

# The Thermal Deformation of the Crystallised Normal Sulphates of Potassium, Rubidium, and Cesium

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X. *The Thermal Deformation of the Crystallised Normal Sulphates of Potassium, Rubidium, and Cæsium.*

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*Communicated by Captain ABNEY, C.B., F.R.S.*

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IN a communication made to the Royal Society in April last ('Phil. Trans.,' A, vol. 191, 313) the author described an interference dilatometer, by the use of which, owing to the introduction of compensation for the expansion of the platinum-iridium interference apparatus by means of a disc of aluminium laid on the object, the delicate method of FIZEAU is rendered equally sensitive in the determination of the expansion of solid substances, notably crystals, which cannot be obtained in blocks of the relatively large size hitherto required. The method is particularly applicable in the cases of those substances, including the crystals of most artificial chemical salts or other preparations, whose ground surfaces will not take a polish equal to that of glass. The author was led to devise it in order to be able to extend his investigations, concerning the relations between the morphological and physical properties of the crystals of isomorphous series of salts on the one hand and their chemical constitution on the other, to the thermal deformation of the salts in question. In previous communications to the Chemical Society the author has described the results of detailed observations of a large number of morphological and physical properties of the crystals of the series of normal alkali sulphates, containing as metal potassium, rubidium, and cæsium respectively ('Journ. Chem. Soc.,' Trans., 1894, 628); of twenty-two double sulphates of the series  $R_2M(SO_4)_2, 6H_2O$  in which R is represented by the same three alkali metals ('Journ. Chem. Soc.,' Trans., 1893, 337 and 1896, 344); and of the normal selenates of these metals ('Journ. Chem. Soc.,' Trans., 1897, 846). The general result of these investigations has been to show that the whole of the investigated morphological and physical properties of the crystals of these salts exhibit progressive variations which follow the order of progression of the atomic weights of the three alkali metals ( $K = 39$ ,  $Rb = 85.2$ ,  $Cs = 132.7$ ), so that the variations may be said to be functions of the atomic weight of the alkali metal, in the broad sense in which the term "function" is usually applied in connection with atomic weight.

Of all the isomorphous series referred to, the normal sulphates alone prove to be

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suitable for an investigation of the thermal deformation. The double sulphates are unsuitable on account of the ease with which most of them lose water of crystallisation when their temperature is raised, and a similar remark applies to the double selenates, whose investigation with respect to their morphological and physical properties is now proceeding. The simple selenates offer great difficulties on account of their excessively hygroscopic nature, which is so marked in the case of caesium selenate, in accordance with the rapidly progressive advance in the solubility of the three salts which has been shown (*loc. cit.* p. 851) to follow the order of the atomic weights of the metals, as to place it in the category of effective desiccating agents. The normal sulphate of potassium is absolutely free from this disadvantage, being one of the least soluble of the salts usually classed as soluble in water, 100 cub. centims. of this liquid at the ordinary temperature only dissolving 10 grams of the salt (*loc. cit.* p. 851 and sulphate memoir *loc. cit.* p. 632). Rubidium sulphate is so slightly hygroscopic, its solubility being only 44 per cent., as to present no difficulty on this ground. Caesium sulphate is decidedly hygroscopic, the solubility being so relatively great as 163 grams in 100 cub. centims. water. Although this characteristic is by no means so strong as in the analogous selenate, the solubility of caesium selenate being no less than 245 grams in 100 cub. centims. water, still it is sufficiently marked to render the use of the salt for the purpose in question impossible in damp weather. The difficulty has, however, been successfully overcome in the case of caesium sulphate, by taking advantage of the driest days of the recent remarkably dry summer, and of a few dry frosty ones of the early winter, together with the expedient of utilising the inner chamber of the air bath of the dilatometer as a desiccator, by placing a vessel containing oil of vitriol therein until the actual moment of commencing the observations.

In the present memoir, therefore, are presented the results of an investigation of the thermal deformation of the orthorhombic normal sulphates of potassium, rubidium, and caesium. It is scarcely necessary to remark that the series of these particular three metals has been chosen throughout the whole of the author's work on the relations between the chemical composition of salts and the properties of their crystals, because of their well-established close relationship, as being in the strictest sense members of the same family group of the periodic system, the definitely established and relatively large differences between their atomic weights, and the fact that they form the most strongly electro-positive series of elements.

#### *Preparation of the Crystals.*

Although the new compensation method does not require crystal blocks of greater thickness than 5 millims., the greatest difficulty has been experienced in obtaining crystals of the commonest of the three salts, potassium sulphate, of adequate thickness in all three of the axial directions along which measurements of expansion or con-

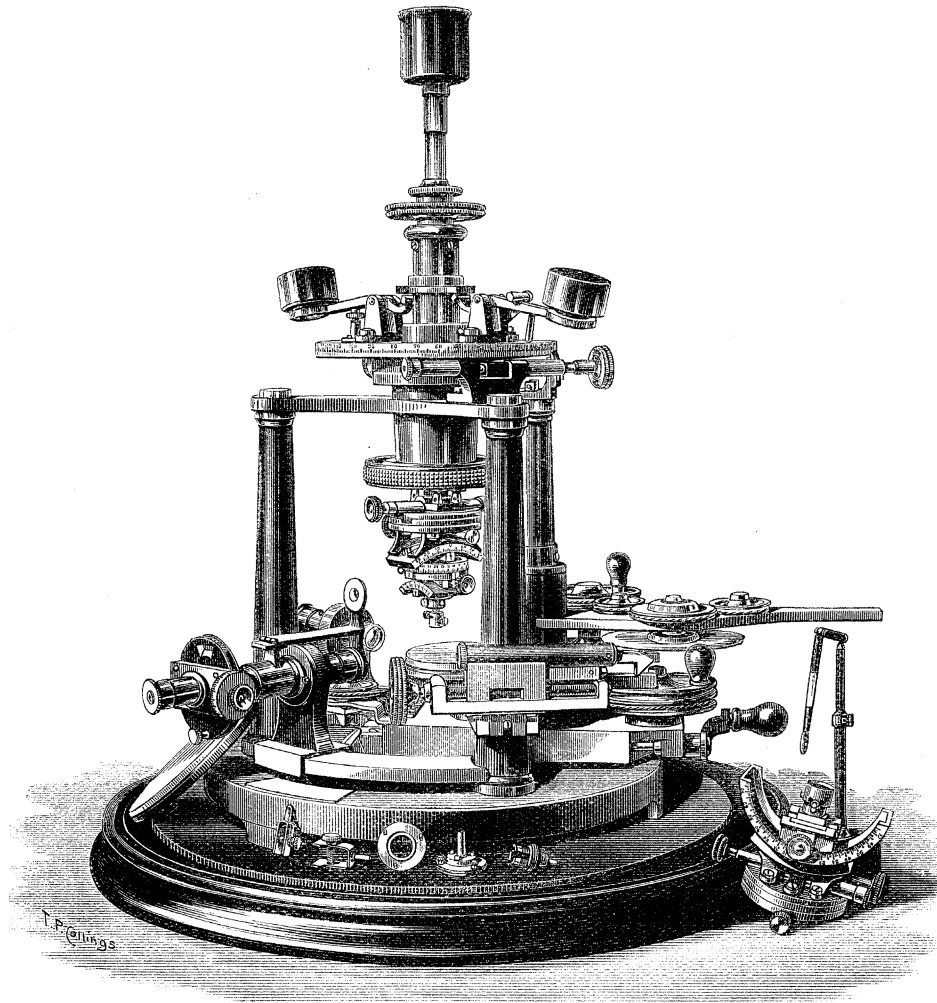
traction by heat were desired. By the slow evaporation of cold saturated solutions over oil of vitriol *in vacuo* it is possible, given adequate length of time and sufficient amount of solution, to obtain excellent crystals of the more soluble sulphates of rubidium and cæsium, of the requisite size to furnish blocks from 5 to 10 millims. thick in the three axial directions. But in the case of the sparingly soluble potassium salt the crystals are almost invariably small. Moreover, when by exception they are larger, they are either pseudo-hexagonal triplets or other twinned forms, useless for the purpose in view owing to the unequal expansion of the interpenetrating parts due to different axial expansion in accordance with orthorhombic symmetry; or otherwise, they are individuals of an elongated prismatic nature, the elongation being in the direction of the axis *a* and the prisms being too narrow for use along the other two axial directions, particularly that of the axis *b*. It was found exceedingly difficult to induce well-formed individual prisms, deposited from a large quantity of a cooling saturated solution, to grow further to the required transverse dimensions in cold saturated solutions over vitriol *in vacuo*. After attaining a thickness of about 4 millims. it almost always happened that, rather than grow further, fresh crystals began to be deposited. After months of fruitless labour, Messrs. HOPKIN and WILLIAMS kindly undertook to attempt to obtain larger crystals by the use of very much larger quantities of solution, and eventually succeeded in producing seven crystals of exceptional thickness, and which, after a little further growth in a cold saturated solution over vitriol *in vacuo*, have at length yielded transparent blocks 6·5 to 9·6 millims. thick along the direction of the axis *c* and 5·1 to 5·9 millims. along the axis *b*. The author desires to express his great indebtedness to the firm in question for so kindly placing their resources at his disposal, and thus enabling this investigation to be completed.

#### PREPARATION OF THE PARALLEL-FACED CRYSTAL-BLOCKS.

##### *Improvements on the Cutting and Grinding Goniometer.*

The preparation of the crystal-blocks, each provided with a pair of truly plane and truly parallel surfaces accurately perpendicular to the particular crystallographical axis along which the linear expansion or contraction was to be measured, was carried out with the aid of the author's new cutting and grinding goniometer. The instrument in question is similar in principle and general appearance to that which was described to the Royal Society in December 1894, ('Roy. Soc. Proc.,' vol. 57, p. 324), and which is now in the National Collection in the South Kensington Museum. It differs from the latter instrument in including a few slight improvements which prolonged use has shown to be advisable for the sake of greater convenience and ease in manipulation. The perfected instrument affords the highest satisfaction, enabling the most accurately orientated and truly plane surfaces of crystals of any degree of

hardness to be obtained with the minimum expenditure of time and trouble. Its cost is necessarily very heavy, and the author wishes it to be clearly understood that it is not intended as an instrument for ordinary laboratory use, but as a means of obtaining, irrespective of cost, plates blocks or prisms of the highest attainable accuracy of orientation and perfection of surface, for the purposes of original investigation. The accompanying illustration represents it.



The following description of the improvements on the instrument previously described is appended for the information of other workers, and in response to several enquiries which the author has received both from investigators in this country and abroad.

The most important is a new method of mounting the grinding table, which admits of its movement in its own plane; this is introduced in order to be able to vary the part used in the grinding more considerably than can be achieved merely by use of

the centering movements of the crystal-adjusting apparatus, and thus avoid concentric grooving of the grinding surface, besides no longer requiring the centering of the crystal to be disturbed. This is achieved by mounting the grinding gear on a slider, which can be made to traverse a bevelled bed resting on the base of the instrument, by rotation of a long screw gearing with a corresponding thread in the bed and manipulated by a winch handle. The gunmetal bed is 20 centims. long, 6 centims. wide at the top surface, the greater portion of which is planed out into a depression so as to reduce friction by only leaving narrow strips along the long edges to act as guides for the slider, and 4 centims. wide at the base, there being thus a bevel of 1 centim. at each side. The bed is fixed firmly to the main base of the instrument by four large screws. At the outer end is a cup-shaped hollow ending in the tapped horizontal hollow cylinder of steel which gears with the steel screw carried by the slider. The latter is slightly longer than the bed, and 8 centims. broad. It is a solid casting of steel hollowed underneath to the shape of the bed; the thickness above the bed is 8 millims., and the sides, bevelled on their interior, have a depth of 24 millims. In order to ensure close but not inconveniently tight fitting of the slider on its bed, room has been left on one side for the insertion of a thick strip of steel between the bevelled edges of the slider and the bed, and this is attached to the slider by five screws whose heads are on its outside, and which serve as adjusting screws to regulate the fitting of bed and slider. At the outer end the slider narrows off laterally and its termination is deepened to the depth of the bevelled sides, so as to form a stout support for the passage of the thick steel cylinder which, beyond this bearing, where it is flanged to prevent its traversing, is cut with a deep screw-thread corresponding to the hollow one in the bed. Immediately outside this bearing, the steel cylinder passes into the brass winch fitted with ebonite handle. As the other end of the screw is unflanged, the slider can be readily removed from, or re-attached to, the bed; on pushing the slider over the bed it slides unimpeded for a dozen centims., when the screw begins to gear, and further movement is effected by the winch. The grinding gear is similar to that permanently fixed to the base in the previous instrument, the grinding table being provided with an efficient means of adjustment exactly perpendicular to the vertical goniometrical axis, and the friction pulley with a means of adjustment for the tightening of the driving band. The former is necessarily effected differently to the method employed in the previous instrument, as it is no longer possible to penetrate the base for the utilisation of the spiral spring and tripod method. It is here effected by an adjustable stout circular base-plate, which is fixed to the slider by six screws, three of which penetrate both plate and slider, and three pass through the plate only and thus act as adjusting screws; after these are adjusted the table is fixed in the adjusted position by means of the other three screws. The adjustment of the friction pulley is effected by carrying it on a bracket which is fixed at the inner end of the slider by two broad-headed screws, working in slots of the required length in the horizontal claws of the

bracket. Both this attachment and the circular-plate-bearing attachment of the driving pulley carried at the outer end of the slider can be slightly tilted if desired, so as to make the pulleys run sufficiently eccentrically to avoid friction of the band at the two crossing points on each side of the grinding table pulley. The slider carries in addition, at the middle of the friction pulley end, a small brass plate supporting a short tube, in which, together with two holes driven into the slider one near each side and on the other side of the grinding table, fit three rod supports for a circular guard to surround the grinding table and prevent projection of the lubricating liquid when grinding. The guard has a window on the side nearest the friction-pulley, for the passage of the crystal and its supporting apparatus as the slider is pushed into position; the window can be closed by a shutter after the passage of the crystal, a strip of metal of similar curvature to the guard itself being fitted round this portion of the guard for this purpose, and made movable with the aid of a little handle along a suitable slot directed by broadheaded guiding pins.

The height of the grinding surface of the lap, when the slider is in position, is exactly the same as that of the cutting disc when the cutting gear is in position, so that no variation of the height of the crystal-carrying axis is required. The cutting gear is exactly as in the former instrument, rotatable about the back pillar, and supported also, when in position, in a traversing apparatus carried by the front pillar. The slider carrying the grinding apparatus is removed when the cutter is in position.

In addition to the laps provided with the previous instrument, two additional ones are furnished. One is a polishing lap for hard crystals, consisting of hard opticians' wax melted into a circular metal tray of the same size as the other laps, and afterwards compressed so as to present a plane surface. This lap, employed with ochre or rouge, enables the opticians' method of polishing glass surfaces to be closely followed in the polishing of hard crystal surfaces. The second is a lap whose grinding surface is formed by a sheet of emery cloth stretched over, and cemented to, a metal base of the size and shape common to all the laps. This lap has been particularly useful for effecting the preliminary grinding down of the relatively large crystals employed in the work whose results are now being communicated, leaving but little for the ground-glass lap to do. The variety of eleven laps now provided, enables any or all of the usual grinding and polishing processes of the optician and lapidary to be followed, besides those described by the author for the grinding and polishing of the softer crystals of artificial salts. One of the laps is shown in position in the illustration, and another to the left leaning against the base of the instrument.

