LII.—*Connection between the Atomic Weight of Contained Metals, and the Crystallographical Characters of Isomorphous Salts. A Comparative Crystallographical Study of the Normal Sulphates of Potassium, Rubidium, and Cæsium.*

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THE interesting relationships brought to light by the detailed goniometrical investigation of the double sulphates of the series $R_2M(SO_4)_2 \cdot 6H_2O$, in which R was represented by potassium, rubidium, and cæsium, communicated to the Society last year (Trans., 1893, **63**, 337), rendered a similar study of the simple normal sulphates of these alkali metals particularly desirable. The problem was a more difficult

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one, however, by reason of the higher symmetry of the crystals of the normal sulphates of potassium, rubidium, and caesium, and the consequent minuteness of the differences between their respective angles. The changes in the magnitudes of the angles in the case of the monoclinic double sulphates, on passing from a potassium to a rubidium salt and from a rubidium to a caesium salt, were shown to be relatively considerable, frequently exceeding a whole degree of arc, and therefore widely removed from the limits of experimental and formational error. In the case of the simple normal sulphates, however, which crystallise in the rhombic system of symmetry, the angular differences are very much less than this; the greatest difference between analogous angles amounts only to between 20 and 30 minutes of arc, and by far the greater number of angles exhibit differences less than 15 minutes of arc. Hence extreme care has been required in order to obtain pure salts and crystals free from formational distortion.

It might be expected that the well-known and important salts which form the subject of this communication would have long ago been fully worked out and described. This, however, is not the case. The data at present current concerning the crystallography of potassium sulphate is inadequate for the purpose in view, while that concerning the sulphates of rubidium and caesium is not only much less adequate than in the case of potassium sulphate, but is also inaccurate, and completely misleading when employed for comparative purposes. For instance, the ratios of the crystallographical axes currently accepted, and apparently the only determinations which have ever been made, are those given by Mitscherlich in the year 1830 for potassium sulphate, Bunsen's values, published in 1861, for rubidium sulphate, and those given by Topsoe from measurements made by von Lang in 1867 for caesium sulphate. These values are as follows, arranged in the axial order now usually employed.

For K_2SO_4	$a : b : c = 0.5727 : 1 : 0.7464$
„ Rb_2SO_4	$a : b : c = 0.5723 : 1 : 0.7522$
„ Cs_2SO_4	$a : b : c = 0.5805 : 1 : 0.7400$

Topsøe (*Tidsskrift for Physik og Chemi*, 8, 5, 193, 321, and 9, 225) adopts these ratios in his celebrated classification of isomorphous series. It will at once be observed that if the above ratios are correct, all idea of progression according to the atomic weight of the contained metal is directly negatived, for the differences between similar ratios in the three salts are sufficiently large to have real significance, particularly in the case of the ratio $c : b$. In view of the very positive evidence that such a progression does exist in the case of potassium, rubidium, and caesium, afforded by the results of the goniometrical investigation of the double sulphates, it was of the first importance

that the simple sulphates should be subjected to a thorough crystallographical examination. That a progression according to atomic weight is to be expected, is further indicated by the recently published work of Muthmann (*Zeitschrift für Krystallographie*, **22**, 497) concerning the permanganates of potassium, rubidium, and caesium. Muthmann finds that the rule established by the author in case of the double sulphates, that "the magnitudes of all the angles upon the crystals of the rubidium salts lie between the magnitudes of the corresponding angles upon the crystals of the potassium and caesium salts," holds throughout in the case of the permanganates. The rule also enunciated in the case of the double sulphates that "the differences between the magnitudes of many of the angles of the caesium and rubidium salts are much larger than those between the rubidium and potassium salts," is likewise followed by the permanganates, the change brought about by the introduction of the heavy caesium atom instead of rubidium being relatively greater than that caused by the replacement of potassium by rubidium. The necessity, therefore, for a detailed study of the sulphates of the three metals is thus seen to have been paramount.

The investigation of the double sulphates above referred to was confined to the goniometrical relationships. The optical and other physical relationships are now being studied, and the author hopes to indicate the results in the course of the next few months. It has been found necessary, in order to be able to prepare the necessary section-plates and prisms required for the optical investigation with greater precision than has hitherto been possible, to devise an instrument for attaining this object. An instrument has likewise been devised for furnishing spectrum monochromatic light of any desired wave-length, in order that observations might be made for a greater number of wave-lengths than hitherto, and in a relatively shorter time, while also enabling the whole field of the observing instrument to be more brightly illuminated than by the use of coloured flames. The instruments have been described to the Royal Society; abstracts of the two papers are given in the *Proceedings* of the Royal Society for this year (**55**, 108 and 111), and full details of their construction and use will appear in the *Philosophical Transactions* in due course. During the construction of these instruments, the normal sulphates of potassium, rubidium, and caesium were subjected to a detailed goniometrical investigation, and the new instruments being to hand when this was finished, the author has completed the work on these three salts by making a similarly detailed study of their optical and other physical properties. The results of the whole are set forth in the following pages.

