraction on heating took place between  $130^{\circ}$  and  $133^{\circ}$  C. Thus, in all, for the temperatures during which the mass contracted, the index moved through 15 revolutions of  $180^{\circ}$  to  $0^{\circ}$  of arc, and these were related to the temperatures in the following manner :—

1	revolution of index took place during heating from $124^{\circ}$ to $128^{\circ}$ C.
2	"      "      "      " $128^{\circ}$ „ $130^{\circ}$ C.
4	"      "      "      " $130^{\circ}$ „ $131^{\circ}$ C.
6	"      "      "      " $131^{\circ}$ „ $133^{\circ}$ C.
2	"      "      "      " $133^{\circ}$ „ $139^{\circ}$ 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  $144^{\circ}$  C. the alloy expanded with a coefficient about three times greater than that which it possessed between  $0^{\circ}$  and  $118^{\circ}$  C.

#### COEFFICIENTS of cubical expansion and contraction of the alloy for $1^{\circ}$ C.

Between	$0^{\circ}$	and	$118^{\circ}$	C.	=	+·0000306
„	$124^{\circ}$	„	$128^{\circ}$	C.	=	-·0003240
„	$128^{\circ}$	„	$130^{\circ}$	C.	=	-·0012990
„	$130^{\circ}$	„	$131^{\circ}$	C.	=	-·0017330
„	$131^{\circ}$	„	$133^{\circ}$	C.	=	-·0039000
„	$133^{\circ}$	„	$139^{\circ}$	C.	=	-·0004329
„	$144^{\circ}$	„	$350^{\circ}$	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 curve is shown in Table A (p. 1145).

The coefficient between  $144^{\circ}$  C. and the fusing point increased rapidly with the temperature.

If we take the volume at  $0^{\circ}$  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. 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 (p. 1140) 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, the amount of contraction by heat of the latter is nearly four 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 compounds 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 <sub>2</sub> , AgI.	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 . . . . .	..	..	..
"    150 . . . . .	.984810	..	..
"    156.5 . . . . .	..	..	..
"    300 . . . . .	1.002060	1.039239	.980510
Volume of solid at melting point . . . . .	1.013790	1.046646	1.005008
"    liquid at solidification point . . . . .	1.024370	1.097486	1.040908
Melting point . . . . .	350° C.	331° C.	527° C.

The Tables (A, p. 1145, B, p. 1147) 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.

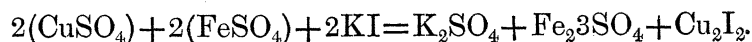
Other alloys of iodide of lead with iodide of silver were made, having the following composition :—

(1)	2AgI.PbI <sub>2</sub> ,	containing	50·517	per cent.	of iodide of silver.
(2)	3AgI.2PbI <sub>2</sub>	„	43·360	„	„
(3)	4AgI.3PbI <sub>2</sub>	„	40·497	„	„
(4)	5AgI.4PbI <sub>2</sub>	„	38·950	„	„
(5)	10AgI.9PbI <sub>2</sub>	„	36·190	„	„

They all possessed the same general appearance as the alloy AgI.PbI<sub>2</sub> described above, which contains 33·794 per cent. of iodide of silver. But with the exception of No. 5 they were 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<sub>2</sub>I<sub>2</sub>.AgBr.AgCl; Ag<sub>3</sub>I<sub>3</sub>.AgBr.AgCl; Ag<sub>4</sub>I<sub>4</sub>.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<sub>4</sub>I<sub>4</sub>.AgBr.AgCl.

#### 10. IODIDE OF COPPER.

The cuprous iodide was prepared by the method of SOUBEIRAN, in which an aqueous solution of two molecules of cupric sulphate and two molecules of ferrous sulphate is precipitated by potassic iodide, according to the equation



The precipitated iodide was washed with dilute sulphuric acid and with water, and was completely dried at 200° C. It then presented the appearance of a nearly white powder, not of a dead white colour like oxide of zinc, but white with a tinge of grey. On heating to a temperature considerably exceeding 200° C. it becomes pale canary-yellow, which just before its fusion changes to orange. When fused it forms a bromide-red liquid, which solidifies to a steel-grey crystalline mass. If the fused mass

be powdered, the powder presents the same grey-white colour as the original precipitate. SOUBEIRAN asserts that cuprous iodide fuses to a brown mass, which yields a green powder, and I imagine from this that he did not entirely wash out all traces of ferrous and ferric sulphate from the precipitate. In thin laminæ it is translucent, transmitting a greenish light. It fuses at  $601^{\circ}$  C. according to the determinations of Mr. THOMAS CARNELLEY. When heated in the air it begins to give off iodine soon after the temperature has passed  $230^{\circ}$  C., but it gives it off most copiously when fused in the air. Oxide of copper is left.

When heated in a current of dry carbonic anhydride the iodide gives off a small amount of iodine, and afterwards remains in tranquil fusion without undergoing decomposition. At a bright red heat it slowly volatilises, the sublimate condensing immediately above the molten mass which is producing it. When heated in a current of dry oxygen, iodine is freely evolved, and oxide of copper ultimately remains in the form of a fine crystalline powder.

A quantity of iodide weighing 9.0080 grms. was heated for many hours in an air-bath to a temperature of  $190^{\circ}$  C. It lost .4551 per cent. On raising the temperature and maintaining it between  $200^{\circ}$  and  $300^{\circ}$  C. for several hours the loss increased to 3.3303. It was then ignited over a one-jet BUNSEN burner for 16 minutes, the cover being retained on the crucible. The total loss amounted to 4.6514. The crucible was now strongly heated over a four-jet BUNSEN burner; the mass of course freely fused, and evolved iodine although the crucible was covered. After heating for 10 minutes the loss due to this heating was 1.3987, and the total loss was equal to 6.0501 per cent. A further ignition of five minutes only raised the total loss to 6.3277. The ignition was then continued with the cover of the crucible removed. Iodine was freely evolved. After more than an hour's ignition no more iodine was evolved, and the weight became constant. The loss amounted to 40.4639 per cent. of the whole, leaving in the crucible 3.6450 grms. of cupric oxide in minute crystals. The calculated weight of the residue, on the supposition that all the  $\text{Cu}_2\text{I}_2$  is converted into  $\text{CuO}$ , is 3.7590 grms. Hence there can be no doubt that the iodine is completely expelled and replaced by oxygen. Subsequent testing of the residue failed to reveal the presence of any iodine.