A further small but important addition to the accessories consists of three gripping crystal-holders, which are shown resting on the base. One of them is a triply and widely split tube of a centimetre bore, narrowing at a centimetre from the orifice into a cone which passes into a grooved stem similar to the stems of the ordinary holders used for wax attachment of the crystal. The wide splits are continued down to the stem, and the conical portion is provided with a screw thread, with which gears a

milled collar, by the screwing of which down the cone the three portions of the tubular holder are compressed together. The latter are padded inside with broad-cloth, within which, on rotating the collar, the crystal is firmly clamped. This holder is suitable for the gripping of prismatic crystals. The other two, which differ only in the size of their apertures, somewhat resemble miniature tuning forks, the stems being of the same size as those of the other holders and similarly grooved to fit the ribbed socket at the base of the crystal-adjusting apparatus. The two prongs are in each case relatively broad, 1·3 centim., are padded inside with broad-cloth and can be drawn together so as to effect the grip by means of a milled-headed clamping screw, passing loosely through one prong and screwing firmly through the other. One of the forks takes crystals 5 millims. thick and the other takes crystals up to 1·2 centim. thick. If the crystal is not sufficiently tabular for direct gripping by one of these two latter holders, and not sufficiently evenly prismatic for the advantageous use of the split-tube gripper, it is packed in a rectangular block of cork held in the larger forked holder; the cork can be cut with a sharp penknife so as to accommodate the most inconveniently shaped crystal in the position required for grinding. When the prongs are screwed together as much as possible so as to tightly grip the cork setting and the contained crystal, the latter is found to be rigidly held without any danger of cracking, the cork lending itself to an even distribution of pressure. These grippers were devised in order to avoid the frequent cracking which large crystals suffer when warm opticians' wax is employed to cement them to the ordinary holders. The importance of this point is obvious, when it is remarked that a cracked crystal is totally unsuitable for use in determinations of thermal expansion by the interference method, the crack being sure to develop further during the observation and derange the interference bands.

Another addition is a special crystal-adjusting apparatus, shown resting on the table to the right in the illustration, intended for use in preparing  $60^\circ$  prisms for refractive index determinations, in cases where it is a difficult matter, by reason of deliquescence or other rapid deterioration of the substance under investigation, to prepare the two inclined surfaces by separate settings on a crystal-holder employed with the ordinary adjusting apparatus. In order to prepare two surfaces inclined at  $60^\circ$  by one setting of the crystal, it is obviously necessary to rotate the crystal for  $60^\circ$  on each side of the particular principal optical plane which has been adjusted vertical to the grinding plane, with the aid of the goniometrical arrangements provided on the instrument, and to which optical plane the two required surfaces are to be symmetrical. The adjusting apparatus provided for ordinary purposes is similar to the second one described in the memoir on the first and smaller pattern grinding goniometer, intended for use in grinding small artificial salt crystals ('Phil. Trans.,' A, 1894, p. 895), but of larger size, corresponding to the larger instrument. It includes two cylindrical adjusting movements provided with divided silver arcs and indicators, and a divided horizontal circle between them to enable the lower movement to be set at any desired



angle, usually  $90^\circ$ , to the upper one. The two cylindrical movements, however, only admit of  $35^\circ$  of rotation on either side of the vertical axis in each case; this amount is ample for ordinary purposes, including the preparation of a  $60^\circ$  prism by separately setting the direction of each required prism-face, by rotation of  $30^\circ$  from the plane perpendicular to the bisecting plane, the former of which planes can usually be as readily goniometrically adjusted with reference to the existing crystal faces as the bisecting plane itself. In the exceptional cases referred to, of which the extremely deliquescent caesium selenate is an excellent instance, it repays to render the adjusting mechanism more cumbrous in order to secure the prime object, and for this reason the new alternative adjusting apparatus is provided.

It is exactly like the one provided for ordinary use as far down as the upper fixed cylindrical segment and its divided silver scale reading  $35^\circ$  on each side, which is suspended by a bracket from the lower disc of the centering arrangement. The latter is given in duplicate, one being always attached to the ordinary and one to the special adjusting apparatus, as it is more readily attached to, or detached from, the inner axis of the goniometer than the adjusting apparatus to or from the centering disc. Sliding in and under the fixed segment, instead of the usual movable segment of the same size, is one of double the size, that is of rather more than  $150^\circ$ . On one face this enlarged movable segment carries a silver index, to indicate the position with respect to the fixed graduated arc above it; and on the other a silver arc graduated to  $75^\circ$  on each side of the centre. In a rabbetted bed on the under side of the large segment slides the carrier of the lower adjusting segments, which are of the same kind as in the ordinary apparatus, arranged permanently at right angles to the two upper ones, the horizontal circle of the ordinary apparatus being omitted in order to avoid complexity. The sliding of the large segment about the upper fixed one is effected, for the  $35^\circ$  of its path on each side, by manipulation of the milled head of a tangent screw arrangement as in the ordinary apparatus. The lowest of the pair of segments arranged at right angles to these upper ones is also manipulated in its segmental bed for  $35^\circ$  each side by a similar tangent screw. But the sliding of the carrier of the two lower segments about the large segment is effected by hand, and fixation at any required position, with reference to the large silver arc as indicated by an index on the carrier, can be brought about by a milled-headed screw-clamp on the opposite side to that on which are situated the manipulating screw of the lower segments and the index just referred to.

The mode of using the apparatus is very simple. The crystal is attached, with the minimum of wax protruding at the sides, to the smallest of the special crystal-holders which are provided with azimuth adjustment, and with the plane which is desired to be the bisectrix of the  $60^\circ$ -prism arranged vertically as nearly parallel to the goniometrical axis as possible and parallel to the lower tangent screw. The latter can be accurately attained by use of the azimuth adjustment of the crystal-holder. The plane referred to is then exactly goniometrically adjusted with the aid of the two tangent screws, that

is, in the case of the upper adjusting movement by slight rotation of the large segment about the upper fixed segment, the clamping screw being fixed, with the indicator on the carrier at zero. The screw is then unloosed and the slider, together with the lower segments carried by it, moved round  $60^\circ$  on one side, as indicated by the silver index on the carrier, which travels closely underneath the large divided arc. If the  $60^\circ$  are not conveniently attained by the hand movement of the carrier, the difference can be nicely made up by movement of the large segment about the upper arc by means of its tangent screw. If the original position of the upper segment had been noted on the silver scale it could readily be re-attained after the grinding of the first surface. When the latter has been achieved, the lower part of the apparatus is transferred to a position  $60^\circ$  on the other side of the centre, by a total sliding underneath the large segment of  $120^\circ$ , and the second surface is ground.

Another smaller but very useful addition is a spring-clutch to keep up the counter-balanced gun-metal axis, the apparatus for varying the pressure of the crystal on the grinding lap, when the left hand is removed from that one of the counterpoising levers which it manipulates during grinding. In order to prevent this axis from moving during the adjustment of the crystal, a hooked spring-clutch is arranged about the bearing of the lever, in such a manner that when it is pushed over into position, it is maintained there by the force of a spring. It consists of an arm rotatable about an axis screwed into the lower part of one side of the bearing, and carrying a short horizontal bar attached at its outer end which presses down on the outer arm of the counterpoising lever when in position; a strong spring fixed to the base of the bearing and which has to be overcome on moving over the little arm, presses up against an angle of the latter below the axis in such a manner as to keep the bar of the clutch, after being brought over into position, firmly down on the counterpoising lever. The lever is thus fixed with its elbow resting on the circle plate, and its other arm carrying the knife edge is maintained pressed up against the collar of the gun-metal axis, and thus the axis and the crystal which it carries at its lower extremity is unable to fall out of position during the adjustment.

The remaining improvements are two additions to the telescope of the goniometer, due to the suggestion of the author's friend Professor H. A. MIERS, who had already had such additions made to the telescope of an inverted goniometer constructed for him by the same firm, Messrs. Troughton and Simms, and which was intended for the study of the vicinal faces of crystals while in the act of growth in a cell of mother liquor. As the author's cutting and grinding goniometer forms a most excellent inverted goniometer, it was considered advisable to adopt these additions. A rectangular cell with truly plane glass sides is also included to contain the saturated solution employed in such investigations.

The first of the two consists of a combined goniometer- and micrometer-eyepiece, which provides two fixed spider-lines arranged at  $90^\circ$ , one vertical and adjusted exactly parallel to the vertical axis of the goniometer and the other horizontal, both

being diameters of the circular field; and also a third spider-line which is both rotatable and capable of movement perpendicular to itself in the focal plane. The fixed lines are attached in the central aperture of a circle-plate 7 centims. diameter fixed round the optical tube of the eyepiece, and which carries near its periphery a circle divided directly into degrees. The movable spider-line is carried in the aperture of a micrometer box carried in front of a similar circular plate, which latter is fitted closely to the former plate in front of it, and partly enveloping it with a milled flange in such a manner as to be rotatable about it. This front plate is pierced by a window above the micrometer box in such a position that the divided circle of the fixed plate is visible through it. The inner edge of the window is bevelled and carries a vernier, with the aid of which the circle reads to minutes. The movable line is fixed to the front of the traversing frame of the micrometer, at the focus of the double eyepiece which slides in the short portion of the optical tube in front of the box. The fixed lines are brought into the focal plane and almost into contact with the movable one by means of a relatively thick annulus capable of penetrating the traversing frame and attached to the aperture of the fixed circle. The traverse of the frame and its spider line is recorded by a divided drum of the usual kind at the right-hand side of the box; the drum is divided into 100 parts, and the reading is indicated by an index mark fixed alongside. The movable circle and the spider line which it carries can be clamped to the fixed circle and the stationary spider lines when desired, by means of a suitable clamping screw provided with milled head, on the lower part of the periphery opposite to that near which the window is situated. These arrangements enable small movements of the image of the collimator signal, reflected from a crystal surface during growth and due to disturbance of the thermal or other conditions of the solution, to be followed and measured, whether they are lateral, angular, or both.

The other addition to the telescope is that of so arranging the removable lens, usually added to the telescopes of goniometers outside the objective for the purpose of converting the optical system into that of a low power microscope focussing the crystal, as to make it capable of being thrown into position either as usual behind the objective or in front of the eyepiece, and further of making it capable of travelling for some distance along the optical axis. The purpose of this is to enable the image of the signal to be actually followed right up to the image of the crystal itself, in order to be quite certain as to the particular face from which it emanates. This is achieved by supplying two such lenses, mounting the pair on a T-piece, and hinging the stem about a small platform carried above a short tube sliding round the main optical tube and prevented from rotation by a suitable rib and groove. It is only necessary to swing the T-piece over one way or the other for the lens to fall into position either adjoining the objective or the eyepiece, the length of the end cross-piece carrying the lenses being arranged so that either lens falls exactly into the optical axis. The one which falls behind the objective is generally employed close up to the latter in the usual manner. The other one which falls in front of the eyepiece is the one employed

to trace an image; it is of such focal length that when it is close up to the eyepiece it permits the image of the signal to be seen almost as well as when it is absent, while as it is drawn more and more in front of and away from the eyepiece it causes the image to pass gradually into that of the particular reflecting face of the crystal itself. The latter is clearly focussed when the sliding tube has been drawn forward to the full extent of its path, and the face affording the signal image is seen brightly illuminated, as well possibly as other vicinal faces, from which it is distinguished by the tracing process just indicated.

The rest of the arrangements of the instrument are precisely as described in the former memoir (*loc. cit.*).

*Procedure in Cutting and Grinding the Crystal-blocks.*

In selecting crystals from which to prepare a parallel-faced block, those were naturally chosen which were free from traces of turbidity and from cracks and distortions. Crystals of cæsium sulphate are readily obtained perfectly free from turbidity; in the case of rubidium sulphate only very slow growth *in vacuo* yields crystals satisfactory in this respect. The exceptional crystals of the potassium salt, eventually obtained after so much trouble, as has been referred to, were also satisfactory from this point of view.

After removal from the mother liquor, the crystals were carefully dried, and then immediately stored in a desiccator for several days at least before use. With two exceptions each selected crystal was only employed for duplicate determinations, on two successive days, of the linear thermal expansion or contraction along some one particular axial direction. In all, 29 different crystals were employed, 11 of potassium sulphate, 8 of rubidium sulphate, and 10 of cæsium sulphate. The two exceptions were crystals of the rubidium and cæsium salts, the former of which was a particularly fine specimen elongated along one axial direction, and which, when cut in two halves transversely to this direction yielded portions so large that they were separately employed for determinations in two different axial directions; the crystal of cæsium sulphate was cut and ground into a rectangular block for successive determinations in all three axial directions, so as to afford an instance of all three linear values, and from these the value for the cubic expansion, being derived from one and the same crystal, for comparison of the cubic deformation thus obtained with that derived by calculation from measurements of the three linear expansions or contractions exhibited by different crystals. The results were so nearly identical, and the comparison therefore so satisfactory, that there will be no occasion to further refer to this point.

The orientation of the various faces, and the consequential identification of the axial directions of the crystals, was usually an easy matter, as the author was familiar with the salts in question owing to the exhaustive morphological and optical study

already made. The identification of the axial directions is such a vital matter, as will be abundantly evident when the results are discussed, that it should be stated that the whole of the work, in common with all the author's previous crystallographical investigations, has been carried out exclusively by the author personally. In every case, the axial directions were actually verified both by goniometrical measurements and by examination of the interference figures in convergent polarised light. Immersion in a cell of benzene, on the inverted goniometrical polariscope, materially facilitates the latter verification, as the refractive index of that liquid is not far removed from the mean of the indices of the three salts, and the interference figures are consequently very clear, and the apparent optic axial angle is very nearly the true angle. Oil cannot be used, as it is apt to penetrate into any minute cavities in the surfaces, and to ooze out during the thermal observations in drops too small to be noticeable without a lens, but which are sufficient to entirely derange the interference bands by lifting the compensator by an amount which is very appreciable in observations of such delicacy.

For the same reason oil cannot be used in grinding the surfaces, and recourse was again made to benzene, which by its volatility rapidly removes itself from cavities. It is naturally unavoidable that greater quantities require to be used than of oil, as it so rapidly dries away. Hence a dropping funnel was arranged above the cutting or grinding disc, to deliver drops sufficiently fast to continually provide adequate lubrication.

The crystal, after verification of the axial direction along which it was desired to determine the linear deformation, was mounted in the grip-holder, in the manner already described, with the axial direction in question approximately vertical, parallel to the goniometrical axis and perpendicular to the cutting disc and grinding table. The approximation was then converted into absolute adjustment, by goniometrical observation and adjustment of the natural zone of faces parallel to the axis in question. If the crystal were so terminated below that much grinding would be necessary to produce the required surface, the cutter was first brought into requisition and the lower end cut off, at such a distance as to afford a surface of the required extent with the least sacrifice of thickness in the axial direction adjusted. The cutting of these crystals of artificial salts, although they are so much more friable than mineral crystals, is nevertheless most successfully performed by the new instrument. No crystal has yet been broken in the process. If no cutting were required the rough grinding of the surface was carried out on the emery-cloth lap, at first with the crystal-holder and lap detached from the instrument and the former held in the hand, and then, after a rough approximation to the desired surface had been attained, with the crystal and its holder and the lap in position. Finally, after verification of the adjustment, which, owing to the mode of fitting of the holder on to the suspended adjusting apparatus, was usually unimpaired, the surface was finely ground with one of the ground-glass laps.