The pure sulphates employed formed part of the stock obtained for

preparing the double sulphates described in the former communication. Analyses of the three salts were given in that memoir (p. 340), and these analyses, together with spectroscopic examination, indicate that the salts are of a very high degree of purity. They have since been several times fractionally recrystallised, during the preparation of crystals of the necessary perfection, by the method of slow evaporation of cold solutions protected from sudden changes of temperature or other disturbance, so that the purity of the crystals actually employed in the work is even greater than is indicated by the analyses.

The spectroscopic examination of the salts was conducted with particular care, using the author's monochromatic light apparatus as spectroscope. This instrument forms an admirable spectroscope when the eye-piece is placed in position in front of the exit slit, the jaws of which may either be opened wide or employed as a pair of more or less separated cross wires for convenience in localising the lines. The table of circle readings corresponding to definite wave-lengths enables a most accurate determination of the position of any line to be made. Erdmann (*Archiv der pharmacie*, 232, 1, 10) has recently shown that the presence of traces of potassium in rubidium salts may be detected with great certainty by observations of the nature of the lines exhibited in the red. The red potassium line consists in reality of two adjacent lines of the wave-lengths, according to Kaiser and Runge, 766.56 m_{μ} and 769.93 m_{μ} . These lines are very well separated in the spectroscope above referred to. The two well-known red rubidium lines have the wave-lengths 781.1 m_{μ} and 795 m_{μ} . A rubidium salt containing 1 to 2 per cent. of potassium exhibits, according to Erdmann, the double potassium line very strongly and the rubidium line 781 faintly, the other rubidium line being absent. A salt analytically pure exhibits both rubidium lines, but the potassium line still predominates, owing to the greater ease with which this line is produced. Approximately pure rubidium sulphate exhibits the rubidium lines predominating, but the potassium line is still visible, while the pure salt of course exhibits no trace of the potassium line.

The rubidium sulphate used in this investigation exhibited the two rubidium lines referred to with great intensity, but no potassium line; the position which the latter ought to occupy, if present, was well defined by having previously brought one of the jaws of the exit slit in close proximity while igniting a potassium salt. The cæsium salt exhibited neither potassium nor rubidium lines, but the whole of the cæsium lines were most brilliant.

Solubilities of the Three Sulphates.

The three sulphates differ remarkably with regard to their solubility. Potassium sulphate, as is well known, is a most sparingly soluble salt compared with other salts of that metal. Mulder found that 100 c.c. of a solution saturated at 10° , contained only 9.7 grams of potassium sulphate, and Bunsen's determinations of the solubility of the salt agree with this value. Rubidium sulphate is very much more soluble. Erdmann (*loc. cit.*) found in 100 c.c. of a solution saturated at the ordinary temperature, 34.4 grams of rubidium sulphate. Bunsen (*Ann. der Chemie*, 119, 110) states that it dissolves in 2.4 times its weight of water at 7° . The author found that at $17-18^{\circ}$, 100 c.c. of water dissolved 44.7 grams of the rubidium sulphate used in this investigation, and 100 c.c. of a solution saturated at $17^{\circ}.5$, which had been allowed to stand until crystals had deposited, left 44 grams on evaporation in a platinum dish. Cæsium sulphate is an extremely soluble salt. Bunsen (*loc. cit.*) states that at 2° it only requires 0.63 of its weight of water for solution. The author finds that 100 c.c. of water at $17-18^{\circ}$ dissolve 163.5 grams of the pure salt, corresponding to a solubility in 0.61 of its weight of water, a result in close agreement with that of Bunsen. On evaporation of a saturated solution standing over crystals at $17^{\circ}.5$, an amount of salt is left corresponding to 131 grams per 100 c.c. of the solution; the volume of the saturated solution is greater than that of the water employed to effect solution by almost exactly one-fourth.

The solubilities are greater at higher temperatures, but at 100° potassium sulphate is still sparingly soluble, so that a large bulk of solution is required in order to obtain crystals of any considerable size, such as are required for certain portions of the optical investigation. Cæsium sulphate dissolves to a very large amount indeed at 100° , producing an extremely heavy liquid; and rubidium sulphate likewise dissolves to a larger extent than at the ordinary temperature, but still retains its intermediate position in this respect. It may therefore be stated concerning the solubilities of the three salts that:—

The solubilities of the normal sulphates of potassium, rubidium, and cæsium are widely different, potassium sulphate being sparingly, rubidium sulphate moderately, and cæsium sulphate extremely, soluble in water. 100 c.c. of water at the ordinary temperature dissolve 10 grams of potassium sulphate, 44 grams of rubidium sulphate, and 163 grams of cæsium sulphate respectively. The solubilities are greater at higher temperatures, but the intermediate position of rubidium sulphate is retained.

GONIOMETRICAL INVESTIGATION.