16.0130 grms. of the iodide only lost 0.6106 per cent. by heating for about 15 hours to a temperature of  $230^{\circ}$  C. 2.8050 grms. heated for some time to  $190^{\circ}$  C. lost .2495 per cent.; at  $231^{\circ}$  C. it lost 1.2830; on raising the temperature to  $260^{\circ}$  C. for some hours the loss increased to 17.7540. Ignition for 20 minutes over a one-jet BUNSEN burner (the cover being kept on the crucible) raised the loss to 25.7932. The cover was then removed, and after strong ignition for more than an hour no more iodine was evolved, and 1.1703 grm. of oxide of copper remained in the crucible. The calculated amount is 1.1755.

The loss of weight on ignition is equal to the difference between the atomic weight of iodine and of oxygen, for the change is expressed by  $\text{Cu}_2\text{I}_2 + \text{O}_2 = 2\text{CuO} + \text{I}_2$ . Hence

for every 126·53 of iodine lost 16 of oxygen is gained. No definite oxyiodide seems to be formed midway, but merely a mixture of CuO and Cu<sub>2</sub>I<sub>2</sub>. Cuprous iodide cannot be fused without some loss of iodine and oxidation of the surface. This mixture of iodide and oxide forms a black scum on the surface of the molten iodide, which is less fusible than the iodide, and which effectually protects it from the air. In casting, the more fluid iodide easily runs from beneath this partially oxidised surface. Some of the latter was fused after running off the pure iodide from beneath, and its specific gravity was taken, and was found, as we should expect, to be lower than that of the iodide; for while the specific gravity of the latter is 5·6936, that of the partially oxidised surface was found to be only 5·6030.

The iodide was found to contract considerably when it solidified. A deep hollow cone sinks into the mass in the act of solidifying. The change of volume which occurs in the passage from the solid to the liquid state was determined by the method of the platinum cone before described.

Good rods of the iodide were cast by quickly fusing the powdered precipitate and pouring the fused iodide from beneath the semi-oxidised crust into warm glass tubes. The resulting cast rod was brittle and possessed a dark steel-grey colour, no doubt due to surface oxidation. The fracture was highly crystalline and the rods somewhat brittle. The rods were reduced by sawing to a length of 6 inches; the ends were rendered plane by rubbing on a level surface of sand-paper, and were furnished with copper caps. The expansion was determined in the apparatus described above (p. 1128). Unlike the iodides of lead and silver, the iodide of copper does not possess more than one coefficient of expansion, at least for temperatures below 300° C.

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

$$·00007317.$$

It increases but slightly with the temperature.

If the cast rod is plunged into hot paraffine and allowed to cool very slowly the coefficient is somewhat lower. The determinations of the volume in the molten state were not satisfactory, owing to the high temperature at which the iodide fuses and the readiness with which it then superficially undergoes oxidation.

The following volumes correspond to the temperatures given:—

Volume at	0° C.	· · · · ·	=1·000000
„	100	· · · · ·	=1·007317
„	200	· · · · ·	=1·014634
„	300	· · · · ·	=1·021951
„	400	· · · · ·	=1·029268
„	500	· · · · ·	=1·036585
„	600	· · · · ·	=1·043902
„	601 (solid)	· · · · ·	=1·043975
„	601 (liquid)	· · · · ·	=1·118401

## 11. COPPER-SILVER IODIDES.

1. *Copper-silver iodide*,  $\text{Cu}_2\text{I}_2\cdot\text{AgI}$ .

Iodide of silver and iodide of copper were fused together in the proportion of one molecule of each. The fusing point was obviously lower than that of either of the constituents; the fusion was tranquil, and the mass did not oxidise at the surface. The alloy contains in 100 parts:—

Iodide of copper . . . . .	=61·7767	Copper . . . . .	=20·5515
Iodide of silver . . . . .	=38·2233	Silver . . . . .	=17·5430
	100·0000	Iodine . . . . .	=61·9055
			100·0000

Specific gravity of the cast-rod = (1) 5·6290, (2) 5·6526. When fused in a tube, instead of being cast into it, the specific gravity was a little higher—

(1) 5·7302                      (2) 5·7500.

The melting point of this, and of each of the other alloys, was determined for me by Mr. CARNELLEY.  $\text{Cu}_2\text{I}_2\cdot\text{AgI}$  melts at  $514^\circ\text{C}$ . Although containing 38 per cent. of iodide of silver the alloy contracted on cooling, and came easily out of the glass tube. It was brown in colour in the mass, but when powdered it was a brilliant yellow, unaffected by light. In thin layers it was yellow and perfectly transparent. Fracture resinous.

Rods one-third of an inch in diameter and six inches long were cast in hot glass tubes. The ends were sawn plane by a fine steel saw, and were afterwards worked smooth on sand-paper, and furnished with copper caps. They were examined in the expansion apparatus in the usual way.

The alloy expanded on heating under a definite coefficient of  $\cdot 00004998$  until a temperature of  $223^\circ\text{C}$ . was attained, when the coefficient began to diminish rapidly, and between  $223^\circ\text{C}$ . and  $256^\circ\text{C}$ . it fell to

$\cdot 00001999$ .

Between  $256^\circ\text{C}$ . and  $284^\circ\text{C}$ . the mass simply absorbed heat without undergoing either contraction or expansion.

At  $284^\circ\text{C}$ . it began to contract, and between that temperature and  $309^\circ\text{C}$ . it underwent slight contraction under a negative coefficient of

$\cdot 00003999$ .

At  $309^\circ\text{C}$ . the contraction ceased and the mass simply absorbed heat without either contracting or expanding, till a temperature of  $319^\circ\text{C}$ . had been attained, at which point rapid expansion set in under a coefficient of

$\cdot 00016665$

which is more than three times greater than the coefficient of expansion between  $0^\circ\text{C}$ . and  $223^\circ\text{C}$ .