As the method of using the aluminium compensator above the crystal was always

adopted in arranging the interference apparatus of the dilatometer, the second of the methods described in the memoir concerning the latter and which is illustrated by a special figure in the German translation of that memoir contributed to the 'Zeitschrift für Krystallographie' (30, 530), there was no necessity to polish the surfaces of the crystal-blocks. For a crystal surface is not required to act as the lower reflecting surface involved in the generation of the interference bands, the upper surface of the compensator performing that function. It was therefore only necessary to complete the block by preparing a similar parallel surface in the same manner, separated from the first one by as much thickness of crystal as the particular specimen admitted of. The crystal-block was then cleaned from crystal dust by washing in benzene, dried with a clean linen cloth free from fluff, and stored in a desiccator until required for the observations. The thickness of the blocks employed varied, as will subsequently be seen from the record of the accurate measurements, from 4·8 to 10·7 millims., the former limit being in the case of the only crystal under 5 millims. in thickness. The great majority were from 7 to 9 millims. thick.

In two or three cases, although only benzene had been used in the treatment of the crystals, the observations of expansion were vitiated by the oozing of minute traces of liquid, which proved to be mother-liquor, between the surfaces of the platinum-iridium tripod table and the crystal, or between the latter and the compensator. For in most cases the three point method of contact was impossible, owing to the prepared crystal surfaces being narrower in one direction than in the other, too narrow to take the third point but not too narrow for stable equilibrium of both crystal and compensator. A comparison of the results for the same direction by the two methods shows, however, no appreciable difference, the surfaces having always been absolutely clean and free from dust. Moreover, the surfaces produced by the author's cutting and grinding goniometer are so absolutely plane, that no rolling, due to slight convexity of surface, has ever been observed with them. Further, the placing of the crystal and compensator in position on the table of the tripod was always effected by sliding, to minimise any intervening compressed air film. In the cases of oozing of mother-liquor referred to, the crystals were subsequently heated slowly to  $105^{\circ}$  in an air-bath, and maintained at this temperature for twelve hours. On repeating the observations of expansion no further disturbance occurred, successful determinations being obtained, and the results agreed satisfactorily with those obtained for the same direction of the same salt in cases where this treatment had been unnecessary.

#### THE DETERMINATIONS OF LINEAR DEFORMATION.

##### *Mode of Conducting the Observations.*

The determinations of thermal expansion or contraction were made in the manner which is very briefly outlined for crystals at the close of the memoir concerning the

dilatometer (*loc. cit.*, lower part of p. 363 and p. 364), after the description and communication of the results of the determinations of the expansion of the platinum-iridium alloy of the interference tripod and of the aluminium of the compensators. The temperatures employed have not been quite so high as in the cases of those metallic substances, the highest limit being in the neighbourhood of  $96^{\circ}$ , in order that there might be no appreciable deformation due to internal strain, provoked by the attempted vaporisation of the water of mother-liquor contained in the inevitable minute internal cavities. It is impossible to altogether prevent the formation of such cavities, even by slow evaporation *in vacuo*, but the remarkable agreement of the results obtained indicates that any variable deformation due to this cause has been infinitesimal.

Every effort has been made to render the conditions of the determinations as rigidly analogous as possible, so that comparisons of the results can be made with confidence. As far as possible the same aluminium compensator has been used throughout, namely, one 5.25 millims. thick and a centimetre diameter, and unprovided with points as the three-point method of contact was so rarely available; where exceptions have been made, results with the compensator mentioned are available for the same direction of the same salt, and the two series of results agree so well that the change has evidently not introduced any error. This, of course, should be so, for the compensators, including the one 12 millims. thick used for the determination of the expansion of the metal, were all cut from the same casting of pure aluminium. In most of the exceptional cases the other compensators were provided with points, and the three-point method was used, and afforded the results which have already been stated to accord with those where points were not used. The 5.25 compensator gives excellent interference bands, particularly from one of the two surfaces, which was marked and invariably used. The bands afforded by it were slightly curved, due to infinitesimal convexity, an additional advantage as it was always possible, by noting whether they moved outwards from or inwards towards the centre of curvature, to at once ascertain whether the movement of the bands were due to expansion or to contraction. There is a further advantage in employing the compensator above rather than below the crystal, namely, that the polished surface of aluminium reflects light almost equally with the other surface involved in the production of the bands, the lower surface of the large cover-glass which is laid on the platinum-iridium tripod screws and which bears about its centre the miniature silver ring whose centre is the point of reference for the micrometric measurement of the position of the bands.

The air-film between the two reflecting surfaces was in nearly all cases very thin; it was not found advisable to strive so much for exact compensation for the expansion of the screws as to produce the most brilliant bands. For the correction for non-compensation is of course in all cases accurately determined from the known expansion of the tripod alloy and aluminium. The screw-length corresponding to 5.25 millims.

of aluminium is about 13·77 millims. which leaves room for a crystal 8·37 millims. thick and an air film of 0·15 millim. As the crystals only usually varied 1 or 2 millims. each side of the thickness mentioned, the amount of under or over compensation was never very large.

The same thermometers have been employed as were fully described in the previous memoir. Their fixed points were carefully redetermined after the completion of the determinations. The inner bent thermometer whose bulb was in contact with the tripod and whose indications were those accepted, was found to have altered only to the extent of  $0^{\circ}\cdot 1$ , the indications at  $0^{\circ}$  and  $100^{\circ}$  in ice and steam, after applying the pressure correction for the latter, being  $0^{\circ}\cdot 1$  and  $100^{\circ}\cdot 1$  respectively. Hence the interval had remained unchanged, and as only differences of the temperatures are employed in calculating the coefficients of expansion, no correction of these latter is required for change of interval.

The usual *modus operandi* was to expend the greater part of three days in carrying out a duplicate pair of determinations, of the linear thermal deformation of any one crystal along the direction perpendicular to the two prepared parallel surfaces. The afternoon of the first day was employed in adjusting the crystal and the whole apparatus so as to afford a suitable field of interference bands. Each of the two succeeding days was utilised for the carrying out of a complete series of observations of the position and transit of bands for two intervals of temperature, the operations on each day occupying 5 to 7 hours, during the whole of which time the author followed the bands without intermission. Naturally, the carrying out of sixty-four such observations has proved very trying and fatiguing, the observer being continually afraid of such highly delicate measurements being vitiated by earth tremors due to street traffic or other disturbance, in spite of the rigid mounting of the apparatus on a slate table. Fortunately, this fear has not proved to have had much foundation, as the author's laboratory is happily situated in an exceptionally quiet part of Oxford well removed from the city and the railway. But the experience has shown that the observations would have been far more difficult, if not impossible, in a large city with a network of underground railways such as London. Although this source of disturbance has been minimised, several observations have been lost, generally after spending hours upon them, by the cracking of the crystal under the influence of the rise of temperature, slow as it always was in order to avoid this catastrophe.

The further experience gained during this work indicates that in the case of crystals the Abbe method, of calculating the number of bands which pass the point of reference between two temperatures from initial and final observations of the positions of the bands nearest the reference point, for two wave-lengths, is generally inapplicable. The only guarantee that the observation has been a trustworthy one, that no disturbance due to any of the causes already referred to has occurred, is obtained by carefully following the bands for the whole of the temperature-interval, and observing that they maintain their regular distances and exhibit no appreciable



twisting round the centre or any other irregularity, throughout the whole of the interval of time. Frequently slight cracking of the crystal is accompanied by widening or narrowing of the bands during one part of the observation and movement in the inverse direction during the other, or possibly by twisting for a whole revolution, and very frequently by merely jumping several bands, the appearance at the end being much the same as at the beginning. Such an observation is, of course, valueless, but the Abbe method would not detect this fact. Undoubtedly, the author's method, although very fatiguing, is the only one which is trustworthy when fragile substances are under investigation.

The counting of the bands was achieved precisely as described in the dilatometer memoir (p. 348) with the aid of the tape-puncturing recorder, the induction coil which illuminated the hydrogen Geissler tube being actuated at sufficiently rapidly succeeding intervals to enable the author to observe the passage of at least every quarter of a band. Timing the transit with the watch is an excellent aid, as, if the observation is trustworthy, there should be no sudden changes of rapidity in the movement of the bands. When the Fletcher ring-gas-burner below the double air-bath is first ignited, the bands move very slowly, the rapidity then growing with a regular increment until it reaches, in the case of large expansions where at least forty bands pass during the interval of  $45^{\circ}$  of temperature, a maximum of two bands per minute; the rapidity then as gradually diminishes until, with the attainment of constancy at the higher limit for that particular interval, the bands cease to move altogether. Moreover, if the temperature recorded by the inner bent thermometer, whose bulb is tied to and in contact with the platinum-iridium tripod, shows any slight tendency to descend a fraction of a degree, the bands should immediately begin to retrace their steps to a corresponding extent. No observation has been accepted during which these conditions were not fulfilled.

The temperature limits employed were respectively the ordinary temperature, obtained as low as possible by commencing work about 7 A.M., the neighbourhood of  $56^{\circ}$ , and that of  $96^{\circ}$ . The determinations of the positions at these temperatures, of the two bands nearest to the reference point, were made precisely as described in the previous memoir (p. 346). The monochromatic light employed throughout was red hydrogen light, corresponding to the C line of the solar and hydrogen spectrum, separated from all other radiations by a train of prisms in the manner described in the dilatometer memoir (pp. 322 and 342). The wave-length of this radiation employed in the calculations was 0.0006562 millim.

When adequate time for complete cooling had elapsed, after the second series of observations, the measurement of the thickness of the crystal and the length of the tripod screws was made, by means of the thickness measurer described on p. 337 of the former memoir. For this purpose the interference chamber was carefully raised out of the bath by means of the rackwork on the pedestal, and the tripod, together with the supported crystal and compensator, after cutting the thread binding the

thermometer to it and gently drawing the latter aside, was removed from the chamber and transferred to the thickness measurer. The greatest care was taken not to disturb the positions of the crystal and compensator on the table of the tripod. The large cover-glass (cover-wedge of the previous memoir) was too large to be taken through one of the windows of the chamber along with the tripod, so was left inside, being raised with the left hand while the tripod was removed with the right to the nearest resting place, the top of the air-bath; the cover-wedge was then turned over so as not to injure the silver reference ring and laid on the floor of the chamber. The tripod was then removed with both hands to such a position on the glass base of the thickness measurer that the agate pointed end of the measuring bar would fall exactly on the centre of the compensator, over which the silver reference ring of the cover-wedge had been situated during the observations. The height of the plane of the tops of the three tripod screws at this point was then first determined by laying on the screws a large circular disc of glass similar to the cover-wedge, and whose surfaces were truly plane and the thickness of which had previously been repeatedly determined at a position near the centre which was conveniently indicated by a small internal bubble. The disc was laid so that the bubble was over the centre of the compensator. The measurement was then made by lowering the counterpoised bar into gentle contact with the top of the disc and reading the scale with the aid of the micrometer. This height, *minus* the known thickness of the disc, gave the height of the plane of the tops of the screws. The disc was then removed and the bar lowered down upon the compensator, and the height again noted. The difference between this and the height of the screws gave the thickness of the air film. The bar was again raised and the compensator next removed, without disturbing the crystal, a matter requiring some nicety of manipulation with a pair of small ivory-tipped forceps; the bar was then allowed to fall gently on the crystal, when another measurement was taken. The difference of this and the last was of course the thickness of the compensator, as nearly as possible 5·250. It then only remained to once more raise the bar, remove the crystal, allow the bar to fall on to the table of the tripod, and take a final measurement of the height of this. The difference between this reading and the previous one afforded the measure of the thickness of the crystal. In cases where the three-point method was employed the only difference was to determine the mean height of the three particular table points used, with the aid of a small disc of glass, of known thickness at the centre, and placed on the same points, instead of determining the height of the surface of the table itself. The length of the screws was evidently afforded by subtracting from the height of the screws the height either of the table itself or of the points, according to the method of supporting the crystal employed.

The four desired basal quantities,  $L_c$  the thickness of the crystal,  $l_a$  the thickness of the compensator,  $l$  the length of the screws, and  $d$  the thickness of the air-film, were thus determined exactly along the vertical line passing through the centre of

reference of the interference band observations, and so any error due to minute lack of parallelism of the surfaces involved was obviated.

An example taken at random from the actual measurements will render the process quite clear. It refers to the fourth crystal of caesium sulphate along the direction of the morphological axis *b*.

	millims.	millims.
Height of top of glass disc . . . . .	40·857	
Known thickness of glass disc . . . . .	6·117	
Height of screws . . . . .	34·740	$d = 0·145$
„ top of compensator . . . . .	34·595	$l_a = 5·253$
„ „ crystal . . . . .	29·342	$L_{t_1} = 8·379$
„ „ tripod table . . . . .	20·963	$l = 13·777$

*The Nature of the Problem with reference to the Crystallographical Symmetry.*

The symmetry of the three salts under investigation being orthorhombic, the three axes of the thermal ellipsoid coincide in direction in each case with the crystallographical axes, just as do the axes of the optical ellipsoid already fully elucidated in a previous memoir. The amounts of thermal deformation along these three axial directions should not, from general considerations, be equal, as in crystals belonging to the cubic system, nor even would any two of them be likely to exhibit the same amount of expansion, as in the case of crystals exhibiting tetragonal or hexagonal symmetry. Orthorhombic symmetry requires that if a sphere of the substance of any one of these crystallised salts could be procured at any specific temperature, at any other temperature such sphere would have become converted into an ellipsoid with three unequal axes, and that these axes would coincide in direction with the three rectangular crystallographical axes. One of these morphological axes would thus be the direction of maximum expansion or contraction, another that of minimum and the remaining one that of intermediate deformation. The problem of the determination of the nature and amount of this thermal deformation consequently resolves itself into the determination of the amount of linear thermal expansion or contraction along the respective directions of the three morphological axes. From these fundamental data can be calculated the cubical expansion, in other words, the difference in volume between the sphere of unit radius and the deformation ellipsoid produced therefrom as the effect of change of temperature.

*The Determinations and Computations.*

The work has thus consisted in the determination of nine quantities, namely, the linear coefficients of thermal expansion or contraction along each of the three crystallographical axes of each of the three salts. It may be at once stated that in no case has contraction been observed, expansion in every direction having been found to be the invariable rule with regard to all three sulphates. Every one of the nine

quantities has been determined at least six independent times on three different crystals, and with respect to five of the quantities eight determinations have been made on four separate crystals. In all sixty-four independent determinations have been carried out, on different days, and using the twenty-nine different crystals of which the details have already been given (p. 465).

Each determination afforded, as already fully explained in connection with the determinations of the expansion of platinum-iridium and aluminium in the dilatometer memoir (*loc. cit.* p. 352), the two constants required for a complete statement of the thermal behaviour, namely, the constant  $a$ , the coefficient of expansion at  $0^\circ$ , and  $b$ , half the increment of the coefficient *per* degree of temperature, the coefficient not being a fixed quantity for all temperatures but varying regularly with the temperature. The coefficient of thermal expansion is signified by  $\alpha$ , and the expression for the actual coefficient at any temperature  $t$ , as also for the mean coefficient between any two temperatures whose mean is  $t$ , is :

$$\alpha = a + 2bt.$$

The mean coefficient of expansion between  $0^\circ$  and  $t^\circ$  is, however

$$a + bt.$$

The data afforded by observations of the positions of the interference bands at three adequately separated temperatures, and of the number of bands passing the reference point during the intervals between these temperatures, together with a knowledge of the original thicknesses of the block of crystal and of the aluminium compensator, and the length of the platinum-iridium screws projecting above the tripod table or its raised points, are ample to enable the two constants  $a$  and  $b$  to be calculated. For it is only necessary to insert respectively in three equations of the form

$$L_t = L_0 (1 + at + bt^2)$$

the known values of the three temperatures and the lengths (thicknesses) of the crystal block at those temperatures, and to solve the three equations thus provided, for the three unknown quantities  $L_0$ ,  $a$ , and  $b$ .