The normal sulphates of potassium, rubidium, and caesium crystallise in the rhombic system. The isomorphism is of a very close description, as will be apparent from the small differences between the magnitudes of analogous angles when the goniometrical relationships are discussed. The same planes are developed upon the crystals of all three salts, but marked differences in the relative amount of development of the various faces are observed, each salt being to a considerable extent characterised by its own peculiar habit. The distinction between the three is not so sharp, however, as was observed in the case of the double sulphates, the three habits shading off more into each other.

The general symmetry of the three sulphates is portrayed in the spherical projection, Fig. 1.

FIG. 1.

The differences between the angles of the salts are so small that a spherical projection drawn on the scale given, correctly represents all three. The most remarkable feature of the symmetry will be at once apparent, namely, the close approximation to hexagonal symmetry. The angles ap , pp' , and $p'b$ are almost exactly 30° ; the angle ap is 12—16 mins. less than 30° , and the angle $p'b$ greater than 30° by the same amounts in the three salts, while curiously enough the angle pp' is found to be exactly 30° in each salt, with a possibility of error which cannot exceed 2 mins. The truly rhombic nature of the crystals, however, is fully proved by the total impossibility of anything like 16' of error in the determination of the angular magnitudes, and by the optical properties of the crystals.

The goniometrical measurements were carried out with the excellent horizontal goniometer of Fuess, model No. 2a. An extraordinarily large number of measurements have been made with crystals of the highest attainable perfection, 10 crystals at least of each salt having been measured along not only the principal but also the minor zones, in order to afford as many different angles as possible for comparison. The total number of goniometrical measurements accepted, as being afforded by faces reflecting irreproachable images of the Websky signal, is 2506. This number, of course, refers to angles formed by different faces. As many as 70 or 80 measurements of the same angular magnitude have sometimes been obtained, certain of the more important angles being repeated eight times on each crystal in accordance with rhombic symmetry. Hence the possible error of the mean of so large a number of measurements between perfect faces upon different crystals belonging to several different crops, must be very small and cannot exceed 2 mins. of arc.

Potassium Sulphate, K₂SO₄.

Several crops of crystals of this salt of superior excellence as regards brilliance of reflection, planeness of the faces, and perfection of development, were obtained by the slow evaporation of cold saturated solutions. These solutions were protected from sudden changes of temperature and from the access of disturbing atmospheric influences by enclosing them under a large vase, and supporting the small, flat bottomed beakers containing them upon, and surrounding them by, badly-conducting materials. The slow evaporation was brought about at ordinary pressure by enclosing along with them a shallow glass dish containing oil of vitriol.

Eleven of the best crystals of suitable small size were selected from these three crops and measured with an amount of completeness which is indicated in the table of measurements. These 11 crystals were all single individuals exhibiting most of the faces marked upon the spherical projection.

The *ratio of the axes* deduced from the very large number of measurements (1160) made upon the 11 crystals above mentioned is

$$a : b : c = 0.5727 : 1 : 0.7418.$$

The value of the ratio given by Mitscherlich is 0.5727 : 1 : 0.7464.

The *forms observed* include the whole of those indicated upon the spherical projection with the exception of the brachydome $q''' \{012\}$. They are:

$$\begin{aligned} a &= \{100\}_{\infty} \bar{P}_{\infty}; & b &= \{010\}_{\infty} \bar{P}_{\infty}; & c &= \{001\}_o P; & p &= \{110\}_{\infty} P; \\ p' &= \{130\}_{\infty} \bar{P}_3; & q &= \{011\} \bar{P}_{\infty}; & q' &= \{021\}_2 \bar{P}_{\infty}; & q'' &= \{031\}_3 \bar{P}_{\infty}; \\ o &= \{111\} P; & o' &= \{112\}_{\frac{1}{2}} P; & o'' &= \{332\}_{\frac{3}{2}} P. \end{aligned}$$

The forms q'' and o'' do not appear to have been observed either by Mitscherlich or by Rammelsberg, who also made a few measurements of crystals of this salt.

The above forms were relatively developed upon the 11 particularly perfect crystals specially studied in such a manner as to produce the four distinct types of habit portrayed in Figs. 2, 3, 4, and 5, which appeared likewise to be more or less characteristic of the whole of the individuals belonging to the numerous crops prepared.

FIG. 2.

FIG. 3.

FIG. 4.

FIG. 5.

In the crystals of the first type a short prismatic habit is exhibited, the prisms being formed by the faces of the brachypinacoid $b\{010\}$ which were usually developed to the largest extent, those of the brachydome $q''\{021\}$ which came next in importance, and those of the primary brachydome $q\{011\}$ and the basal plane $c\{001\}$, both of which latter forms were usually represented by much narrower faces. The end faces were relatively developed as shown in Fig. 2, and consisted of narrow faces of the macropinacoid $a\{100\}$, and broader faces of the primary prism $p\{110\}$ and of the prismatic form $p'\{130\}$, which two latter forms were more or less equally developed, the faces

of the primary prism as a rule slightly predominating. Of the pyramidal forms, the faces of the primary pyramid $o\{111\}$ were always well developed, those of the pyramid $o'\{112\}$ being generally smaller but always bright and plane. The brachydome $q''\{031\}$ was occasionally found well developed, but the pyramidal form $o''\{332\}$ was only rarely observed and was then small and not very bright.