The following volumes correspond to the temperatures given:—

Volume at	0° C.	. . . . .	=1.000000
„	100	. . . . .	=1.004998
„	200	. . . . .	=1.009996
„	223	. . . . .	=1.011145
„	256	. . . . .	=1.011804
„	284	. . . . .	=1.011804
„	309	. . . . .	=1.010805
„	319	. . . . .	=1.010805
„	400	. . . . .	=1.024303
„	500	. . . . .	=1.040968
„	melting point (514° C.) solid	. . . . .	=1.043301
„	„ „ (514 C.) liquid	. . . . .	=1.103307

The fact that the alloy does not commence to expand again after its phase of contraction till a temperature of 324° C. has been attained, necessitated the raising of the temperature to an unusual height. The ceresine employed for heating, ignites when air has free access to it at 300° C. Moreover, ordinary thermometers which contain a vacuum above the mercury cannot be heated above 330° C. as the mercury then commences to boil. But these difficulties were overcome, and the ceresine was even carried to a temperature of 340° C. by closely covering the experimental trough with a brass plate so as to shut out direct access of air, leaving room only for the thermometer and for the working of the levers. Great care was taken to screen the rest of the apparatus by bright metal plates from the effects of radiation. The thermometer difficulty was got over by leaving a little air in the tube above the mercury, by which means it could be heated to 350° C. with readiness, but, of course, it must be borne in mind that the readings at these high temperatures are less reliable than those at lower ranges. It was not found to be practicable to work above 340° C., as at such a temperature the ceresine is liable at any moment to ignite; moreover it fumes furiously, and begins to decompose. The dense acrid vapours are particularly irritating to the lungs and eyes. Nevertheless for temperatures up to 340° C., ceresine or a paraffine of high boiling point, is, I believe, the most convenient medium that we possess.

2. *Copper-silver iodide alloy, Cu<sub>2</sub>I<sub>2</sub>.2AgI.*

The percentage of iodide of silver was now augmented to 55 by the addition of another molecule.

Cu<sub>2</sub>I<sub>2</sub>.2AgI contains:—

Iodide of copper . . .	= 44.6934	Copper. . . . .	= 14.8624
Iodide of silver . . .	= 55.3066	Silver . . . . .	= 25.3939
		Iodine . . . . .	= 59.7437
	<hr/>		<hr/>
	100.0000		100.0000

The alloy fused at 496° C.

Specific gravity = 5·7225 to 5·7377.

It did not expand on solidifying. The fracture was resinous, and it was more brittle than the preceding. Annealing in paraffine did not diminish the brittleness. In the mass it was brown; in thin layers yellow and transparent; in powder a brilliant yellow. Unaffected by light.

The alloy expanded on heating from 0° C. to 221° C. with a cubical coefficient for 1° C. of

$$·00003750.$$

Between 221° C. and 233° C. it simply absorbed heat without either expanding or contracting.

At 233° C. it commenced to contract, with a negative coefficient of

$$·00010587.$$

This continued until a temperature of 298° C. had been attained, viz.: through 65° C., when expansion commenced with a coefficient of

$$·00009474 \text{ for } 1^\circ \text{ C.}$$

and continued until the melting point had been attained.

The following volumes correspond to the temperatures given:—

Volume at	0° C.	. . . . .	. . . . .	=1·000000
	221	. . . . .	. . . . .	=1·008287
	233	. . . . .	. . . . .	=1·008287
	298	. . . . .	. . . . .	=1·001406
	300	. . . . .	. . . . .	=1·001595
	400	. . . . .	. . . . .	=1·011069
	melting point (496° C.)	(solid). . . . .	. . . . .	=1·020164
	”	” (496° C.)	(liquid) . . . . .	=1·062958

### 3. *Copper-silver iodide alloy, Cu<sub>2</sub>I<sub>2</sub>.3AgI.*

The percentage of iodide of silver was further increased to 65 by the addition of another molecule.

Cu<sub>2</sub>I<sub>2</sub>.3AgI contains:—

Iodide of copper . . .	= 35·0116	Copper . . . . .	= 11·6558
Iodide of silver . . .	= 64·9884	Silver. . . . .	= 29·8335
		Iodine. . . . .	= 58·5107
	100·0000		100·0000

The alloy was more brittle than the preceding. Fracture, as before, resinous. Colour: in the mass, brown; in thin laminae, yellow and transparent; in powder, a brilliant yellow. Unaffected by light.



Melting point = 494° C.

Specific gravity 5·716.

The alloy expanded on heating from 0° C. to 194° C., then it simply absorbed heat without either expanding or contracting till it attained a temperature of 214° C. Rapid contraction now took place, and continued through 66° C., viz.: to 280° C. At this temperature the mass began to expand with the same coefficient as that possessed by the previous alloy (No. 2) above 298° C.

The coefficient of cubical expansion for 1° C. from 0° C. to 177° C. was  
 ·00002307.

Between 177° C. and 194° C. the coefficient diminished to  
 ·000012855.

Then the alloy simply absorbed heat without change of volume.  
 At 214° C. it commenced to contract under a negative coefficient of  
 ·00017424.

This continued until a temperature of 280° C. had been reached, when expansion commenced under the coefficient of  
 ·00009474 for 1° C.

This continued to the melting point.

The following volumes correspond to the temperatures given :—

Volume at	0° C.					
	177	.	.	.	.	= 1·000000
	194	.	.	.	.	= 1·004083
	214	.	.	.	.	= 1·004301
	280	.	.	.	.	= ·992902
	300	.	.	.	.	= ·994796
	400	.	.	.	.	= 1·004270
	melting point (494° C.)	(solid)	.	.	.	= 1·013225
	"	"	(494° C.)	(liquid)	.	= 1·081637

#### 4. Copper-silver iodide alloy, $Cu_2I_2 \cdot 4AgI$ .

The percentage of silver iodide was further increased to 71 by the addition of a fourth molecule.

$Cu_2I_2 \cdot 4AgI$  contains :—

Cu <sub>2</sub> I <sub>2</sub> . . . . .	= 28·7775	Copper . . . . .	= 9·5820
AgI . . . . .	= 71·2225	Silver. . . . .	= 32·6994
		Iodine. . . . .	= 57·7186
	<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>
	100·0000		100·0000

The alloy resembled the preceding. It was, however, slightly more brittle, and the fracture was more crystalline. The colour in the mass was brownish-yellow; in thin laminæ bright yellow; and in powder a brilliant yellow. Unaffected by light.

Melting point = 493° C.

Specific gravity = 5.7064.

The alloy expanded on heating from 0° C. to 159° C. under a coefficient of

·00001999.

Between 159° C. and 180° C. the coefficient fell to

·00001056.

From 180° C. to 199° C. it simply absorbed heat without undergoing either expansion or contraction.

At 199° C. contraction commenced, and continued under a negative coefficient of

·00007200

till 213° C., when it increased to

·0003798,

and so continued till 234° C., when it fell again to

·00007200,

under which coefficient it contracted till a temperature of 282° C. was attained.