The solution of these equations furnishes expressions for the three required quantities of the forms

$$a = \frac{\theta}{L_0}, \quad b = \frac{\phi}{L_0}, \quad \text{and} \quad L_0 = L_{t_1} - \theta t_1 - \phi t_1^2,$$

in which  $\theta$  and  $\phi$  are terms involving the differences of the lengths,  $L_{t_1}$ ,  $L_{t_2}$ ,  $L_{t_3}$ , at the three temperatures  $t_1$ ,  $t_2$ , and  $t_3$ , and the sums and differences of those temperatures.

The actual expressions for  $\theta$  and  $\phi$  employed throughout the observations were :

$$\theta = \frac{(t_1 + t_3)(L_{t_3} - L_{t_1})}{(t_2 - t_1)(t_3 - t_2)} - \frac{(t_1 + t_2)(L_{t_3} - L_{t_1})}{(t_3 - t_1)(t_3 - t_2)},$$

$$\phi = \frac{L_{t_3} - L_{t_1}}{(t_3 - t_1)(t_3 - t_2)} - \frac{L_{t_2} - L_{t_1}}{(t_2 - t_1)(t_3 - t_2)}.$$

The results of the determinations of linear thermal expansion are presented in the next section in tabular form. Each table represents the results for one axial direction of a particular salt, and is divided into three portions. In the first portion is given the essential experimental data afforded by the observations and measurements.  $L_c$  is the measured thickness of the crystal block,  $l_c$  that of the compensator,  $l$  the length of the platinum-iridium screws, and  $d$  the thickness of the air-film, each measured in the manner described on p. 471. Next come the temperatures, and subsequently the corresponding barometric pressures. The next column contains  $f_2$ , the number of interference bands which effected their transit past the reference point during the interval between  $t_1$  and  $t_2$ . In the succeeding column is given the small correction to be applied to the number of bands, rendered necessary by the alteration in the wave-length of the monochromatic light employed, which accompanies the change in the refraction of air consequent on the considerable rise of temperature and possible alteration of pressure. The nature and amount of this correction were fully discussed in the previous memoir (*loc. cit.* p. 350), and the formula for it there given was invariably followed. The barometric pressures and  $d$  are essential terms of that formula. The corrected number of bands,  $f_2'$ , is given in the next column, and the three remaining columns contain  $f_3$ , the number of bands for the temperature interval between  $t_1$  and  $t_3$ , its correction, and  $f_3'$  the corrected number for that interval.

In the second portion are given, in the first two columns, the calculated values of the apparent expansion, obtained by multiplying the corrected number of bands by half the wave-length of the red C hydrogen light employed, 0.0003281 millim., according to the fundamental principle of the method; in the next six columns the calculated quantities involved in the correction to be applied to the apparent expansion for lack of compensation are recorded; and in the last two columns the actual expansion of the crystal obtained by use of the correction. For a fuller discussion of the principle of the method as touching the first two columns, the memoir concerning the dilatometer may be referred to; it need only be remarked here that the transit of each band past the reference spot corresponds to an alteration in the thickness of the air-film  $d$ , between the compensator and the cover-wedge at the position of the reference spot, equal to half a wave-length of the monochromatic light employed. The determination of the correction for non-compensation involves the calculation of the actual expansion of the platinum-iridium screws, which is given in the third and fourth columns for the two respective temperature-intervals, and of the aluminium compensator, which is given in the fifth and sixth columns. These values were calculated with the aid of the coefficients of linear expansion of the two metals, as previously determined with the greatest care by the author and published in the memoir concerning the dilatometer (pp. 356 and 360). The following were the actual expressions used,  $l$  and  $l_c$  being the values given in the fourth and third columns respectively of the first portion of the table

For the screws:  $l \left[ 10^{-9} \left( 8600 + 4.56 \frac{t_1 + t_2}{2} \right) \right] (t_2 - t_1)$  for the first interval, and similarly for the second interval, substituting  $t_3$  for  $t_2$ .

For the compensator:  $l_a \left[ 10^{-8} \left( 2204 + 2.12 \frac{t_1 + t_2}{2} \right) \right] (t_2 - t_1)$  for the first interval, and a like expression for the second interval with  $t_3$  substituted for  $t_2$ .

In each case the actual expansion of the metal is thus calculated by multiplying the length (thickness) of the metal by the mean coefficient of the linear expansion between the two temperatures, that is by  $a + 2bt$  for that metal where  $t$  is the mean of the limiting temperatures of the interval, namely  $\frac{1}{2}(t_1 + t_2)$  or  $\frac{1}{2}(t_1 + t_3)$ ; and also by the amount of the temperature interval, that is,  $t_2 - t_1$  or  $t_3 - t_1$ . Actually, of course, one uses  $b(t_1 + t_2)$  instead of  $2b \cdot \frac{1}{2}(t_1 + t_2)$ .

The differences between the amounts of expansion of the screws and the compensator are given in the next two columns headed "correction for non-compensation." The correction is obviously positive, given an expanding crystal, when the screws expand most, and negative when the compensator expands to the greater extent. For in the former case the effect is to increase the thickness of the air-film, and consequently the amount of diminution of the thickness of the air-film due to the expansion of the crystal is not fully evident, the actually observed amount being less than that really effected by the expanding crystal by the amount of this excess of expansion on the part of the screws. This latter amount should, therefore, be added. The inverse is the case when the excess is on the part of the compensator; causing, as it does, additional diminution of the thickness of the air-film, it should be subtracted. The values given in the last two columns, representing the actual expansions of the crystal during the two intervals of temperature,  $L_{t_2} - L_{t_1}$  and  $L_{t_3} - L_{t_1}$ , were obtained by applying the correction for non-compensation, in the sense just indicated, to the apparent expansions  $f_2'\lambda/2$  and  $f_3'\lambda/2$ .

In the last portion of the table are given the calculated values of  $\theta$ ,  $\phi$ , and  $L_0$ , and of the two required constants of the coefficient of linear expansion,  $a$ , the coefficient at  $0^\circ$  and  $b$ , half the increment of the coefficient *per* degree of temperature. In the last column are given the values of the coefficient of linear expansion,  $\alpha$ , for  $50^\circ$ , calculated by means of the formula  $\alpha = a + 2bt$ . FIZEAU invariably gave the coefficient at  $40^\circ$ , a specific temperature in the neighbourhood of the mean of the extreme limits employed by him, in addition to  $a$  and  $b$ . As  $50^\circ$  is nearer the mean of the author's limiting temperatures, this specific temperature has been chosen in preference, for which to record a particular calculated value of  $\alpha$ .

### THE RESULTS.

In the following tables are presented the results of the determinations and calculations.

*Potassium Sulphate, Direction of Axis  $\alpha$ .*

Experimental Data.

Crystal.	$L_{t_1}$	$l_a$	$l$	$d$	$t_1$	$t_2$	$t_3$	$b_1$	$b_2$	$b_3$	$f_2$	Corrn.	$f'_2$	$f_3$	Corrn.	$f'_3$
	millims.	millims.	millims.	millims.	°	°	°	millims.	millims.	millims.						
1	10.355	5.237	15.786	0.194	17.2	56.4	96.6	766.5	765.0	763.5	43.90	-0.02	43.88	90.42	-0.04	90.38
2	7.834	5.250	13.337	0.253	11.6	56.5	96.6	752.4	752.6	752.9	39.98	-0.03	39.95	77.32	-0.05	77.27
3	8.814	5.254	14.223	0.155	13.2	56.7	96.8	753.0	754.0	755.0	43.36	-0.02	43.34	84.36	-0.03	84.33
4	6.568	5.248	12.055	0.239	15.8	58.1	97.5	760.2	760.1	760.0	33.10	-0.03	33.07	65.10	-0.05	65.05

Calculated Actual Expansions.

Diminution of thickness of air-layer.		Expansion of tripod screws.		Expansion of aluminium compensator.		Correction for non-compensation.		Expansion of crystal.	
$f'_2 \lambda/2$	$f'_3 \lambda/2$	1st interval.	2nd interval.	1st interval.	2nd interval.	1st interval.	2nd interval.	$L_{t_2} - L_{t_1}$	$L_{t_3} - L_{t_1}$
{ 0.0143970	{ 0.0296540	0.0054256	0.0110887	0.0046848	0.0096523	+ 0.0007408	+ 0.0014364	0.0151378	0.0310904
{ 0.131078	{ 0.253525	0.0052430	0.100291	0.0053656	0.103471	- 0.001226	- 0.0003180	-0.129852	-0.250345
{ 0.130945	{ 0.252046	0.0054194	0.105240	0.0052065	0.101930	+ 0.002129	+ 0.0003310	-0.144329	-0.279998
{ 0.142200	{ 0.276688	0.0056953	0.105085	0.0054731	0.101756	+ 0.002222	+ 0.0003950	-0.102553	-0.201031
{ 0.148892	{ 0.276720	0.0044714	0.087245	0.0099646	0.099646	- 0.0006125	- 0.0012567	-0.107334	-0.206113
{ 0.113459	{ 0.218680	0.0046353	0.088967	0.0052478	0.101534	- 0.0006125	- 0.0012567	-0.107334	-0.206113

Calculated Coefficients of Linear Expansion.

$\theta$	$\phi$	$L_0$	$\alpha$	$\beta$	$\alpha_{50^\circ}$
{ 0.000 375 23	{ 0.000 000 148 5	10.3485	0.000 036 26	0.000 000 014 4	0.000 037 70
{ 0.000 280 17	{ 0.000 000 132 7	7.8307	0.000 035 78	0.000 000 016 9	0.000 037 47
{ 0.000 326 32	{ 0.000 000 078 1	8.8097	0.000 037 04	0.000 000 008 9	0.000 037 93
{ 0.000 235 66	{ 0.000 000 091 8	6.5643	0.000 035 90	0.000 000 014 0	0.000 037 30
Mean values . . . . .					0.000 000 014 4
					0.000 037 60

Potassium Sulphate, Direction of Axis *b*.

Experimental Data.

Crystal.	$L_4$ .	$l_4$ .	$d$ .	$t_1$ .	$t_2$ .	$t_3$ .	$b_1$ .	$b_2$ .	$b_3$ .	$f_2$ .	Corrn.	$f_2'$ .	$f_3$ .	Corrn.	$f_3'$ .
	millims.	millims.	millims.	°	°	°	millims.	millims.	millims.						
1	5.392	5.250	0.111	12.3	56.9	95.7	753.8	753.9	754.0	27.81	-0.01	27.80	53.02	-0.02	53.00
				13.1	56.9	95.9	754.7	754.8	754.9	27.28	-0.01	27.27	52.70	-0.02	52.68
2	5.931	5.253	0.138	8.5	57.0	96.2	764.8	764.7	764.6	31.69	-0.02	31.67	58.74	-0.03	58.71
				8.7	57.3	96.4	763.9	763.7	763.5	31.94	-0.02	31.92	58.77	-0.03	58.74
3	5.103	5.255	0.156	12.4	57.8	95.9	757.2	756.6	756.0	27.17	-0.02	27.15	50.87	-0.03	50.84
				12.7	57.1	95.9	747.0	746.0	745.0	26.52	-0.02	26.50	50.72	-0.03	50.69
4	5.210	5.250	0.143	10.0	57.6	96.0	735.0	734.5	734.0	29.57	-0.02	29.55	54.50	-0.03	54.47
				9.8	56.3	95.3	731.0	730.5	730.0	28.62	-0.02	28.60	53.53	-0.03	53.50

Calculated Actual Expansions.

$f_2' \lambda/2$ .	Diminution of thickness of air-layer.		Expansion of tripod screws.		Expansion of aluminium compensator.		Correction for non-compensation.		Expansion of crystal.	
	$f_3' \lambda/2$ .	$f_3' \lambda/2$ .	1st interval.	2nd interval.	1st interval.	2nd interval.	1st interval.	2nd interval.	$L_3 - L_{t_1}$ .	$L_3 - L_{t_1}$ .
{ 0.0091212	{ 0.0173896	{ 0.0173896	0.0042001	0.0079334	0.0053325	0.0101517	-0.0011324	-0.0022183	0.0079888	0.0151713
{ 0.0089475	{ 0.0172846	{ 0.0172846	0.048043	0.087763	0.057920	0.106650	-0.009877	-0.018887	0.094034	0.173741
{ 0.0103911	{ 0.0192628	{ 0.0192628	0.048149	0.087771	0.058055	0.106669	-0.009906	-0.018898	0.094824	0.173828
{ 0.0104730	{ 0.0192726	{ 0.0192726	0.041816	0.077669	0.054358	0.101747	-0.012542	-0.024078	0.076538	0.142731
{ 0.0089080	{ 0.0166809	{ 0.0166809	0.040889	0.077396	0.053150	0.101393	-0.012261	-0.023997	0.074687	0.142317
{ 0.0086948	{ 0.0166314	{ 0.0166314	0.044182	0.080625	0.056871	0.104585	-0.012689	-0.023960	0.084266	0.154759
{ 0.0096955	{ 0.0178719	{ 0.0178719	0.043144	0.080136	0.055516	0.103935	-0.012372	-0.023799	0.081466	0.151734

Calculated Coefficients of Linear Expansion.

$\theta$ .	$\phi$ .	$L_{60}$ .	$a$ .	$b$ .	$\alpha_{50^\circ}$ .
{ 0.000 174 15	{ 0.000 000 071 7	{ 5.3898	{ 0.000 032 31	{ 0.000 000 013 3	{ 0.000 033 64
{ 0.000 173 02	{ 0.000 000 083 5	{ 5.3897	{ 0.000 032 10	{ 0.000 000 015 5	{ 0.000 033 65
{ 0.000 186 83	{ 0.000 000 107 7	{ 5.9294	{ 0.000 031 51	{ 0.000 000 018 2	{ 0.000 033 33
{ 0.000 189 89	{ 0.000 000 079 2	{ 5.9293	{ 0.000 032 03	{ 0.000 000 013 4	{ 0.000 033 37
{ 0.000 164 25	{ 0.000 000 061 6	{ 5.1010	{ 0.000 032 20	{ 0.000 000 012 1	{ 0.000 033 41
{ 0.000 163 11	{ 0.000 000 073 2	{ 5.1009	{ 0.000 031 98	{ 0.000 000 014 4	{ 0.000 033 42
{ 0.000 171 87	{ 0.000 000 076 2	{ 5.2083	{ 0.000 032 99	{ 0.000 000 014 6	{ 0.000 034 45
{ 0.000 171 36	{ 0.000 000 058 1	{ 5.2083	{ 0.000 032 90	{ 0.000 000 011 2	{ 0.000 034 02
Mean values . . . . .					0.000 033 66



*Potassium Sulphate, Direction of Axis c.*  
Experimental Data.