In the crystals of the second type, represented in Fig. 3, the brachypinacoid $b\{010\}$ is so largely the predominating form as to impart to them a tabular habit. The crystals of this type present the appearance of square, flat plates, bevelled by the same prismatic and brachydomal forms mentioned in the description of the first type, and modified at the corners by the same pyramidal forms.

The crystals of potassium sulphate of the third type observed are distinguished by the large predominance of the faces of the brachydome $q'\{021\}$, at the expense of the faces of the brachypinacoid $b\{010\}$, which are frequently reduced to a narrow strip as shown in Fig. 4, and often to a line. The faces of the primary pyramid $o\{111\}$ are also relatively very largely developed in crystals of this type, the faces of the primary prism $p\{110\}$ and of the prism $p'\{130\}$ being reduced to the relative dimensions attributed to them in the figure.

A considerable number of the larger crystals belonging to certain crops were found to exhibit an abnormal development of the brachydome $q''\{031\}$, as represented in Fig. 5, giving them the appearance of flat double-wedges. They were frequently elongated parallel to the edges of the wedges, and their ends were principally formed by faces of the primary prism $p\{110\}$, the corners being but relatively slightly modified by small faces of the pyramids $o\{111\}$ and $o'\{112\}$. The faces of the prismatic form $p'\{130\}$ and of the other brachydomes $q\{011\}$ and $q'\{021\}$ were all relatively very small.

Numerous triplet or twin crystals, resembling hexagonal pyramids, twinned upon a plane nearly perpendicular to the faces of the primary prism, or the prism $p'\{130\}$, in the well-known manner described by Mitscherlich and Scacchi, were also observed.

The whole of the faces of the generally occurring forms above described, with the exception of the faces of the brachydome $q'\{021\}$, afforded as a rule excellent single images of the signal, frequently of the most brilliant and perfectly defined character. In a number of cases the q' faces likewise yielded unexceptionable single images, and in such cases the values obtained for the angles involving these faces coincided almost to a minute with the calculated values. In other cases these faces were slightly affected by striation and distortion, and only those values were accepted where the uncertainty was very slight.

Following is a table exhibiting the results of the very large number of measurements made:

Angle measured.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.
$\begin{cases} ap = 100 : 110 \\ pp' = 110 : 130 \\ p'b = 130 : 010 \end{cases}$	$\begin{matrix} 29 \\ 30 \\ 32 \end{matrix}$	$\begin{matrix} 29^{\circ} 45' - 29^{\circ} 52' \\ 29 55 - 30 4 \\ 30 8 - 30 15 \end{matrix}$	$\begin{matrix} 29^{\circ} 48' \\ 30 0 \\ 30 11 \end{matrix}$	$\begin{matrix} 29^{\circ} 48' \\ 30 0 \\ 30 12 \end{matrix}$	$\begin{matrix} 0' \\ 0 \\ 1 \end{matrix}$
$\begin{cases} cq = 001 : 011 \\ qq' = 011 : 021 \\ cq' = 001 : 021 \\ q'q'' = 021 : 031 \\ q'b = 031 : 010 \\ q'b = 021 : 010 \end{cases}$	$\begin{matrix} 16 \\ 16 \\ 29 \\ 7 \\ 8 \\ 30 \end{matrix}$	$\begin{matrix} 36 31 - 36 41 \\ 19 20 - 19 31 \\ 55 55 - 56 9 \\ 9 40 - 9 55 \\ 24 7 - 24 19 \\ 33 52 - 34 5 \end{matrix}$	$\begin{matrix} 36 36 \\ 19 26 \\ 56 2 \\ 9 44 \\ 24 13 \\ 33 59 \end{matrix}$	$\begin{matrix} 36 34 \\ 19 27 \\ 56 1 \\ 9 47 \\ 24 12 \\ 33 59 \end{matrix}$	$\begin{matrix} 2 \\ 1 \\ 1 \\ 3 \\ 1 \\ 0 \end{matrix}$
$\begin{cases} ao = 100 : 111 \\ oq = 111 : 011 \end{cases}$	$\begin{matrix} 68 \\ 58 \end{matrix}$	$\begin{matrix} 43 45 - 44 0 \\ 46 4 - 46 15 \end{matrix}$	$\begin{matrix} 43 52 \\ 46 8 \end{matrix}$	$\begin{matrix} * \\ 46 8 \end{matrix}$	$\begin{matrix} \\ 0 \end{matrix}$
$\begin{cases} ao' = 100 : 112 \\ o'o' = 112 : 112 \end{cases}$	$\begin{matrix} 27 \\ 7 \end{matrix}$	$\begin{matrix} 58 38 - 58 47 \\ 62 30 - 62 38 \end{matrix}$	$\begin{matrix} 58 44 \\ 62 34 \end{matrix}$	$\begin{matrix} 58 44 \\ 62 32 \end{matrix}$	$\begin{matrix} 0 \\ 2 \end{matrix}$
$\begin{cases} bo = 010 : 111 \\ oo = 111 : 111 \end{cases}$	$\begin{matrix} 73 \\ 33 \end{matrix}$	$\begin{matrix} 65 32 - 65 41 \\ 48 40 - 48 52 \end{matrix}$	$\begin{matrix} 65 36 \\ 48 47 \end{matrix}$	$\begin{matrix} 65 37 \\ 48 46 \end{matrix}$	$\begin{matrix} 1 \\ 1 \end{matrix}$
$\begin{cases} bo' = 010 : 112 \\ o'o' = 112 : 112 \end{cases}$	$\begin{matrix} 25 \\ 7 \end{matrix}$	$\begin{matrix} 72 38 - 72 48 \\ 34 31 - 34 41 \end{matrix}$	$\begin{matrix} 72 42 \\ 34 36 \end{matrix}$	$\begin{matrix} 72 42 \\ 34 36 \end{matrix}$	$\begin{matrix} 0 \\ 0 \end{matrix}$
$\begin{cases} co' = 001 : 112 \\ o'o = 112 : 111 \\ co = 001 : 111 \\ oo'' = 111 : 332 \\ o'p = 332 : 110 \\ op = 111 : 110 \end{cases}$	$\begin{matrix} 35 \\ 37 \\ 80 \\ 1 \\ 1 \\ 84 \end{matrix}$	$\begin{matrix} 36 38 - 36 51 \\ 19 16 - 19 33 \\ 56 6 - 56 17 \\ - \\ - \\ 33 42 - 33 57 \end{matrix}$	$\begin{matrix} 36 45 \\ 19 26 \\ 56 11 \\ 9 49 \\ 24 8 \\ 33 49 \end{matrix}$	$\begin{matrix} 36 44 \\ 19 27 \\ * \\ 9 45 \\ 24 4 \\ 33 49 \end{matrix}$	$\begin{matrix} 1 \\ 1 \\ \\ 4 \\ 4 \\ 0 \end{matrix}$
$\begin{cases} po = 110 : 111 \\ oq' = 111 : 021 \\ q'p = 021 : 110 \end{cases}$	$\begin{matrix} 55 \\ 45 \\ 49 \end{matrix}$	$\begin{matrix} 65 2 - 65 13 \\ 49 6 - 49 15 \\ 65 32 - 65 50 \end{matrix}$	$\begin{matrix} 65 9 \\ 49 11 \\ 65 40 \end{matrix}$	$\begin{matrix} 65 8 \\ 49 12 \\ 65 40 \end{matrix}$	$\begin{matrix} 1 \\ 1 \\ 0 \end{matrix}$
$\begin{cases} po' = 110 : 112 \\ o'q = 112 : 011 \\ qp = 011 : 110 \end{cases}$	$\begin{matrix} 21 \\ 15 \\ 23 \end{matrix}$	$\begin{matrix} 72 19 - 72 27 \\ 34 49 - 34 57 \\ 72 43 - 72 52 \end{matrix}$	$\begin{matrix} 72 23 \\ 34 52 \\ 72 46 \end{matrix}$	$\begin{matrix} 72 23 \\ 34 50 \\ 72 47 \end{matrix}$	$\begin{matrix} 0 \\ 2 \\ 1 \end{matrix}$
$\begin{cases} p'o = 130 : 111 \\ oo' = 111 : 112 \\ o'q' = 112 : 021 \\ oq' = 111 : 021 \\ q'p' = 021 : 130 \end{cases}$	$\begin{matrix} 46 \\ 23 \\ 20 \\ 39 \\ 42 \end{matrix}$	$\begin{matrix} 43 54 - 44 6 \\ 45 44 - 45 52 \\ 45 53 - 46 7 \\ 91 38 - 91 55 \\ 44 5 - 44 23 \end{matrix}$	$\begin{matrix} 43 59 \\ 45 47 \\ 46 0 \\ 91 47 \\ 44 13 \end{matrix}$	$\begin{matrix} 43 59 \\ 45 47 \\ 46 1 \\ 91 48 \\ 44 13 \end{matrix}$	$\begin{matrix} 0 \\ 0 \\ 1 \\ 1 \\ 0 \end{matrix}$
$\begin{cases} p'o' = 130 : 112 \\ o'q' = 112 : 011 \\ q'p' = 011 : 130 \end{cases}$	$\begin{matrix} 19 \\ 12 \\ 18 \end{matrix}$	$\begin{matrix} 58 43 - 58 53 \\ 62 10 - 62 18 \\ 58 55 - 59 1 \end{matrix}$	$\begin{matrix} 58 48 \\ 62 14 \\ 58 58 \end{matrix}$	$\begin{matrix} 58 48 \\ 62 12 \\ 59 0 \end{matrix}$	$\begin{matrix} 0 \\ 0 \\ 2 \end{matrix}$

Total number of measurements, 1160.