Somewhat rapid expansion then set in, with a coefficient of

·0002050.

The following volumes correspond to the temperatures given:—

Volume at	0° C.	· · · · ·	= 1.000000
„	159	· · · · ·	= 1.003180
„	180	· · · · ·	= 1.003296
„	199	· · · · ·	= 1.003296
„	213	· · · · ·	= 1.002288
„	234	· · · · ·	= .994313
„	282	· · · · ·	= .990857
„	300	· · · · ·	= .994547
„	400	· · · · ·	= 1.015047
„	melting point (493° C.) (solid)	· · · · ·	= 1.034112
„	„ „ (493° C.) (liquid)	· · · · ·	= 1.065601

##### 5. *Copper-silver iodide alloy, Cu<sub>2</sub>I<sub>2</sub>.12AgI.*

The percentage of silver iodide was finally increased to 88 by alloying one molecule of iodide of copper with twelve of iodide of silver. This extreme was employed in order to test the extent to which a small percentage of iodide of copper may mask for a while the prominent characteristics of the iodide of silver. None of the alloys

hitherto prepared contain so large a percentage of iodide of silver.  $\text{Ag}_4\text{I}_4\cdot\text{AgCl}\cdot\text{AgBr}$  contains 74 per cent.

$\text{Cu}_2\text{I}_2\cdot 12\text{AgI}$  contains :—

$\text{Cu}_2\text{I}_2$ . . . . .	= 11·8696	$\text{Copper}$ . . . . .	= 3·9535
$\text{AgI}$ . . . . .	= 88·1304	$\text{Silver}$ . . . . .	= 40·4770
	100·0000	$\text{Iodine}$ . . . . .	= 55·5695
			100·0000

The alloy possessed a yellowish-green colour in the mass, but thin layers of it were yellow and transparent. The powder was yellow : much brighter than that of iodide of silver, but not quite so brilliant as that of the other alloys. It turned slightly green on exposure to light. The fracture was crystalline ; the grain being much finer than that of the iodide of silver. The alloy violently broke the tube in which it was cast by expansion during cooling, but no rifts appeared in the rod ; nor was it nearly so brittle as iodide of silver.

Melting point =  $513^\circ \text{C}$ .

Specific gravity = 5·6950.

The alloy expanded on heating from  $0^\circ \text{C}$ . to  $124^\circ \text{C}$ . under a coefficient of  
 $\cdot 00000636$ .

Between  $124^\circ \text{C}$ . and  $153^\circ \text{C}$ . it simply absorbed heat without undergoing either expansion or contraction.

At  $153^\circ \text{C}$ . contraction commenced, and continued under a negative coefficient of  
 $\cdot 0000831$

till a temperature of  $168^\circ \text{C}$ . had been attained, when it increased to  
 $\cdot 00028899$ ,

and so continued till the temperature had risen to  $225^\circ \text{C}$ ., when expansion commenced under the coefficient  
 $\cdot 00006666$ .

The following volumes correspond to the temperatures given :—

Volume at	0° C.	. . . . .	=1·000000
„	124	. . . . .	=1·000788
„	153	. . . . .	=1·000788
„	168	. . . . .	= ·998985
„	225	. . . . .	= ·982512
„	300	. . . . .	= ·987511
„	400	. . . . .	= ·994177
„	500	. . . . .	=1·000843
„	502 (solid)	. . . . .	=1·000976
„	502 (liquid)	. . . . .	=1·042612

## DISCUSSION OF THE RESULTS.

1. The copper-silver iodide alloys described in the foregoing pages vary in regard to the quantity of iodide of silver which they possess to the extent of 50 per cent.; the lowest,  $\text{Cu}_2\text{I}_2\cdot\text{AgI}$ , containing 38 per cent. of iodide of silver, and the highest,  $\text{Cu}_2\text{I}_2\cdot 12\text{AgI}$ , 88 per cent.

2. It will be noticed, however, that the percentage of iodine varies but little, for while  $\text{Cu}_2\text{I}_2\cdot\text{AgI}$  contains 61.9055 per cent.,  $\text{Cu}_2\text{I}_2\cdot 12\text{AgI}$  contains 55.5695.

3. The specific gravity of the alloys varies slightly, and is a little above the mean specific gravity of their constituents. This was also observed in the case of the five chlorobromiodides of silver previously described (p. 1140), and in that of the lead-silver iodide alloy (p. 1146), and while the specific gravity of  $\text{Cu}_2\text{I}_2$  is 5.6936, and of  $\text{AgI}$  5.6750, that of the alloys is as follows:—

$\text{Cu}_2\text{I}_2\cdot\text{AgI}$	. . . . .	5.7302
$\text{Cu}_2\text{I}_2\cdot 2\text{AgI}$	. . . . .	5.7225
$\text{Cu}_2\text{I}_2\cdot 3\text{AgI}$	. . . . .	5.7160
$\text{Cu}_2\text{I}_2\cdot 4\text{AgI}$	. . . . .	5.7064
$\text{Cu}_2\text{I}_2\cdot 12\text{AgI}$	. . . . .	5.6950

4. The melting points do not differ much from each other, in fact those of  $\text{Cu}_2\text{I}_2\cdot 2\text{AgI}$ ,  $\text{Cu}_2\text{I}_2\cdot 3\text{AgI}$ ,  $\text{Cu}_2\text{I}_2\cdot 4\text{AgI}$ , and  $\text{Cu}_2\text{I}_2\cdot 12\text{AgI}$ , are practically the same; but they are considerably lower than those of their constituents: *i.e.*, more than 100° C. lower than that of iodide of copper, and more than 30° C. lower than that of iodide of silver. This was also noticed in the case of the chlorobromiodides of silver, and in that of the lead-silver iodide alloy.

5. While both the iodide of copper and the iodide of silver are highly crystalline in structure, even in thin layers, the copper-silver iodides are resinous in fracture and transparent in thin layers, even when they contain as much as 65 per cent. of iodide of silver. With greater percentages the structure becomes slightly crystalline.

6. It is obvious that some of the alloys possess three points of similar density; and others two, at different temperatures. Thus, in the case of  $\text{Cu}_2\text{I}_2\cdot 2\text{AgI}$ , the density is the same at 133° C., 265° C., and 334° C.