Crystal.	$L_{t_1}$	$l_{t_1}$	$d$	$t_1$	$t_2$	$t_3$	$b_1$	$b_2$	$b_3$	$f_2$	Corrn.	$f_2'$	$f_3$	Corrn.	$f_3'$
	millims.	millims.	millims.	°	°	°	millims.	millims.	millims.						
1	6.871	5.251	0.182	12.8	57.1	96.6	735.1	736.3	737.6	38.00	-0.02	37.98	75.24	-0.04	75.20
				9.0	56.1	96.6	740.4	740.3	740.2	40.28	-0.02	40.26	78.28	-0.04	78.24
2	6.537	5.254	0.046	14.3	57.7	96.8	766.0	766.5	767.0	36.29	0.00	36.29	71.84	-0.01	71.83
				13.5	56.6	96.8	767.4	767.7	768.0	35.97	0.00	35.97	72.45	-0.01	72.44
3	9.642	5.250	0.131	13.3	57.7	97.3	761.9	762.5	763.1	49.16	-0.02	49.14	97.31	-0.03	97.28
				13.0	57.1	96.6	764.7	765.3	765.9	48.96	-0.02	48.94	96.96	-0.03	96.93

Calculated Actual Expansions.

Diminution of thickness of air-layer.	Expansion of tripod screws.		Expansion of aluminium compensator.		Correction for non-compensation.		Expansion of crystal.	
	$f_2' \lambda / 2$		$f_3' \lambda / 2$		2nd interval.		$L_{t_3} - L_{t_1}$	
	1st interval.	2nd interval.	1st interval.	2nd interval.	1st interval.	2nd interval.	$L_{t_3} - L_{t_1}$	$L_{t_3} - L_{t_1}$
{ 0.0124615	0.0047744	0.0091243	0.0052992	0.0102087	-0.0005248	-0.0010844	0.0119367	0.0235890
{ 0.0132093	0.0050699	0.0095288	0.0056216	0.0106527	-0.0005517	-0.0011239	-0.0126576	-0.0245469
{ 0.0119069	0.0045024	0.0086457	0.0051996	0.0100638	-0.0006972	-0.0014181	-0.0112097	-0.0221498
{ 0.0118019	0.0044690	0.0087279	0.0051592	0.0101578	-0.0006902	-0.0014299	-0.0111117	-0.0223380
{ 0.0161232	0.0058444	0.0111709	0.0053130	0.0102365	+0.0005314	+0.0009344	-0.0166546	-0.0328520
{ 0.0160572	0.0058035	0.0111150	0.0052748	0.0101836	+0.0005287	+0.0009314	-0.0165859	-0.0327345

Calculated Coefficients of Linear Expansion.

$\theta$	$\phi$	$L_{t_0}$	$a$	$b$	$\alpha_{50}^\circ$
{ 0.000 248 14	0.000 000 304 9	6.8678	0.000 036 13	0.000 000 044 4	0.000 040 57
{ 0.000 250 28	0.000 000 283 5	6.8687	0.000 036 44	0.000 000 041 3	-0.000 040 57
{ 0.000 239 50	0.000 000 260 9	6.5335	0.000 036 66	0.000 000 039 9	-0.000 040 65
{ 0.000 239 77	0.000 000 257 4	6.5337	0.000 036 70	0.000 000 039 4	-0.000 040 64
{ 0.000 346 44	0.000 000 403 8	9.6373	0.000 035 95	0.000 000 041 9	-0.000 040 14
{ 0.000 348 64	0.000 000 391 5	9.6374	0.000 036 18	0.000 000 040 6	-0.000 040 24
Mean values . . . . .					0.000 040 47

*Rubidium Sulphate, Direction of Axis a.*

Experimental Data.

Crystal.	$L_{a_1}$ millims.	$l$ millims.	$d$ millims.	$t_1$ °	$t_2$ °	$t_3$ °	$b_1$ millims.	$b_2$ millims.	$b_3$ millims.	$f_2$	Corrn.	$f'_2$	$f_3$	Corrn.	$f'_3$
1	7.824	13.751	0.674	13.0	56.3	97.3	749.0	749.4	749.8	39.24	-0.09	39.15	78.24	-0.16	78.08
	9.217	14.722	0.253	12.9	56.2	97.4	752.2	752.7	753.1	39.15	-0.09	39.06	78.33	-0.16	78.17
				17.7	56.9	96.4	758.6	758.9	759.2	40.48	-0.03	40.45	83.06	-0.05	83.01
2	5.252	14.722	0.253	17.9	56.6	96.0	757.4	757.6	757.8	40.55	-0.03	40.52	84.13	-0.05	84.08
				13.1	56.8	96.1	759.0	758.9	758.8	47.58	-0.02	47.56	92.26	-0.03	92.23
3	9.918	15.306	0.155	12.3	57.0	95.7	757.9	757.5	757.3	48.66	-0.02	48.64	92.68	-0.03	92.65

Calculated Actual Expansions.

Diminution of thickness of air-layer.	Expansion of tripod screws.		Expansion of aluminium compensator.		Correction for non-compensation.		Expansion of crystal.	
	$f'_2 \lambda/2$	$f'_3 \lambda/2$	1st interval.	2nd interval.	1st interval.	2nd interval.	1st interval.	2nd interval.
{	0.0128450	0.0256180	0.0052147	0.0102610	0.0051804	0.0102780	+ 0.0000343	- 0.0000170
	0.0128160	0.0257000	0.0052264	0.0103010	0.0051916	0.0103140	+ 0.0000348	- 0.0000130
	0.0132718	0.0272358	0.0050613	0.0102655	0.0047003	0.0096093	+ 0.0003610	+ 0.0006562
	0.0132947	0.0275867	0.0049966	0.0101869	0.0046402	0.0095354	+ 0.0003564	+ 0.0006515
	0.0156045	0.0302608	0.0058615	0.0112417	0.0052319	0.0101144	+ 0.0006296	+ 0.0011273
0.0159588	0.0304089	0.0059920	0.0112925	0.0053479	0.0101137	+ 0.0006441	+ 0.0011788	

Calculated Coefficients of Linear Expansion.

$e$	$\phi$	$L_0$	$a$	$b$	$a_{50^\circ}$
{	0.000 286 84	0.000 000 152 9	7.8202	0.000 036 68	0.000 000 019 6
	0.000 283 48	0.000 000 182 6	7.8203	0.000 036 25	0.000 000 023 4
	0.000 335 23	0.000 000 168 2	9.2110	0.000 036 39	0.000 000 018 3
	0.000 336 04	0.000 000 224 0	9.2109	0.000 036 48	0.000 000 024 3
	0.000 359 60	0.000 000 170 0	9.9133	0.000 036 27	0.000 000 017 1
0.000 358 31	0.000 000 189 3	9.9136	0.000 036 14	0.000 000 019 1	
Mean values . . . . .					
0.000 000 020 3					
0.000 038 40					

*Rubidium Sulphate, Direction of Axis b.*

Experimental Data.

Crystal.	$L_{t_1}$ millims.	$l_{a_0}$ millims.	$l$ millims.	$d$ millims.	$t_1$ °	$t_2$ °	$t_3$ °	$b_1$ millims.	$b_2$ millims.	$b_3$ millims.	$f_2$	Corrn.	$f'_2$	$f_3$	Corrn.	$f'_3$
1	6.324	5.255	11.756	0.177	13.0 12.5	56.7 56.6	96.6 96.4	763.1 764.2	763.4 764.4	763.6 764.6	30.62 30.18	-0.02 -0.02	30.60 30.16	60.10 58.94	-0.04 -0.04	60.06 58.90
2	7.697	5.250	13.050	0.103	14.9 15.1	58.4 57.2	96.4 96.3	753.5 757.7	753.3 758.5	753.1 759.3	35.33 33.85	-0.01 -0.01	35.32 33.84	68.51 66.66	-0.02 -0.02	68.49 66.64
3	8.027	5.255	13.398	0.116	13.9 13.7	57.4 57.3	97.9 96.8	762.0 760.0	761.7 759.7	761.3 759.3	35.54 35.97	-0.01 -0.01	35.53 35.96	70.13 69.88	-0.02 -0.02	70.11 69.86

Calculated Actual Expansions.

Diminution of thickness of air layer.		Expansion of tripod screws.		Expansion of aluminium compensator.		Correction for non-compensation.		Expansion of crystal.	
$f'_2 \lambda/2$	$f'_3 \lambda/2$	1st interval.	2nd interval.	1st interval.	2nd interval.	1st interval.	2nd interval.	$L_{t_2} - L_{t_1}$	$L_{t_3} - L_{t_1}$
{ 0.0100399	0.0197061	0.0044998	0.0086978	0.0052309	0.0101932	-0.0007311	-0.014954	0.0093088	0.0182107
{ .0098956	.0193255	.0045403	.0087273	.0052773	.0102261	.0007370	.014988	.0091586	.0178267
{ .0115886	.0224719	.0049746	.0094167	.0052109	.0099353	.0002363	.005186	.0113523	.0219533
{ .0111030	.0218650	.0048154	.0093823	.0050407	.0098992	.0002253	.005169	.0108777	.0213481
{ .0116576	.0230033	.0051069	.0099655	.0052110	.0102520	.0001041	.002865	.0115535	.0227168
{ .0117986	.0229213	.0051184	.0098555	.0052223	.0101358	.0001039	.002803	.0116947	.0226410

Calculated Coefficients of Linear Expansion.

$\theta$	$\phi$	$L_0$	$a$	$b$	$\alpha_{50^\circ}$
{ 0.000 204 61	0.000 000 120 7	6.3213	0.000 032 37	0.000 000 019 1	0.000 034 28
{ .000 199 35	.000 000 120 5	.6.3215	.000 031 54	.000 000 019 1	.000 033 45
{ .000 244 79	.000 000 220 9	7.6933	.000 031 82	.000 000 028 7	.000 034 69
{ .000 250 02	.000 000 115 7	7.6932	.000 032 50	.000 000 015 0	.000 034 00
{ .000 257 06	.000 000 120 3	8.0234	.000 032 04	.000 000 015 0	.000 033 54
{ .000 260 61	.000 000 107 1	8.0234	.000 032 56	.000 000 013 3	.000 033 89
Mean values . . . . .					0.000 033 98

*Rubidium Sulphate, Direction of Axis c.*  
Experimental Data.

Crystal.	$L_{t_1}$ .	$l_a$ .	$l$ .	$d$ .	$t_1$ .	$t_2$ .	$t_3$ .	$b_1$ .	$b_2$ .	$b_3$ .	$f_2$ .	Corrn.	$f_2'$ .	$f_3$ .	Corrn.	$f_3'$ .
	millims.	millims.	millims.	millims.	°	°	°	millims.	millims.	millims.						
1	8.638	5.250	14.153	0.265	12.9	56.6	96.2	755.8	755.9	756.0	42.25	-0.03	42.22	84.35	-0.05	84.30
					12.7	56.4	95.6	757.0	757.2	757.4	42.34	-0.03	42.31	83.70	-0.05	83.65
2	6.797	5.247	12.169	0.125	14.9	57.2	96.1	755.4	755.5	755.6	34.38	-0.02	34.36	68.90	-0.03	68.87
					13.4	55.7	96.4	756.1	756.3	756.5	34.26	-0.02	34.24	70.19	-0.03	70.16
3	10.490	5.250	15.877	0.137	11.1	56.7	96.0	737.5	735.9	734.3	51.68	-0.02	51.66	100.18	-0.03	100.15
					11.0	56.7	95.8	732.1	731.7	731.4	51.65	-0.02	51.63	99.77	-0.03	99.74

Calculated Actual Expansions.

$f_2' \lambda/2$ .	Diminution of thickness of air-layer.		Expansion of tripod screws.		Expansion of aluminium compensator.		Correction for non-compensation.		Expansion of crystal.	
	$f_3' \lambda/2$ .		1st interval.	2nd interval.	1st interval.	2nd interval.	1st interval.	2nd interval.	$L_{t_2} - L_{t_1}$ .	$L_{t_3} - L_{t_1}$ .
{ 0.0138526	{ 0.0276592	{ 0.0054170	0.0104323	0.0052256	0.0101443	+ 0.0001914	+ 0.0002880	+ 0.0004440	0.0140440	0.0279472
{ 0.0112735	{ 0.0225964	{ 0.0045114	0.0087480	0.050613	0.098919	-0.005499	-0.011439	-0.107236	-0.214525	
{ 0.0112342	{ 0.0230197	{ 0.0045079	0.0089390	0.050542	0.101053	-0.003463	-0.011663	-0.106879	-0.218534	
{ 0.0169496	{ 0.0328594	{ 0.0063383	0.119217	0.054484	0.103298	-0.008899	+ 0.015919	-0.178395	-0.344513	
{ 0.0169399	{ 0.0327250	{ 0.0063521	0.119067	0.054602	0.103162	-0.008919	+ 0.015905	-0.178318	-0.3443155	

Calculated Coefficients of Linear Expansion.

$\theta$ .	$\phi$ .	$L_0$ .	$a$ .	$b$ .	$\alpha_{50^\circ}$ .
{ 0.000 296 58	0.000 000 356 7	8.6341	0.000 034 35	0.000 000 041 3	0.000 038 48
{ 0.000 300 02	-0.000 000 318 7	8.6341	-0.000 034 75	-0.000 000 036 9	-0.000 038 44
{ 0.000 233 71	-0.000 000 274 6	6.7935	-0.000 034 40	-0.000 000 040 4	-0.000 038 44
{ 0.000 234 63	-0.000 000 261 1	6.7938	-0.000 034 54	-0.000 000 038 4	-0.000 038 38
{ 0.000 366 08	-0.000 000 370 8	10.4859	-0.000 034 91	-0.000 000 035 4	-0.000 038 45
{ 0.000 365 14	-0.000 000 370 0	10.4859	-0.000 034 82	-0.000 000 035 3	-0.000 038 35
Mean values . . . . .			0.000 034 63	0.000 000 038 0	0.000 038 43

*Cæsium Sulphate, Direction of Axis a.*  
Experimental Data.

Crystal.	$L_t$ .	$l_a$ .	$l$ .	$d$ .	$t_1$ .	$t_2$ .	$t_3$ .	$b_1$ .	$b_2$ .	$b_3$ .	$f_2$ .	Corrn.	$f_2'$ .	$f_3$ .	Corrn.	$f_3'$ .
1	5.864	3.879	10.271	0.528	12.8	56.3	95.1	756.0	754.0	752.6	26.69	-0.07	26.62	52.38	-0.12	52.26
	5.792*	3.907†	10.779	1.080	14.6	55.9	94.2	754.8	754.6	754.5	24.52	-0.14	24.38	48.88	-0.24	48.64
2	10.737	5.249	16.230	0.244	19.6	56.5	95.6	752.0	751.8	751.7	40.50	-0.03	40.47	85.35	-0.05	85.30
	8.277	5.254	13.851	0.320	18.0	56.3	96.1	755.0	755.6	756.2	41.65	-0.03	41.62	85.65	-0.05	85.60
3	8.324	5.252	13.783	0.207	18.5	57.1	96.3	761.8	762.0	762.0	34.64	-0.04	34.60	71.58	-0.07	71.51
					12.4	57.0	95.9	747.2	746.0	745.0	40.66	-0.02	40.64	77.99	-0.04	77.95
4					10.9	56.1	95.6	736.5	735.0	733.5	40.98	-0.02	40.96	78.65	-0.04	78.61

Calculated Actual Expansions.