The two angles ao and co , represented in the "calculated" column by asterisks, were fundamental angles occurring eight times upon each fully developed crystal, and which on account of the usual excellence of the faces involving them together with the large number of measurements made of them, were employed as the two necessary basal measured angles from which the remaining angles were all calculated in order to afford a check on the accuracy of the measure-

ments. The remarkably close agreement between the mean observed and the calculated values affords ample justification for the exhaustive method of work adopted, a method which it was considered particularly advisable to follow in view of the small angular differences expected between the three salts.

Rubidium Sulphate, Rb_2SO_4 .

Rubidium sulphate is only to be obtained in the form of good single crystals from cold saturated solutions; it usually crystallises from warm solutions in feathery aggregates of minute individuals. Five crops of particularly well-defined and eminently suitable single crystals were obtained, among others, by very slow evaporation of cold solutions in the manner described in the case of the potassium salt, and ten excellent individuals were chosen and subjected to measurement.

The ratio of the axes calculated from the measurements made upon the 10 selected crystals is—

$$a : b : c = 0.5723 : 1 : 0.7485.$$

The ratio given by Bunsen in 1861 is 0.5723 : 1 : 0.7522 (*Annalen*, 119, 110).

The forms observed include all those marked on the spherical projection with the exception of $o''\{332\}$ and $q''\{031\}$. They are—

$$\begin{aligned} a &= \{100\}\infty\bar{P}\infty; & b &= \{010\}\infty\bar{P}\infty; & c &= \{001\}0P; & p &= \{110\}\infty P; \\ p' &= \{130\}\infty\bar{P}3; & q &= \{011\}\bar{P}\infty; & q' &= \{021\}2\bar{P}\infty; & q'' &= \{012\}\frac{1}{2}\bar{P}\infty; \\ o &= \{111\}P; & o' &= \{112\}\frac{1}{2}P. \end{aligned}$$

The habit of the crystals of rubidium sulphate differs considerably from that of potassium sulphate represented in Fig. 2 and in Fig. 3, and resembles more that depicted in Fig. 4, inasmuch as the faces of the brachypinacoid $b\{010\}$ are usually extremely narrow, as shown in Fig. 6, while those of the brachydome $q'\{021\}$ are so largely predominating as to impart to the crystals a prismatic habit, the prisms being mainly formed by q' faces. The terminations of the prisms are formed by relatively large faces of the macropinacoid $a\{100\}$ and smaller faces of the prism $p'\{130\}$ and the pyramids $o\{111\}$ and $o'\{112\}$. The primary prism $p\{110\}$ is but rarely developed, it was only found well developed upon two of the crystals measured. The primary pyramid $o\{111\}$ was usually a prominent form, but its faces were frequently equalled in size and brilliancy by those of the pyramid $o'\{112\}$, which were, as a rule, much more largely developed than upon the crystals of potassium sulphate. The basal plane $c\{001\}$ was usually but narrow; the edges cq' were modified as a rule by equally narrow faces of the primary brachydome $q\{011\}$. Upon

one crystal a good face of the exceptionally occurring brachydome $q'''\{012\}$ was observed.

In certain crops, the faces of the brachypinacoid $b\{010\}$ were somewhat more largely developed, as shown in Fig. 7. A characteristic

FIG. 6.

FIG. 7.

FIG. 8.

FIG. 9.

form of rubidium sulphate is also exhibited in Fig. 8; the habit is that of a low pyramid constructed upon a broad base parallel to the macropinacoid $a\{100\}$, and, owing to growth being impeded in a downward direction by the horizontal surface of the vessel in which the crystal is growing, the pyramid faces $o\{111\}$ and $o'\{112\}$ are either only formed, or only to any considerable extent, upon one side (that is, at one end of the axis a). The summit of the pyramid is usually formed by a fairly broad macropinacoid face, of less extent, however, than the basal macropinacoid face. Occasionally similar low pyramids are met with whose bases are parallel to the brachypinacoid $b\{010\}$ or the basal plane $c\{001\}$.

Crystals of rubidium sulphate of still another type were not infrequently observed. They were apparently hexagonal pyramids, as represented in Fig. 9, and the close approximation of the angles in

the prism zone to 30° , and the closeness of the angles po and bq' , rendered them difficult at first to distinguish from truly hexagonal pyramids. The form is entirely due to the almost equal development of the faces of the primary pyramid $o\{111\}$ and the brachydome $q'\{021\}$, while the o' and q faces are relatively very small.