7. When strongly heated in a current of carbonic anhydride the alloys remained in tranquil fusion, undergoing an extremely slow volatilization. Heated in a current of dry oxygen, iodine was freely evolved, and oxide of copper appeared on the surface of the mass. When heated in dry hydrogen, hydriodic acid was formed, and the iodides were reduced.

8. The general colour of the alloys was in the mass from brown-yellow to green-yellow, as the percentage of iodide of silver was increased. In thin laminæ bright yellow, and in a powder a brilliant dark yellow, becoming slightly lighter as the percentage of iodide of silver was increased.

9. The coefficient of expansion of the alloys below the point at which contraction on heating commences, was found to decrease as the percentage of iodide of silver was augmented :—

Percentage of AgI.	Coefficient of expansion.
38·2232	·00004998
55·3066	·00003750
64·9884	·00002307
71·2225	·00001998
88·1304	·00000636

It was in all cases considerably less than that of iodide of copper.

The same fact was observed in the case of the chlorobromiodides of silver :—

Percentage of AgI.	Coefficient of expansion.
26·1692	·00012216
41·4840	·00009529
58·6404	·00008307
68·0171	·00006000
73·9285	·00005400

10. On the other hand, the expansion above the point at which contraction on heating finishes, was greater than that of either the iodide of silver or the iodide of copper.

11. MATTHIESSEN asserts that the coefficient of expansion of a metallic alloy is the mean of the coefficients of expansion of the several volumes of the metals composing it, and in the case of ordinary alloys this law undoubtedly holds good. But in the iodide of silver alloys the conditions are so complex that we can scarcely hope for the same result. Nor do we find it. We are dealing, on the one hand, with a substance which possesses several allotropic modifications; several distinct coefficients of contraction on heating, and one coefficient of expansion; and, on the other hand, with bodies, which like the iodides of lead and mercury also possess allotropic modifications, each with its own coefficient of expansion, or with a single coefficient of expansion and no allotropic modification like the iodide of copper.

12. MATTHIESSEN considers that in nearly all cases two-metal alloys may be regarded as solidified solutions of the one metal in the other, as glass is a solidified solution of different silicates, or gold and silver in the gold-silver alloys.

13. The lowering of the fusing point of alloys undoubtedly means that the cohesion of the particles in the alloy is less than that of the particles in its constituents; and

admitting the supposition that alloys are solidified solutions of one body in another (12), this lessening of cohesion is not difficult to explain. For it is well known that particles of matter of similar composition attract each other (*cohesion*) more readily, and with greater force, than particles of different composition (*adhesion*), and hence the homogeneous diffusion of one substance in another must make the molecular attraction less than that of either body by itself. Hence, molecular motion is more readily assimilated, and sooner produces any given effect, such as the fusion of the mass.

14. It was thought that the same explanation would apply to the curious fact that the five chlorobromiodides of silver, and the lead-silver iodide alloy, all commenced their period of contraction on heating at a lower temperature than the iodide of silver, to which substance alone can they owe their contraction on heating, but the results obtained with the copper-silver iodide alloys appear to discredit this.

15. For it is most noteworthy in this connexion to observe that while the iodide of silver commences to contract considerably on heating, that is to pass from its crystalline into its amorphous plastic condition, at  $142^{\circ}$  C., the five chlorobromiodides of silver, the percentage of iodide of silver in which varies from 26.1692 to 73.9285, and the lead-silver iodide alloy, the percentage of iodide of silver in which amounts to 33.794, all commence their contraction at  $124^{\circ}$  C., that is  $18^{\circ}$  C. lower, although the coefficients of expansion of the associated bodies necessarily differ. It would thus appear that  $124^{\circ}$  C. is the temperature at which iodide of silver commences its passage from the crystalline into the amorphous condition when freed from the attraction of its own molecules, provided no other attraction or influence supervenes; while the attraction exerted when it exists unalloyed with any other substance, and when its molecules are hence much nearer to each other, raises the point of commencement of change  $18^{\circ}$  C. higher, viz.: to  $142^{\circ}$  C.

16. The same result was looked for in the case of the copper-silver iodide alloys, but it was not found. The temperature at which contraction commences was in all cases raised, instead of being lowered, so that the presence of the iodide of copper hinders the assimilation of molecular motion by the molecules, although the coefficient of expansion of the iodide of copper is lower than that of either the chloride or bromide of silver, or of the iodide of lead which enter into the composition of the other alloys.

Percentage of iodide of copper in the silver-copper iodide alloys.	Temperature at which expansion on heating finishes.
61.7767	$256^{\circ}$ C.
44.6934	$221^{\circ}$ C.
35.0116	$194^{\circ}$ C.
28.7775	$180^{\circ}$ C.
11.8696	$124^{\circ}$ C.

But the contraction did not begin when the expansion ceased; the mass simply absorbed heat without undergoing change of volume through a varying range of degrees, which removes the point of contraction still further from that of the iodide of silver.

Thus, while in the case of the chlorobromiodide of silver containing only 26.1692 per cent. of iodide of silver, and of the lead-silver iodide alloy containing 33.794 per cent., the contraction commenced at 124° C., the following temperatures were those at which the contraction commenced in the case of the copper-silver iodide alloys containing in all cases more iodide of silver than either of the alloys mentioned above:—

Percentage of iodide of silver.	Temperature at which contraction on heating commenced.
38.2232	284° C.
55.3066	233° C.
64.9884	214° C.
71.2225	199° C.
88.1304	153° C.

Thus the effect of 61.7767 per cent. of iodide of copper was to raise the point at which the iodide of silver commences to pass from the crystalline to the amorphous condition 142° C., viz.: from 142° C. to 284° C.; and the influence of 28.7775 of iodide of copper was sufficient to raise the temperature of the point of change to 199° C., while the presence of 66.206 per cent. of iodide of lead, and of 74 per cent. of chloride and bromide of silver, not only did not raise the temperature at which contraction commences, but lowered it 18° C. When the percentage of iodide of silver in the copper-silver iodide alloys was very considerable the temperature at which contraction commenced fell to 153° C.