Diminution of thickness of air layer.	Expansion of tripod screws.		Expansion of aluminium compensator.		Correction for non-compensation.		Expansion of crystal.	
	$f_2' \lambda / 2$ .	$f_3' \lambda / 2$ .	1st interval.	2nd interval.	1st interval.	2nd interval.	$L_{t_2} - L_{t_1}$ .	$L_{t_3} - L_{t_1}$ .
{ 0.0087341	0.0171470	0.0039128	0.0074776	0.0074013	+ 0.0000703	+ 0.0000763	0.0088044	0.0172233
	-0.079991	-0.039000	-0.075917	-0.072129	+ 0.002331	+ 0.003788	-0.082222	-0.163378
{ 0.132780	-0.279870	-0.052544	-0.109320	-0.092794	+ 0.008291	+ 0.016526	-0.141071	-0.296396
	-0.136555	-0.055095	-0.111885	-0.094960	+ 0.008702	+ 0.016925	-0.145257	-0.297779
{ 0.113230	-0.236004	-0.046521	-0.095719	-0.095273	+ 0.000584	+ 0.000446	-0.113814	-0.236450
	-0.113525	-0.046902	-0.095495	-0.095065	+ 0.000579	+ 0.000430	-0.114104	-0.235058
{ 0.133340	-0.255759	-0.053837	-0.101817	-0.101688	+ 0.000488	+ 0.000129	-0.133828	-0.255888
	-0.134389	-0.054529	-0.103231	-0.103065	+ 0.000523	+ 0.000166	-0.134912	-0.258089

Calculated Coefficients of Linear Expansion.

$\theta$ .	$\phi$ .		$L_0$ .		$a$ .	$b$ .	$\alpha_{50^\circ}$ .
	1st interval.	2nd interval.	1st interval.	2nd interval.			
{ 0.000 190 15	0.000 000 177 2	0.007 477 6	5.8615	0.007 401 3	0.000 032 44	0.000 000 030 2	0.000 035 46
	-0.000 187 74	-0.039 000	5.7892	-0.072 12 9	-0.000 032 43	-0.000 000 027 8	-0.000 035 21
{ 0.000 367 34	-0.000 000 196 6	-0.052 54 4	10.7297	-0.092 79 4	-0.000 034 24	-0.000 000 018 3	-0.000 036 07
	-0.000 361 09	-0.055 09 5	10.7303	-0.094 96 0	-0.000 033 65	-0.000 000 017 6	-0.000 035 41
{ 0.000 285 97	-0.000 000 150 6	-0.046 52 1	8.2718	-0.095 27 3	-0.000 034 57	-0.000 000 018 2	-0.000 036 39
	-0.000 283 02	-0.046 90 2	8.2717	-0.095 06 5	-0.000 034 22	-0.000 000 020 1	-0.000 036 23
{ 0.000 288 68	-0.000 000 164 1	-0.053 83 7	8.3204	-0.101 68 8	-0.000 034 69	-0.000 000 019 7	-0.000 036 66
	-0.000 287 91	-0.054 52 9	8.3208	-0.103 06 5	-0.000 034 60	-0.000 000 019 0	-0.000 036 50
Mean values . . . . .							
0.000 000 021 4							

\* Crystal surfaces were ground for second observation; natural faces were used in first. † Different compensator.

*Cæsium Sulphate, Direction of Axis b.*  
Experimental Data.

Crystal.	$L_t$ , millims.	$l_a$ , millims.	$l$ , millims.	$d$ , millims.	$t_1$ , °	$t_2$ , °	$t_3$ , °	$b_s$ , millims.			$f_2$	Corrn.	$f'_2$	$f_3$	Corrn.	$f'_3$
								$b_1$	$b_2$	$b_3$						
1	8.218	5.255	13.672	0.199	21.0	56.6	95.9	762.0	761.0	760.0	30.00	-0.02	29.98	64.27	-0.04	64.23
					22.0	57.2	95.6	760.2	760.1	760.0	29.81	-0.02	29.79	63.30	-0.04	63.26
2	8.003	5.252	13.489	0.234	20.9	57.3	97.5	758.6	757.9	757.2	29.73	-0.03	29.70	64.53	-0.05	64.48
					20.4	56.7	95.5	755.2	754.8	754.4	30.14	-0.03	30.11	63.64	-0.05	63.59
3	8.348	5.261	13.903	0.294	20.4	56.0	95.4	754.8	754.6	754.4	29.53	-0.04	29.49	64.73	-0.06	64.67
					19.5	56.6	94.8	756.0	755.8	755.5	30.81	-0.04	30.77	64.20	-0.06	64.14
4	8.379	5.253	13.777	0.145	8.8	56.3	96.3	745.0	744.0	743.0	40.49	-0.02	40.47	76.17	-0.03	76.14
					12.4	56.7	96.4	741.0	740.0	739.0	37.10	-0.02	37.08	72.10	-0.03	72.07

Calculated Actual Expansions.

Diminution of thickness of air-layer.		Expansion of tripod screws.		Expansion of aluminium compensator.		Correction for non-compensation.		Expansion of crystal.	
$f'_2 \lambda/2$	$f'_3 \lambda/2$	1st interval.		2nd interval.		1st interval.		2nd interval.	
		{	0.0098365	0.0042719	0.0090795	0.0042771	0.0091625	-0.0000052	-0.0000830
.0042256	.0089236			.0042320	.0090066	-0.000064	-0.000830	.0097678	.0206730
{	0.0097742	0.0043101	0.0091649	0.0043719	0.0093715	-0.0000618	-0.002066	0.0096829	0.0209497
		.0042971	.0089797	.0043576	.0091778	-0.000605	-0.001981	.0098187	.0206660
{	0.0098792	0.0043428	0.0092427	0.0042797	0.0091806	-0.0000631	-0.000621	0.0097387	0.0212804
		.0045253	.0092762	.0045793	.0092115	-0.0000660	-0.000647	.0101618	.0211093
{	0.0100958	0.0057249	0.0106559	0.0056715	0.0108427	-0.0000534	-0.000132	0.0133316	0.0249948
		.0053448	.0102395	.0052992	.0102341	-0.0000456	-0.000054	.0122117	.0236515

Calculated Coefficients of Linear Expansion.

$\theta$	$\phi$	$L_0$	$a$	$b$	$\alpha_{50^\circ}$	
						{
{	.000 000 088 1	8.2120	.000 032 94	.000 000 010 7	.000 034 01	
{	.000 000 186 0	7.9977	.000 031 44	.000 000 023 3	.000 033 77	
{	.000 000 121 1	7.9976	.000 032 65	.000 000 015 1	.000 034 16	
{	.000 000 258 5	8.3427	.000 030 42	.000 000 031 0	.000 033 52	
{	.000 000 168 2	8.3428	.000 031 30	.000 000 020 2	.000 033 32	
{	.000 000 124 6	8.3765	.000 032 54	.000 000 014 9	.000 034 03	
{	.000 000 148 6	8.3757	.000 031 69	.000 000 017 7	.000 033 46	
Mean values . . . . .					0.000 000 018 2	0.000 033 77

*Cæsium Sulphate, Direction of Axis c.*  
Experimental Data.

Crystal.	$L_{c_1}$ millims.	$l_a$ millims.	$l$ millims.	$d$ millims.	$t_1$ °	$t_2$ °	$t_3$ °	$b_1$ millims.	$b_2$ millims.	$b_3$ millims.	$f_2$	Corrn.	$f_2'$	$f_3$	Corrn.	$f_3'$
1	5.883	3.879	10.604	0.842	13.0	56.4	96.0	751.4	752.5	753.0	30.07	-0.11	29.96	60.63	-0.19	60.44
					12.9	56.5	96.0	758.5	757.5	757.0	30.21	-0.12	30.09	60.73	-0.20	60.53
2	5.122	3.879	10.165	1.164	9.5	56.0	95.4	760.5	759.0	758.0	28.10	-0.17	27.93	54.10	-0.28	53.82
					10.3	56.5	95.9	762.0	762.4	762.8	28.01	-0.17	27.84	53.90	-0.28	53.62
3	4.816	3.879	10.566	1.870	14.8	56.0	95.3	753.1	753.1	753.0	23.33	-0.24	23.09	47.42	-0.42	47.00
					15.9	56.2	96.0	752.9	752.4	751.9	22.57	-0.23	22.34	47.22	-0.41	46.81
4	6.712	5.256	12.085	0.117	9.5	56.8	95.9	768.0	768.1	768.1	38.93	-0.01	38.92	73.81	-0.02	73.79
					9.6	56.1	96.4	768.3	768.4	768.5	38.15	-0.01	38.14	74.09	-0.02	74.07

Calculated Actual Expansions.

Diminution of thickness of air-layer.	$f_3' \lambda/2$	Expansion of tripod screws.		Expansion of aluminium compensator.		Correction for non-compensation.		Expansion of crystal.	
		1st interval.	2nd interval.	1st interval.	2nd interval.	1st interval.	2nd interval.	$L_{c_2} - L_{c_1}$	$L_{c_3} - L_{c_1}$
{	0.0098299	0.0040306	0.0077879	0.0038343	0.0074678	+0.0001963	+0.0003201	0.0100262	0.0201501
	.0098726	.0040492	.0077970	.0038520	.0074765	.0001972	.0003205	.0100698	.0201805
{	.0091639	.0041355	.0077181	.0041006	.0077144	.0000349	.0000037	.0091988	.0176617
	.0091344	.0041103	.0076938	.0040766	.0076920	.0000337	.0000018	.0091681	.0175948
{	.0075758	.0038140	.0075284	.0036422	.0072467	.0001718	.0002817	.0077476	.0157027
	.0073303	.0037320	.0074943	.0035648	.0072164	.0001672	.0002779	.0074975	.0156369
{	.0127697	.0050024	.0092306	.0056542	.0105160	.0006518	.0012854	.0121179	.0229255
	.0125138	.0049170	.0092749	.0055567	.0105679	.0006397	.0012930	.0118741	.0230094

Calculated Coefficients of Linear Expansion.

$e$	$\phi$	$L_0$	$a$	$b$	$\alpha_{30^\circ}$
{	0.000 210 43	5.8802	0.000 035 79	0.000 000 050 5	0.000 040 84
	.000 210 07	.5.8802	.000 035 73	.000 000 051 2	.000 040 85
{	.000 184 89	5.1202	.000 036 11	.000 000 038 6	.000 039 97
	.000 186 39	.5.1201	.000 036 40	.000 000 035 2	.000 039 92
{	.000 175 42	4.8134	.000 036 44	.000 000 037 1	.000 040 15
	.000 169 41	.4.8132	.000 035 20	.000 000 047 9	.000 039 99
{	.000 240 69	6.7097	.000 035 87	.000 000 034 9	.000 039 36
	.000 239 49	.6.7097	.000 035 69	.000 000 036 0	.000 039 29
Mean values . . . . .					0.000 040 04

## SUMMARY OF THE RESULTS FOR THE LINEAR COEFFICIENTS OF EXPANSION.

Collating the mean values given at the foot of each of the foregoing tables, the following is a statement of the essential results of the work as regards the linear coefficients.

MEAN Coefficients of Linear Expansion,  $a + bt$ , between  $0^\circ$  and  $t^\circ$ .

*Potassium Sulphate.*

For the direction of the axis	$a$	. . .	$0\cdot000\ 036\ 16 + 0\cdot000\ 000\ 014\ 4t.$
„	„	$b$	. . . $0\cdot000\ 032\ 25 + 0\cdot000\ 000\ 014\ 1t.$
„	„	$c$	. . . $0\cdot000\ 036\ 34 + 0\cdot000\ 000\ 041\ 3t.$

*Rubidium Sulphate.*

For the direction of the axis	$a$	. . .	$0\cdot000\ 036\ 37 + 0\cdot000\ 000\ 020\ 3t.$
„	„	$b$	. . . $0\cdot000\ 032\ 14 + 0\cdot000\ 000\ 018\ 4t.$
„	„	$c$	. . . $0\cdot000\ 034\ 63 + 0\cdot000\ 000\ 038\ 0t.$

*Cæsium Sulphate.*

For the direction of the axis	$a$	. . .	$0\cdot000\ 033\ 85 + 0\cdot000\ 000\ 021\ 4t.$
„	„	$b$	. . . $0\cdot000\ 031\ 95 + 0\cdot000\ 000\ 018\ 2t.$
„	„	$c$	. . . $0\cdot000\ 035\ 90 + 0\cdot000\ 000\ 041\ 4t.$

In abbreviated notation will next be given a list of the true coefficients. The suffix attached to  $\alpha$  indicates the axial direction.

TRUE Coefficients  $\alpha$  of Linear Expansion at  $t^\circ$ , or Mean Coefficients between any Two Temperatures whose Mean is  $t$ .  $\alpha = a + 2bt$ .

*Potassium Sulphate.*

$$\begin{aligned}\alpha_a &= 10^{-8} (3616 + 2\cdot88t). \\ \alpha_b &= 10^{-8} (3225 + 2\cdot82t). \\ \alpha_c &= 10^{-8} (3634 + 8\cdot26t).\end{aligned}$$

*Rubidium Sulphate.*

$$\begin{aligned}\alpha_a &= 10^{-8} (3637 + 4\cdot06t). \\ \alpha_b &= 10^{-8} (3214 + 3\cdot68t). \\ \alpha_c &= 10^{-8} (3463 + 7\cdot60t).\end{aligned}$$

*Cæsium Sulphate.*

$$\begin{aligned}\alpha_a &= 10^{-8} (3385 + 4\cdot28t). \\ \alpha_b &= 10^{-8} (3195 + 3\cdot64t). \\ \alpha_c &= 10^{-8} (3590 + 8\cdot28t).\end{aligned}$$



A comparison of the coefficients of expansion along analogous directions in the three salts is presented in the following table, which also includes a comparison of the coefficients for the particular temperature of  $50^{\circ}$ .

*Comparative Table of the Linear Coefficients of Expansion for the Three Salts.*

THE Constant  $a$ , the Coefficient of Expansion at  $0^{\circ}$ .

Crystallographical axial direction.	$K_2SO_4$ .	$Rb_2SO_4$ .	$Cs_2SO_4$ .
$a$	0·000 036 16	0·000 036 37	0·000 033 85
$b$	·000 032 25	·000 032 14	·000 031 95
$c$	·000 036 34	·000 034 63	·000 035 90
Sums of values for all three directions :	0·000 104 75	0·000 103 14	0·000 101 70

THE Constant  $b$ , Half the Increment of the Coefficient per Degree.

Axial direction.	$K_2SO_4$ .	$Rb_2SO_4$ .	$Cs_2SO_4$ .
$a$	0·000 000 014 4	0·000 000 020 3	0·000 000 021 4
$b$	·000 000 014 1	·000 000 018 4	·000 000 018 2
$c$	·000 000 041 3	·000 000 038 0	·000 000 041 4
Sums of values for all three directions :	0·000 000 069 8	0·000 000 076 7	0·000 000 081 0

$\alpha_{50^{\circ}}$ , the Coefficient of Expansion,  $\alpha = a + 2bt$ , for  $50^{\circ}$ .

Axial direction.	$K_2SO_4$ .	$Rb_2SO_4$ .	$Cs_2SO_4$ .
$a$	0·000 037 60	0·000 038 40	0·000 035 99
$b$	·000 033 66	·000 033 98	·000 033 77
$c$	·000 040 47	·000 038 43	·000 040 04
Sums of values for all three directions :	0·000 111 73	0·000 110 81	0·000 109 80

It will be observed that in the preceding table the sums of the values of each constant for the three axial directions of each particular salt are taken. These sums represent the constants of the cubical coefficients of expansion. For when the

expression for the product of the expansions in the three rectangular axial directions, which naturally gives the expansion of the solid, is examined, it is found to consist of a large number of terms of which the only ones that affect the fourth and last place of significant figures in the coefficient of expansion for any temperature are the sums of the constants  $a$  and  $b$  respectively.

In the next table is presented a summary of the constants of the cubical coefficients of expansion, and of the cubical coefficients for  $50^\circ$ , in a form which readily admits of a comparison of the values for the three salts.