Moreover, triplet crystals of the same type as the well-known ones of potassium sulphate, twinned upon a plane almost perpendicular to the primary prism faces, were also observed. They frequently formed complete doubly-terminated hexagonal pyramids, and the

Angle measured.	No. of measure- ments.	Limits.	Mean. observed.	Calculated.	Diff.
$\left\{ \begin{array}{l} ap = 100 : 110 \\ pp' = 110 : 130 \\ ap' = 100 : 130 \\ p'b = 130 : 010 \end{array} \right.$	$\left\{ \begin{array}{l} 2 \\ 2 \\ 21 \\ 25 \end{array} \right.$	$\left\{ \begin{array}{l} 29^\circ 45' - 29^\circ 46' \\ 30 \quad 0 - 30 \quad 4 \\ 59 \quad 43 - 59 \quad 54 \\ 30 \quad 10 - 30 \quad 17 \end{array} \right.$	$\left\{ \begin{array}{l} 29^\circ 46' \\ 30 \quad 2 \\ 59 \quad 47 \\ 30 \quad 12 \end{array} \right.$	$\left\{ \begin{array}{l} 29^\circ 47' \\ 30 \quad 0 \\ 59 \quad 47 \\ 30 \quad 13 \end{array} \right.$	$\left\{ \begin{array}{l} 1' \\ 2 \\ 0 \\ 1 \end{array} \right.$
$\left\{ \begin{array}{l} cq''' = 001 : 012 \\ q'''q = 012 : 011 \\ cq = 001 : 011 \\ qq' = 011 : 021 \\ cq' = 001 : 021 \\ q'b = 021 : 010 \end{array} \right.$	$\left\{ \begin{array}{l} 1 \\ 1 \\ 18 \\ 16 \\ 29 \\ 28 \end{array} \right.$	$\left\{ \begin{array}{l} - \\ - \\ 36 \quad 44 - 36 \quad 55 \\ 19 \quad 21 - 19 \quad 31 \\ 56 \quad 8 - 56 \quad 25 \\ 33 \quad 33 - 33 \quad 53 \end{array} \right.$	$\left\{ \begin{array}{l} 20 \quad 29 \\ 16 \quad 18 \\ 36 \quad 50 \\ 19 \quad 26 \\ 56 \quad 17 \\ 33 \quad 42 \end{array} \right.$	$\left\{ \begin{array}{l} 20 \quad 31 \\ 16 \quad 18 \\ 36 \quad 49 \\ 19 \quad 26 \\ 56 \quad 15 \\ 33 \quad 45 \end{array} \right.$	$\left\{ \begin{array}{l} 2 \\ 0 \\ 1 \\ 0 \\ 2 \\ 3 \end{array} \right.$
$\left\{ \begin{array}{l} ao = 100 : 111 \\ oq = 111 : 011 \end{array} \right.$	$\left\{ \begin{array}{l} 64 \\ 43 \end{array} \right.$	$\left\{ \begin{array}{l} 43 \quad 33 - 43 \quad 48 \\ 46 \quad 10 - 46 \quad 24 \end{array} \right.$	$\left\{ \begin{array}{l} 43 \quad 41 \\ 46 \quad 19 \end{array} \right.$	$\left\{ \begin{array}{l} * \\ 46 \quad 19 \end{array} \right.$	$\left\{ \begin{array}{l} \\ 0 \end{array} \right.$
$\left\{ \begin{array}{l} ao' = 100 : 112 \\ o'q''' = 112 : 012 \\ o'o' = 112 : 112 \end{array} \right.$	$\left\{ \begin{array}{l} 39 \\ 1 \\ 12 \end{array} \right.$	$\left\{ \begin{array}{l} 58 \quad 25 - 58 \quad 34 \\ - \\ 62 \quad 56 - 63 \quad 2 \end{array} \right.$	$\left\{ \begin{array}{l} 58 \quad 30 \\ 31 \quad 34 \\ 62 \quad 59 \end{array} \right.$	$\left\{ \begin{array}{l} 58 \quad 31 \\ 31 \quad 29 \\ 62 \quad 58 \end{array} \right.$	$\left\{ \begin{array}{l} 1 \\ 5 \\ 1 \end{array} \right.$
$\left\{ \begin{array}{l} bo = 010 : 111 \\ oo = 111 : 111 \end{array} \right.$	$\left\{ \begin{array}{l} 38 \\ 17 \end{array} \right.$	$\left\{ \begin{array}{l} 65 \quad 28 - 65 \quad 38 \\ 48 \quad 48 - 49 \quad 2 \end{array} \right.$	$\left\{ \begin{array}{l} 65 \quad 33 \\ 48 \quad 54 \end{array} \right.$	$\left\{ \begin{array}{l} 65 \quad 33 \\ 48 \quad 54 \end{array} \right.$	$\left\{ \begin{array}{l} 0 \\ 0 \end{array} \right.$