17. This difference in the commencement of the period of contraction on heating would lead us to look for differences of structure in the case of those alloys which begin to contract at 124° C., and those in which the contraction is masked and annulled until a higher temperature is attained. Such differences we have no difficulty in finding. If we compare the lead-silver iodide alloy,  $\text{PbI}_2 \cdot \text{AgI}$ , previously described (p. 1146), which contains 33.794 per cent. of iodide of silver, with the copper-silver iodide alloy,  $\text{Cu}_2\text{I}_2 \cdot \text{AgI}$ , which contains 38.2232 per cent. of iodide of silver, and which, hence, most nearly approaches it in composition, the differences are very conspicuous.  $\text{PbI}_2 \cdot \text{AgI}$  is crystalline in structure, and in cooling it expands considerably and breaks the tube in which it is cast. Harsh noises are emitted during cooling, and strong tremors are propagated through the mass. The expansion of the alloy ceases at 118° C., contraction commences at 124° C., and continues to 139° C. rapidly, almost equalling that of iodide of silver itself; the mass decreasing in volume to .984120.  $\text{Cu}_2\text{I}_2 \cdot \text{AgI}$  is resinous in structure, and in cooling it contracts considerably, and comes out of the tube in which it is cast. No harsh sounds are emitted during cooling, and no tremors are propagated through the mass. The expansion of the alloy ceases at

256° C., contraction commences feebly and under a very low coefficient at 284° C., and continues till a temperature of 309° C. has been attained, when rapid expansion sets in. The difference in the volume due to this contraction is very slight: thus, volume at 284° C. = 1.011804, and volume at 309° C. when the contraction is finished = 1.010805.

18. The microscope, when applied to the examination of thin layers, also shows differences.  $\text{PbI}_2 \cdot \text{AgI}$  in a thin layer is opaque owing to the presence of multitudes of small crystals.  $\text{Cu}_2\text{I}_2 \cdot \text{AgI}$  is transparent. It would therefore appear that the presence of the  $\text{Cu}_2\text{I}_2$  has prevented the iodide of silver from changing from the amorphous plastic condition to the crystalline condition: a change which, as above stated, is usually accomplished at 142° C.

19. The researches of petrologists in connexion with the examination of thin slices of minerals under the microscope, have shown that if rocks be fused and suddenly cooled no structure is developed, while, if slowly cooled, they not only become crystalline, but may be built up entirely of crystals. Thus basalt perfectly fused and suddenly cooled in water forms a black glass, which exhibits no structure under the highest power. Less rapid cooling develops *microliths* or *crystallites*, and as the cooling is still further retarded the microliths group themselves into gem-like forms, into radial forms about a centre, into small definite crystals, and into large definite crystals. Thus the glassy basalt or tachylyte, passes into ordinary basalt; and the ordinary basalt, into the highly crystallised gabbro. Also it is noted that the specific gravity increases as the crystalline structure is more and more developed. Thus glassy basalt has a lower specific gravity than basalt, and the latter than gabbro. We are also very familiar with the difference in the size of the crystals of any substance which separates out from solution if the evaporation be rapid or slow.

Now  $\text{AgI}$  above 142° C. corresponds to the glassy basalt.

„ below „ „ gabbro.

Or octohedral sulphur corresponds to the gabbro.

„ plastic „ „ tachylyte.

The crystals of felspar, quartz, &c., doubtless separate out from solution in the ground mass of the mineral, as a soluble salt separates from its solution in water.

20. We have obviously to deal with—

(a) The crystalline forces which tend to build up the substance into crystals.

(b) The force of cohesion exerted by the crystals whether microliths or large crystals for each other.

(c) The attraction subsisting between the surrounding mass or medium and the crystals.

On the other hand we have the molecular motion tending to disunite them.



21. It would therefore appear that in the case of the lead-silver iodide alloy,  $\text{PbI}_2 \cdot \text{AgI}$ , the ground mass of  $\text{PbI}_2$ , with which the iodide of silver is surrounded, offers no opposition to the passage of the iodide from the plastic to the crystalline condition, but rather, by separating the crystals from the influence of their own attraction, promotes it. While, on the other hand, that in the case of the copper-silver iodide alloy the ground mass of  $\text{Cu}_2\text{I}_2$ , by its attraction or by other influence, prevents the passage of the iodide of silver from the plastic to the crystalline condition, or at least considerably hinders it, and allows it only to take place at a temperature far above the usual point, or when the percentage of iodide of silver is so considerable that the adverse influence of the  $\text{Cu}_2\text{I}_2$  is overcome, as in the last alloy containing 88 per cent. of  $\text{AgI}$ .

22. If a small thin layer of sulphur be melted on a piece of mica and suddenly cooled in cold water, and placed under the microscope, it is seen to be perfectly transparent; gradually, as we watch it from day to day, crystals are seen forming themselves out of the ground mass, and these increase rather in number than in size, until the whole is converted into a crystalline opaque brittle mass. In this case molecular motion being, as we know, slowly lost, the crystalline forces become more and more able to build up crystals out of the ground mass. On the other hand, if a thin layer of iodide of silver be melted on a slip of mica, and placed, while in the plastic condition, under the microscope, it is seen to be transparent, but at the moment when the temperature sinks to  $142^\circ \text{C}$ . the mass suddenly crystallises all over. Between these two extremes we, of course, have instances in which the passage from the amorphous to the crystalline state takes place with greater or lesser readiness. If iodide of lead be fused on a piece of mica, and placed under the microscope, it is seen to crystallise rapidly, and it presents the appearance of crystalline plates with numerous veined markings (fig. 7). When alloyed with iodide of silver the mass is seen to be made up of a multitude of small tabular crystals (fig. 8), altogether different from either the iodide of lead, or the iodide of silver when similarly and separately treated. The copper-silver iodide alloys (except when the percentage of iodide of silver is very large) present the network appearance under the microscope shown in fig. 9. They are transparent moreover in thin layers, and translucent in thicker layers, while the chlorobromiodides, and the iodide of lead, and the lead-silver iodide alloy are opaque from the presence of multitudes of crystals.

23. It is conceivable that the iodide of lead possesses so strong a tendency to crystallise, and so little attraction for the molecules of iodide of silver, that it in no way interferes with the crystallisation of the latter; while the iodide of copper may possess but little tendency to crystallise itself and considerable attraction for the iodide of silver homogeneously diffused throughout. Or, in the one case we may have an actual chemical attraction of the molecule of the one iodide for that of the other;

while in the other case they may exist as a literal alloy—a solidified solution of the one substance in the other, like glass.

Fig. 7.



Fig. 8.