COEFFICIENTS of the Cubical Expansion of the three Sulphates.

	$a.$	$b.$	$\alpha_{50^\circ}.$
$K_2SO_4$ . . .	0·000 104 75 Diff. 161	0·000 000 069 8 Diff. 69	0·000 111 73 Diff. 92
$Rb_2SO_4$ . . .	0·000 103 14 Diff. 144	0·000 000 076 7 Diff. 43	0·000 110 81 Diff. 101
$Cs_2SO_4$ . . .	0·000 101 70	0·000 000 081 0	0·000 109 80

The mean coefficients of the cubical expansion of the three salts between  $0^\circ$  and  $t^\circ$  are therefore as follows :

For potassium sulphate .  $0\cdot000\ 104\ 75 + 0\cdot000\ 000\ 069\ 8t$ , or  $10^{-8} (10475 + 6\cdot98t)$ .  
 „ rubidium sulphate .  $0\cdot000\ 103\ 14 + 0\cdot000\ 000\ 076\ 7t$ , or  $10^{-8} (10314 + 7\cdot67t)$ .  
 „ cæsium sulphate .  $0\cdot000\ 101\ 70 + 0\cdot000\ 000\ 081\ 0t$ , or  $10^{-8} (10170 + 8\cdot10t)$ .

The actual coefficients of cubical expansion,  $\alpha$ , at any temperature  $t$ , and also the mean coefficients of cubical expansion between any two temperatures whose mean is  $t$ , are the following, in which  $\alpha = a + 2bt$  :

For potassium sulphate .  $0\cdot000\ 104\ 75 + 0\cdot000\ 000\ 139\ 6t$ , or  $10^{-8} (10475 + 13\cdot96t)$ .  
 „ rubidium sulphate .  $0\cdot000\ 103\ 14 + 0\cdot000\ 000\ 153\ 4t$ , or  $10^{-8} (10314 + 15\cdot34t)$ .  
 „ cæsium sulphate .  $0\cdot000\ 101\ 70 + 0\cdot000\ 000\ 162\ 0t$ , or  $10^{-8} (10170 + 16\cdot20t)$ .

#### DISCUSSION OF THE RESULTS, AND CONCLUSIONS THEREFROM.

##### *The Cubical Expansion.*

The most striking result of the investigation is apparent from an inspection of the comparative table of the cubical coefficients of expansion. It may be stated in the following words :

*The coefficients of cubical expansion of the normal sulphates of potassium,*

*rubidium, and caesium exhibit a progression, corresponding to the progression of the atomic weights of the three respective metals. This is true of both the constants  $a$  and  $b$  in the general expression for the coefficient of cubical expansion, the values of each constant for the rubidium salt being intermediate between the corresponding values for the potassium and caesium salts.*

It may be further stated that :

*The differences between the values of the constant  $a$ , which represents the coefficient of cubical expansion for  $0^\circ$ , for the three salts, are small, amounting to only one and a half per cent. ; this is an amount, however, which is five times as great as the possible experimental error in the determinations.*

Also that :

*The order of progression of the two constants of the cubical coefficient of expansion is inverted ;  $a$ , the coefficient at  $0^\circ$ , diminishes with increasing atomic weight of the metal contained in the salt, while  $b$ , half the increment of the coefficient per degree, increases.*

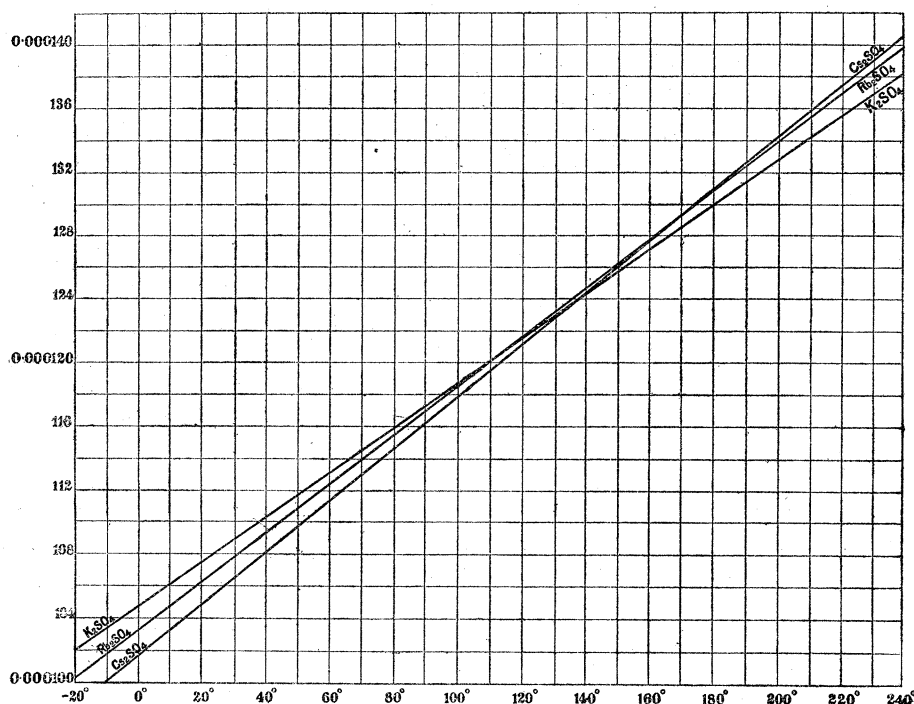
This latter fact leads to an interesting result, namely, that the coefficients, in increasing with rise of temperature, approach each other in value, until for three certain temperatures between  $110^\circ$  and  $170^\circ$  they become identical in pairs ; moreover, in the neighbourhood of the second of these temperatures the three values approximate so closely to each other that their difference comes within the limits of experimental error. For temperatures higher than those of coincidence, the values diverge and exhibit an inverted order of progression. This will be rendered clear by a table showing the true coefficients of cubical expansion,  $a + 2bt$ , for intervals of  $50^\circ$  up to  $200^\circ$ , and for the three temperatures of coincidence. These latter are  $114^\circ$  for the identity of cubical expansion of potassium and rubidium sulphates,  $136^\circ$  for potassium and caesium sulphates, and  $168^\circ$  for the coincidence of expansion of the rubidium and caesium salts.

COEFFICIENTS of Cubical Expansion for Various Temperatures from  $0^\circ$  to  $200^\circ$

Salt.	$0^\circ$ .	$50^\circ$ .	$100^\circ$ .	$114^\circ$ .	$136^\circ$ .	$150^\circ$ .	$168^\circ$ .	$200^\circ$ .
$K_2SO_4$	$10^{-8}$ 10475	11173	11871	12066	12373	12569	12820	13267
$Rb_2SO_4$	$10^{-8}$ 10314	11081	11848	12065	12400	12615	12891	13382
$Cs_2SO_4$	$10^{-8}$ 10170	10980	11790	12017	12373	12600	12891	13410

The point may be graphically demonstrated by plotting out the values on curve paper, taking temperatures as abscissæ and coefficients of cubical expansion as ordinates. The three straight lines thus obtained, shown in the reproduction given, will be observed to converge from  $0^\circ$  towards the three temperatures of coincidence, where crossing of the lines in pairs occurs, beyond which they diverge. The relative nearness of the lines to each other in the middle of the part where crossing occurs,

together with the fact that the increment  $2b$  is not determinable with the accuracy of the constant  $a$ , the coefficient at  $0^\circ$ , suggests the probability that the three lines should all cross at one point, somewhere near  $136^\circ$ . At this temperature the value for rubidium sulphate only exhibits a difference of one in five hundred from the two identical values for the two other salts, so that the three values are identical within the limits of experimental error.



Graphical Expression of Cubical Expansions.

These considerations may be summarised in the following addition to the last italicised statement.

*In consequence of this fact the coefficients of cubical expansion of the three salts converge with rise of temperature towards equality, which, within the limits of experimental error, they reach at  $136^\circ$ . Beyond the temperature at which identity of expansion occurs the coefficients of expansion exhibit increasing divergence, the order of progression being inverted, an increase in the atomic weight of the metal being now accompanied by an increase in the coefficient of cubical expansion.*

#### *The Linear Expansion.*

The first conclusions to be drawn from an inspection of the coefficients of linear deformation are the following :

*The thermal deformation is of the nature of an expansion along all directions in the crystals of the three sulphates, no contraction occurring in any direction.*

*The amount of the expansion is relatively large, compared with the expansions of metals, being four times that of platinum and one and a half times as great as the large expansion of aluminium.*

*The differences between the amounts of linear expansion along the three axial directions of any one salt are small, the difference between the maximum and minimum being about twelve per cent. of the total expansion in the case of each salt. But the differences between the values for the same direction of the three salts are much smaller; in the case of the direction of the axis *b*, the difference is only one per cent., and in that of the axis *a* where the greatest divergence is shown, it is only six per cent. of the total amount of expansion.*

*The increment of the coefficient of expansion, per degree of temperature, is about twice as large for the direction of the axis *c* of each salt as for the other two axial directions, for which the increment is nearly identical.*

It is interesting to point out, in connection with the last fact, that it agrees in a remarkable manner with the observation previously recorded ('Journ. Chem. Soc.,' Trans., 1894, p. 715, §14), that the change of optical refractive power brought about by rise of temperature is considerably greater for the direction of the axis *c*, than for the directions of the *a* and *b* axes, along which the amount of change is approximately the same.

The fact that the differences of expansion exhibited by the three salts are so small, compared with the differences in the amounts of expansion in the three axial directions, would render it probable that if any considerable changes were introduced in the relations of the values for these three directions by the replacement of one metal by another, particularly if such changes were not simply proportional to the atomic weight of the metal but expressed by a higher function of the atomic weight, such change would suffice to negative the possibility of a direct progression of the linear coefficients of expansion for each axial direction of the three salts, corresponding to the atomic weights of the metals present. That simple proportionality to the atomic weight was not to be expected directionally, has been indicated by the whole of the morphological and physical work on both sulphates and selenates. In the case of the refractive indices, however, the directional changes were small in comparison with the differences exhibited by different salts; hence in the case of these, as of other, optical constants, the interesting progression according to the atomic weight of the metal was not interfered with. But although such perturbations of a directional character are able, in the case of the thermal constants, to obliterate such a progression of the linear coefficient of expansion, they would mutually compensate each other when the total solid change was considered. Hence it must be apparent that if the influence of atomic weight were indeed a progressive one it would only be clearly revealed in the case of the coefficients of cubical expansion. These latter constants have been shown to exhibit such a progression in the clearest possible manner.

In accordance with the above considerations, a progression of the linear coefficients

of expansion is found to be prevented by the slight directional perturbations due to the different natures of the molecules of the three salts. The replacement of the atoms of one metal by those of another of higher atomic weight is possibly, and even probably, accompanied by movement of the relative positions of the constituents of the molecules of their spheres of motion, as well as by the purely chemical change; for not only is the substitution accompanied by an increase of mass, but also by an increase in the electro-positive energy of the metallic atoms, which may very reasonably be expected to result in a closer approximation to the negative atoms, probably of oxygen, to which they are attracted. There are, however, several interesting facts exhibited by the linear coefficients, which connect their relations very intimately with those of the optical constants, for which a true progression in the order of atomic weight has been clearly demonstrated. Before passing to the consideration of these indications of parallelism between the thermal and optical behaviour of the crystals of the three salts, attention must be drawn to the two following salient facts which are apparent from an inspection of the linear coefficients. It is that :

*The amount of expansion along the direction of the crystallographical axis  $b$  is practically identical for all three sulphates, indicating that the interchange of the three metals is without influence on the thermal behaviour along the macrodiagonal axis of the crystals. Moreover, the crystals of all three salts expand least along this direction, which is therefore that of the minimum axis of the thermal ellipsoid.*

These two facts are doubtless of significance with respect to the structure of the molecule, apparently indicating absence of the metallic atoms or their spheres of motion from the immediate proximity of the axis  $b$ . The significance becomes enhanced in view of the fact that the author has shown ('Journ. Chem. Soc. Trans.,' 1896, p. 507) that the whole of the work on the sulphates and double sulphates points to the conclusion that the structural unit of the crystals of the simple sulphates is the simple chemical molecule, a conclusion which is supported by the work of Fock (referred to *loc. cit.*) on the solubility of mixed crystals.

The relations between the amounts of expansion along the directions of the other two crystallographical axes,  $a$  and  $c$ , are much more complicated, and are evidently influenced by the replacement of one metal by another. Considering the coefficients of expansion for  $0^\circ$ , the amount of expansion along the direction of the axis  $c$  is the greater in the case of both the potassium and cæsium salts; and for all three salts the increment is, as already indicated, greater for this than for any other direction. But in the case of the rubidium salt a remarkable excess of expansion is observed to occur along the direction of the  $a$  axis, which is the maximum thermal axis at  $0^\circ$ , at the expense of that along the  $c$  axis, which becomes reduced to the intermediate thermal axis. The increments per degree, however, for these two directions in the rubidium salt, remain of the same order as for the other two salts. Now it is an interesting fact, and doubtless not without significance, that the directions of maximum thermal effect coincide with those of the first median line of the optic axial angles of all three

salts, which is the axis  $c$  in both the potassium and caesium salts and the axis  $a$  in the case of the rubidium salt. In order to follow the parallelism further, it will be necessary to compare the linear coefficients of expansion for higher temperatures, the values for  $50^\circ$  and  $100^\circ$  sufficing for the purpose. In the following table are given the values of  $\alpha = a + 2bt$  for  $0^\circ$ ,  $50^\circ$  and  $100^\circ$ . The directions are also indicated of the axes of the optical indicatrix, namely, the first median line, the second median line, and the intermediate axis of the optical ellipsoid. The sign of the double refraction of the crystals is also given, as this determines whether the first median line is the maximum or the minimum axis of the optical indicatrix, the former being the case for positive double refraction and the latter for negative.

COMPARISON of Linear Expansions at Different Temperatures with the Optical Indicatrix.

Salt.	Sign of double refraction.	Crystallographical axis.	Direction in optical ellipsoid.	Linear coefficients of expansion—		
				At $0^\circ$ .	At $50^\circ$ .	At $100^\circ$ .
$K_2SO_4$	Positive . . .	$a$	Intermediate axis . . . . .	$10^{-8}$ 3616	3760	3904
		$b$	Second median line . . . . .	3225	3366	3507
		$c$	First median line . . . . .	3634	4047	4460
$Rb_2SO_4$	Very feebly positive	$a$	First median line . . . . .	3637	3840	4043
		$b$	Second median line below $50^\circ$	3214	3398	3582
		$c$	Intermediate axis below $50^\circ$	3463	3843	4223
$Cs_2SO_4$	Negative . . .	$a$	Second median line . . . . .	3385	3599	3813
		$b$	Intermediate axis . . . . .	3195	3377	3559
		$c$	First median line . . . . .	3590	4004	4418

It will be apparent from the table that the relations of the linear expansions at  $0^\circ$  still hold good, as the temperature is raised, in the cases of the potassium and caesium salts. A similar observation has been shown to be valid with respect to the optical properties. But in the case of the rubidium salt a remarkable change occurs. Owing to the greater increment of the expansion along the direction of the axis  $c$ , the preponderance of the expansion along the axis  $a$  diminishes, until at  $50^\circ$  the amounts of expansion along these two axial directions become equal. That is to say, in the neighbourhood of  $50^\circ$  the crystals of rubidium sulphate simulate uniaxial symmetry as regards their thermal behaviour. This is rendered the more interesting by the fact that about this temperature the crystals of this salt also exhibit uniaxial optical properties. Owing to the extremely feeble double refraction, it was shown (*loc. cit.*, p. 693) that the slight alterations of the relations of the refractive power in the three

axial directions, brought about by rise of temperature according to a rule common to all three salts, result in bringing two of the refractive indices to equality about the temperature indicated, and the optic axial angle diminishes until about the same temperature the circular rings and rectangular cross of an uniaxial crystal are exhibited in convergent polarised light. The exact temperatures at which the uniaxial interference figure is produced differ slightly according to the wave-length of the light, owing to there being a large amount of dispersion of the optic axes. They are respectively  $42^\circ$  for red lithium light,  $44^\circ$  for red C. hydrogen light,  $48^\circ$  for sodium light,  $52^\circ$  for green thallium light and  $58^\circ$  for greenish blue F. hydrogen light; the average is thus exactly  $50^\circ$ , the temperature at which the crystals of rubidium sulphate are thermally uniaxial. But the two ellipsoids of revolution for the two properties are not similarly orientated, the principal axis for the optical property being the crystallographical axis  $a$ , while for the thermal property it is the axis  $b$ .