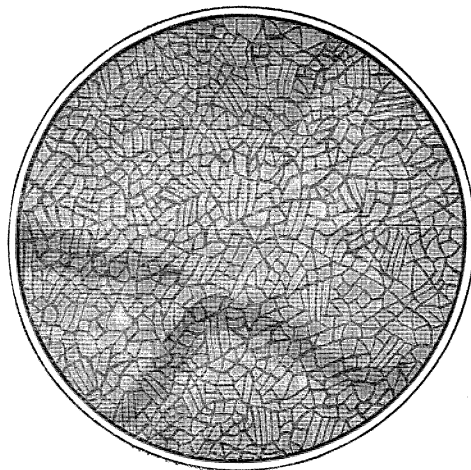
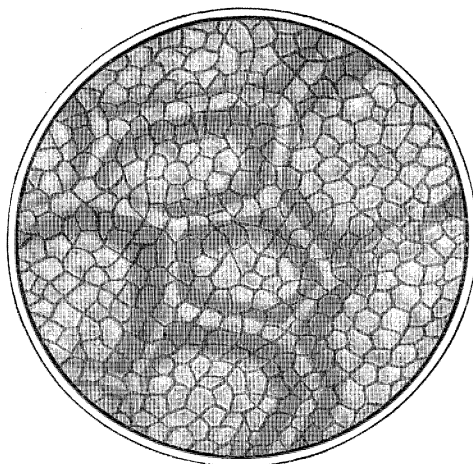


Fig. 9.



24. In the case of the alloy  $\text{Cu}_2\text{I}_2\text{AgI}$ , which contains 61·7767 per cent. of iodide of copper, the effect of the 38·2233 per cent of iodide of silver has been—

(a) To diminish the coefficient of expansion below  $256^\circ\text{C}$ . from ·00007317 to ·00004998.

(b) To annul the expansion altogether between  $256^\circ\text{C}$ . and  $284^\circ\text{C}$ . and between  $309^\circ\text{C}$ . and  $319^\circ\text{C}$ .

(c) To produce contraction on heating between  $284^\circ\text{C}$ . and  $309^\circ\text{C}$ ., viz.: through  $25^\circ\text{C}$ .

(d) To augment more than two-fold the coefficient of expansion above  $319^\circ\text{C}$ ., viz.: from ·00007317 to ·00016665.

25. The effect of the addition of the second molecule of AgI, raising the percentage to 55.3066, has been—

(a) To diminish the coefficient of expansion below 221° C. to .00003750.

(b) To annul the expansion between 221° C. and 233° C.

(c) To produce contraction on heating between 233° C. and 298° C., viz.: through 65° C.

(d) To augment slightly the coefficient of expansion above 298° C., viz.: from .00007317 to .00009474.

26. The addition of the third molecule of AgI in  $\text{Cu}_2\text{I}_2.3\text{AgI}$  raises the percentage of iodide of silver to 64.9884, and the effect has been—

(a) To diminish the coefficient of expansion below 177° C. to .00002307, and between 177° C. and 194° C. to .00001285.

(b) To annul the expansion between 194° C. and 214° C.

(c) To produce contraction on heating between 214° C. and 280° C., viz.: through 66° C.

(d) To augment to the same extent as the preceding the coefficient of expansion above 280° C., viz.: from .00007317 to .00009474.

It will be noticed in the case of this alloy, which differs from the preceding one ( $\text{Cu}_2\text{I}_2.2\text{AgI}$ ) by containing nearly 10 per cent. more of iodide of silver and nearly 10 per cent. less of iodide of copper—(1) that the contraction takes place through the same range of temperature (65° C.), beginning, however, 19° C. lower; (2) that the coefficient of expansion above the point at which contraction finishes is the same; (3) that the specific gravity and fusing point are practically the same. In fact, the almost sole effect of the additional 10 per cent. of iodide of silver has been to increase the coefficient of contraction between 214° C. and 280° C.

27. The addition of the fourth molecule of AgI in  $\text{Cu}_2\text{I}_2.4\text{AgI}$  raises the percentage of AgI to 71.2225, and the effect has been—

(a) To diminish the coefficient of expansion below 159° C. to .00001999, and between 159° C. and 180° C. to .00001056.

(b) To annul the coefficient of expansion between 180° C. and 199° C.

(c) To produce contraction on heating between 199° C. and 282° C., viz.: through 83° C.

(d) To augment more than two-fold the coefficient of expansion above 282° C., viz.: from .00007317 to .0002050.

28. The addition of the twelfth molecule of AgI in  $\text{Cu}_2\text{I}_2.12\text{AgI}$  raised the percentage of AgI to 88.1304, and, as might be expected, altered the character of the alloy from that of the preceding, approximating it more to the iodide of silver, and diminishing the influence of the iodide of copper. The effect has been—

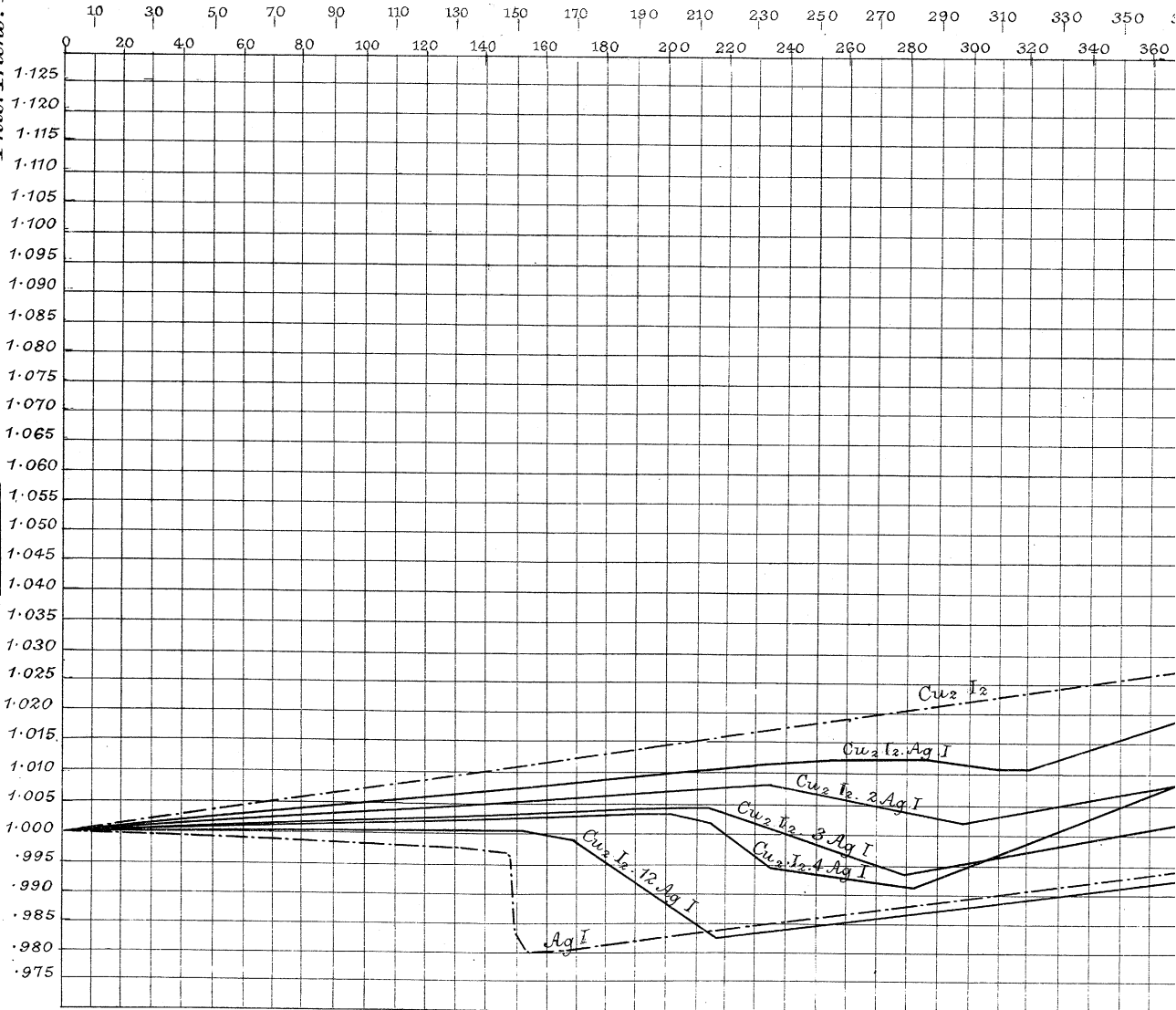
- (a) To diminish the coefficient of expansion below  $124^{\circ}$  C. to  $\cdot 00000636$ .
- (b) To annul the coefficient of expansion between  $124^{\circ}$  C. and  $153^{\circ}$  C.
- (c) To produce contraction on heating between  $153^{\circ}$  C. and  $225^{\circ}$  C., viz.: through  $72^{\circ}$  C.
- (d) To produce a coefficient of expansion above  $225^{\circ}$  C. almost identical with that of iodide of silver.

Plate 96 shows the effects of heat upon the copper-silver iodide alloys.

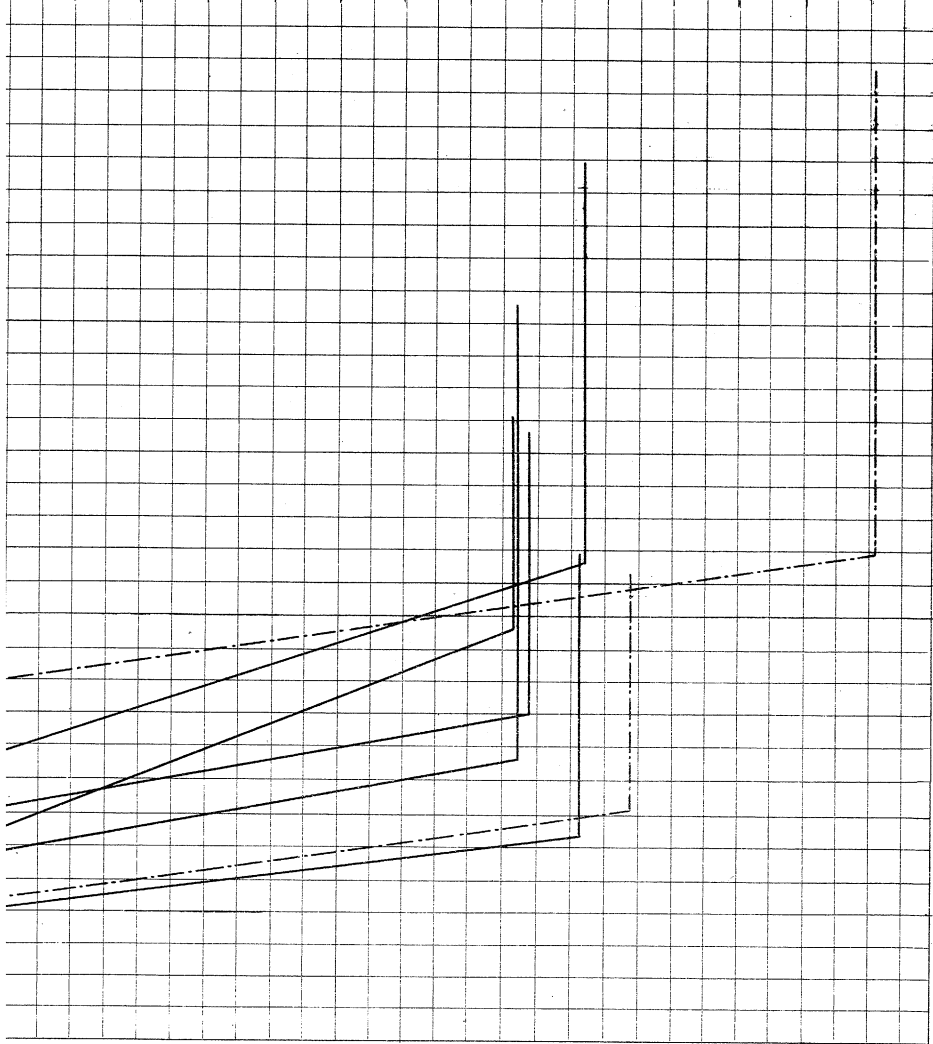
Professor M. BELLATI and Dr. R. ROMANESE, of the University of Padua, have lately determined the specific heat, and heat of transformation, of the iodide of silver and the copper-silver iodides above described, using for their determinations the same specimens as those with which I worked, and which were forwarded to Padua at their request. Their results are given in this volume (page 1169).

I beg to express my indebtedness to the Royal Society for several grants which it has allowed for the prosecution of these researches.

TEMPERATURES.



350 370 390 410 430 450 470 490 510 530 550 570 590 610  
40 360 380 400 420 440 460 480 500 520 540 560 580 600 620 °C.



West Newman & Co lith.

TEMPERATURES.