This close parallelism between the thermal and optical properties is of considerable importance, inasmuch as the optical constants were shown to exhibit a clear progression corresponding to the progression of the atomic weights of the three metals, the differences between the optical constants for the three salts being much greater relatively to their variations in the three axial directions of any one salt, than in the case of the thermal properties.

On following the growth of the coefficients of linear expansion further to  $100^\circ$ , it is observed that the continued gain on the part of the  $c$  value has now rendered the expansion along this axis clearly the maximum, thus reversing the order of the axial expansions which had obtained below  $50^\circ$ . The maximum axis of the thermal ellipsoid for  $100^\circ$ , and temperatures superior to this, is thus the crystallographical axis  $c$  for all three sulphates; moreover the axis  $b$  is the minimum thermal axis, and the axis  $a$  the axis of intermediate thermal expansion for all three salts. To complete the parallelism of the thermal and optical properties, it may be mentioned that at temperatures superior to the neighbourhood of  $50^\circ$ , where the uniaxial optical interference figure is produced, the figure again breaks up into a biaxial one, but with the optic axes separated in the plane perpendicular to that which formerly contained them, and the optic axes separate more and more in this new plane until about  $180^\circ$  the axis  $c$  becomes the first median line instead of the axis  $a$ . At this temperature, therefore, the crystallographical axis  $c$  is the first median line for all three salts. It has been shown that at temperatures superior to  $100^\circ$  the axis  $c$  is also the direction of maximum thermal expansion. Hence, at higher temperatures the rule observed for the lower ones, that the direction of maximum thermal expansion is that of the optical first median line, is equally valid.

The foregoing considerations, concerning the relations of the linear coefficients of expansion, may be summarised as follows:—

*The smallness of the difference in the coefficient of expansion along any particular direction in the crystals, which is introduced by the replacement of one alkali metal*



by another, compared with the larger differences of expansion exhibited in the three axial directions of any one salt, together with the fact that the change of metal is accompanied by considerable modifications of these latter relative expansions for two of the axial directions,  $a$  and  $c$ , prevent the coefficients of expansion for any one direction of the three salts from exhibiting any progression corresponding to that of the atomic weights of the three metals. These directional perturbations are, however, mutually compensative, the increase of expansion in one of the two directions referred to being more or less balanced by the diminution in the other; consequently the effect of interchange of the metals is clearly exhibited by the solid deformation, the cubical expansion, the coefficients and increments of which have been shown to exhibit a well-defined progression following the order of the atomic weights of the three metals.

Before proceeding to summarise the interesting analogy between the thermal and the optical properties, it may be of advantage to consider what the dimensions of the linear change, on replacing one metal by another, would probably be, provided no directional perturbations occurred. The difference between the cubical coefficients of expansion of potassium and rubidium sulphates is 0·00000161, and of the rubidium and caesium salts 0·00000144. The mean is 0·0000015, and the linear differences might be reasonably expected to be about one-third of this, namely 0·0000005. Even if the linear expansions along the axis  $b$  are accepted as free from perturbation and unaffected by change of metal, the linear differences for the other two directions could not exceed 0·0000008. Now the directional perturbation in which the rubidium salt exhibits a reversal of the relative directions of the maximum and intermediate thermal axis compared with the potassium salt, amounts to more than twice this amount, namely 0·0000017. Hence it is clearly apparent that a progressive change, of the maximum possible amount, would be completely masked by the larger directional perturbation. A brief summary of the nature of the perturbation and its relation to the optical changes may next be given.

*The chief directional perturbation consists of a reversal, for temperatures below 50°, of the directions of the maximum and intermediate axes of the thermal ellipsoid in the rubidium salt, compared with their directions in the potassium and caesium salts. The maximum thermal axis is the crystallographical axis  $c$  for the two latter salts, but the  $a$  axis for the rubidium salt. A similar reversal of the direction of the first median line, the maximum axis of the optical ellipsoid (the indicatrix), from the direction  $c$  to the direction  $a$ , occurs for similar temperatures, in the case of the rubidium salt. Hence, the maximum thermal axis is identical in all three salts with the first median line.*

*At higher temperatures the same relations still hold for the potassium and caesium salts, both thermally and optically. But owing to the increment of expansion along the axis  $c$  being so much greater than for other directions, the exceptional intermediate expansion along the axis  $c$  of rubidium sulphate is rapidly brought up to*

equality, at  $50^\circ$ , with the expansion along the axis  $a$ ; and beyond this temperature  $c$  becomes the maximum thermal axis for the rubidium salt, as it is for the other two sulphates. Hence, at  $50^\circ$  the crystals of rubidium sulphate are apparently thermally uniaxial. At temperatures varying  $10^\circ$  each side of  $50^\circ$  for different wave-lengths of light, they are also apparently optically uniaxial. The thermal and optical ellipsoids of revolution, however, are not identically orientated, the axis of the former being the crystallographical axis  $b$ , and of the latter  $a$ . Further, the change of direction of the maximum thermal axis of rubidium sulphate, from  $a$  to  $c$ , is followed optically at  $180^\circ$  by the change of the first median line from  $a$  to  $c$ . Thus the first optical median line corresponds, as at lower temperatures, to the maximum thermal axis, for all three sulphates.

This parallelism between the linear thermal expansions and the optical constants is of significance, inasmuch as the latter constants, which, unlike the former ones, exhibit differences between the three salts of much greater magnitude than the directional differences for any one salt, show a clear progression, in the order of the atomic weights of the metals contained in the three sulphates.

It will be interesting in conclusion, to compare the results for the thermal deformation thus obtained by the refined interference method, with those previously obtained from the much cruder method of combining determinations of specific gravity at the ordinary and higher temperatures with measurements of the morphological angles at those temperatures. Such an attempt to determine the coefficients of expansion was described in the previous memoir on the sulphates ('Journ. Chem. Soc., Trans.,' 1894, p. 653). It naturally depended for success on the possibility of employing a liquid in the pycnometer which was absolutely without action on the salts, as well as upon the degree of accuracy with which such determinations and angular measurements, the latter involving total deviations of less than two minutes of arc, can be carried out, even with the aid of the extremely delicate instruments employed.

The actual values found for the total cubical expansion for  $40^\circ$  (between  $20^\circ$  and  $60^\circ$ ) were :—

For potassium sulphate	. . .	0·0053
„ rubidium	„ . . .	0·0052
„ cæsium	„ . . .	0·0051.

Thus a diminution of expansion was found to occur as the atomic weight of the metal increased, a result which is fully borne out by the more accurate determinations now presented. The figures for the three salts were so near, however, that they were taken as identical, having reference to the method by which they were obtained, for the purpose of calculating the coefficients of linear expansion with the aid of the angular deviations for the same temperatures. For the linear coefficients of expansion  $\lambda$  for  $100^\circ$  the following numbers were given :—

$$\lambda_a = 0\cdot00437, \quad \lambda_b = 0\cdot00385, \quad \lambda_c = 0\cdot00479,$$

It was therefore concluded that "the crystals of the three salts, on heating, expand most in the direction of the vertical axis  $c$ , and least along the macrodiagonal axis  $b$ ." We have seen that this is indeed the case, except for temperatures below  $50^\circ$  in the case of  $\lambda_a$  and  $\lambda_c$  of the rubidium salt, a fact which the method could not possibly have indicated, as at  $60^\circ$ , the temperature of the higher density determinations, the rule found is really true.

The actual values now published for the total expansion of potassium sulphate, taking this salt as an example, for the  $100^\circ$  between  $20^\circ$  and  $120^\circ$ , calculated by the formula  $\alpha = a + 2b \left( \frac{20 + 120}{2} \right)$ , are as follows :

$$\alpha_a = 0.003818, \quad \alpha_b = 0.003422, \quad \alpha_c = 0.004212.$$

The difference between these highly accurate values and the approximate ones obtained by the rougher method is not great considering the nature of the latter, and the order is the same.

An attempt to determine the expansion of crystals of potassium and rubidium sulphates, by means of the weight-thermometer method, has been described by SPRING ('Bull. de l'Acad. de Belgique,' 1882, 197, and 'Ber. Deut. Chem. Ges.,' 15, 1940). Olive oil was employed as the liquid, and the density determinations were carried up to  $100^\circ$ . The value obtained for the cubical expansion of potassium sulphate for  $100^\circ$  was 0.0126, and for rubidium sulphate 0.0111. The latter value is extraordinarily near the truth according to the results now presented, the value for  $0^\circ$  to  $100^\circ$  being actually 0.01108. But the impossibility of trusting this method, equally with all the relatively coarser density methods, to afford correct differences between the values for different salts, is clearly demonstrated by the fact that the difference shown between the values for the potassium and rubidium salts, namely 0.00150, is seventeen times as great as the real difference ( $0.01117 - 0.01108 = 0.00009$ ), which is now shown to exist.

#### SUMMARY OF CONCLUSIONS.

The principal results of the investigation are presented in the following summary.

1. The coefficients of cubical expansion of the orthorhombic crystals of the normal sulphates of potassium, rubidium and caesium exhibit a progression, corresponding to the progression of the atomic weights of the three respective metals. This is true of both the constants  $a$  and  $b$  in the general expression for the coefficient of cubical expansion,  $\alpha = a + 2bt$ , for any temperature  $t$ .
2. The order of progression of the two constants is inverted;  $a$ , the coefficient for  $0^\circ$ , diminishes with increasing atomic weight of the metal, while  $b$ , half the increment of the coefficient per degree of temperature, increases.
3. In consequence of rule 2 the coefficients of cubical expansion of the three salts converge, with rise of temperature, and attain equality, within the limits of

experimental error, at  $136^{\circ}$ . Beyond the temperature of identity divergence occurs and an increase of atomic weight is now accompanied by an increase in the coefficient of cubical expansion.

4. The thermal deformation is of the nature of an expansion in all directions in the crystals of all three sulphates.

5. The differences between the coefficients of linear expansion along the three crystallographical axial directions of any one salt, although only amounting to one-eighth of the total coefficient, are large compared with the differences between the values for the same direction of the three salts.

6. The operation of rule 5, together with the fact that the replacement of one metal by another is accompanied by considerable modifications of the relations of two of the three values for the original salt, those corresponding to the axes  $a$  and  $c$ , prevent the coefficients of linear expansion for any one direction of the three salts from exhibiting any progression corresponding to that of the atomic weights of the three metals. These directional perturbations are, however, mutually compensative, so that the effect of interchange of the metals is clearly exhibited by the solid deformation, the cubical expansion, the coefficients of which and their increments have been shown to exhibit a progression according to the atomic weight of the metal, as stated in rule 1.

7. The increment of the linear coefficient of expansion for the direction of the vertical axis  $c$  of each salt, is about twice as large as the increments for the other two directions  $a$  and  $b$ , for which latter the increments are nearly equal. This thermal property is analogous to the optical behaviour, the refractive power being altered (diminished) by rise of temperature much more in the direction of the axis  $c$  than in the other two directions, in which the lesser amounts of change are nearly equal.

8. The amount of expansion along the direction of the crystallographical axis  $b$  is approximately identical for all three sulphates, indicating that interchange of the metals is without influence on the thermal behaviour along the macrodiagonal axis of the crystals. The crystals of all three salts also expand least in this direction, which is therefore the common minimum axis of the thermal ellipsoid.

9. The chief of the directional perturbations, referred to under 6, consists of a reversal, for temperatures below  $50^{\circ}$ , of the directions of the maximum and intermediate axes of the thermal ellipsoid for rubidium sulphate, compared with their directions in the potassium and cæsium salts. The maximum thermal axis is the crystallographical axis  $c$  for the two latter salts, but  $a$  for the rubidium salt. A similar reversal of the direction of the first median line, the maximum axis of the optical ellipsoid (the indicatrix), from  $c$  to  $a$  occurs for the same temperatures, in the case of rubidium sulphate. The maximum thermal axis is identical in all three salts with the optical first median line.

10. At higher temperatures the same relations still obtain for the potassium and cæsium salts, both thermally and optically. But owing to the increment of expansion

along the axis  $c$  being so much greater than for the other directions, the intermediate expansion along  $c$  for rubidium sulphate attains equality at  $50^\circ$  with the expansion along  $a$ , and beyond this temperature  $c$  becomes the maximum thermal axis for this salt, as it is for the other two sulphates. Consequently, at  $50^\circ$  the crystals of rubidium sulphate are apparently thermally uniaxial. At temperatures varying  $10^\circ$  each side of  $50^\circ$  for different wave-lengths of light, they have previously been shown to simulate uniaxial optical properties. The thermal and optical ellipsoids of revolution are not, however, identically orientated, the axis of the former being the axis  $b$  and of the latter  $a$ . Further, the change of direction of the maximum thermal axis of rubidium sulphate from  $a$  to  $c$  is followed optically at  $180^\circ$  by the change of the first median line from  $a$  to  $c$ , rendering the last sentence of rule 9 again valid.

11. A close parallelism between the linear thermal expansion and the directional optical behaviour is thus shown to exist, and is indicative that the same progressive effect of variation of the atomic weight of the metal is in operation with regard to the former, as was clearly demonstrated in a former memoir with respect to the latter, and that this effect would be manifest in the former were it not masked by the larger effect indicated under 6.

12. The thermal deformation constants best capable of indicating the effect of the replacement of one alkali metal by another, in the crystals of the normal alkali sulphates, have thus been shown to be the cubical coefficients of expansion and their increments; and these have been further demonstrated to exhibit a regular progression, which follows the order of progression of the atomic weights of the metals in question. Moreover, the linear coefficients and their increments have been shown to exhibit variations which present a remarkable analogy to those of the optical constants, for which, the values for the three salts being very much more widely separated and consequently undisturbed by the modification of the directional differences for the same salt which are relatively so much more important in the case of the linear thermal constants, a clear progression according to the atomic weight of the alkali metals has been proved.

The final conclusion of this investigation, therefore, is that :

*The thermal deformation constants of the crystals of the normal sulphates of potassium, rubidium, and caesium exhibit variations, which, in common with the morphological, optical, and other physical properties previously investigated, follow the order of progression of the atomic weights of the alkali metals which the salts contain.*

This result is, therefore, in perfect agreement with the principle enunciated at the conclusion of the memoir concerning the alkaline selenates ('Journ. Chem. Soc., Trans.,' 1897, p. 920), which reads as follows :

*The difference in the nature of the elements of the same family group which is manifested in their regularly varying atomic weights, is also expressed in the similarly regular variation of the characters of the crystals of an isomorphous series of salts of which these elements are the interchangeable constituents.*