$\left\{ \begin{array}{l} bo' = 010 : 112 \\ o'o' = 112 : 112 \end{array} \right.$	$\left\{ \begin{array}{l} 20 \\ 13 \end{array} \right.$	$\left\{ \begin{array}{l} 72 \quad 32 - 72 \quad 42 \\ 34 \quad 42 - 34 \quad 52 \end{array} \right.$	$\left\{ \begin{array}{l} 72 \quad 37 \\ 34 \quad 47 \end{array} \right.$	$\left\{ \begin{array}{l} 72 \quad 37 \\ 34 \quad 46 \end{array} \right.$	$\left\{ \begin{array}{l} 0 \\ 1 \end{array} \right.$
$\left\{ \begin{array}{l} co' = 001 : 112 \\ o'o = 112 : 111 \\ co = 001 : 111 \\ op = 111 : 110 \\ oo = 111 : 111 \end{array} \right.$	$\left\{ \begin{array}{l} 51 \\ 42 \\ 62 \\ 7 \\ 22 \end{array} \right.$	$\left\{ \begin{array}{l} 36 \quad 52 - 37 \quad 6 \\ 19 \quad 19 - 19 \quad 31 \\ 56 \quad 19 - 56 \quad 33 \\ 33 \quad 28 - 33 \quad 38 \\ 67 \quad 1 - 67 \quad 14 \end{array} \right.$	$\left\{ \begin{array}{l} 37 \quad 0 \\ 19 \quad 26 \\ 56 \quad 26 \\ 33 \quad 34 \\ 67 \quad 8 \end{array} \right.$	$\left\{ \begin{array}{l} 37 \quad 0 \\ 19 \quad 26 \\ * \\ 33 \quad 34 \\ 67 \quad 8 \end{array} \right.$	$\left\{ \begin{array}{l} 0 \\ 0 \\ \\ 0 \\ 0 \end{array} \right.$
$\left\{ \begin{array}{l} po = 110 : 111 \\ oq' = 111 : 021 \\ q'p = 021 : 110 \end{array} \right.$	$\left\{ \begin{array}{l} 5 \\ 19 \\ 5 \end{array} \right.$	$\left\{ \begin{array}{l} 64 \quad 59 - 65 \quad 5 \\ 49 \quad 18 - 49 \quad 27 \\ 65 \quad 32 - 65 \quad 37 \end{array} \right.$	$\left\{ \begin{array}{l} 65 \quad 3 \\ 49 \quad 22 \\ 65 \quad 35 \end{array} \right.$	$\left\{ \begin{array}{l} 65 \quad 2 \\ 49 \quad 22 \\ 65 \quad 36 \end{array} \right.$	$\left\{ \begin{array}{l} 1 \\ 0 \\ 1 \end{array} \right.$
$\left\{ \begin{array}{l} po' = 110 : 112 \\ o'q = 112 : 011 \\ qp = 011 : 110 \end{array} \right.$	$\left\{ \begin{array}{l} 4 \\ 10 \\ 2 \end{array} \right.$	$\left\{ \begin{array}{l} 72 \quad 12 - 72 \quad 19 \\ 35 \quad 2 - 35 \quad 7 \\ 72 \quad 35 - 72 \quad 41 \end{array} \right.$	$\left\{ \begin{array}{l} 72 \quad 15 \\ 35 \quad 5 \\ 72 \quad 38 \end{array} \right.$	$\left\{ \begin{array}{l} 72 \quad 15 \\ 35 \quad 4 \\ 72 \quad 41 \end{array} \right.$	$\left\{ \begin{array}{l} 0 \\ 1 \\ 3 \end{array} \right.$
$\left\{ \begin{array}{l} p'o = 130 : 111 \\ oo' = 111 : 112 \\ o'q' = 112 : 021 \\ q'p' = 021 : 130 \end{array} \right.$	$\left\{ \begin{array}{l} 36 \\ 23 \\ 30 \\ 45 \end{array} \right.$	$\left\{ \begin{array}{l} 43 \quad 44 - 43 \quad 55 \\ 45 \quad 51 - 46 \quad 1 \\ 46 \quad 6 - 46 \quad 16 \\ 43 \quad 59 - 44 \quad 8 \end{array} \right.$	$\left\{ \begin{array}{l} 43 \quad 48 \\ 45 \quad 57 \\ 46 \quad 11 \\ 44 \quad 3 \end{array} \right.$	$\left\{ \begin{array}{l} 43 \quad 49 \\ 45 \quad 55 \\ 46 \quad 12 \\ 44 \quad 4 \end{array} \right.$	$\left\{ \begin{array}{l} 1 \\ 2 \\ 1 \\ 1 \end{array} \right.$
$\left\{ \begin{array}{l} p'o' = 130 : 112 \\ o'q = 112 : 011 \\ qp' = 011 : 130 \end{array} \right.$	$\left\{ \begin{array}{l} 30 \\ 15 \\ 22 \end{array} \right.$	$\left\{ \begin{array}{l} 58 \quad 31 - 58 \quad 40 \\ 62 \quad 35 - 62 \quad 41 \\ 58 \quad 45 - 58 \quad 52 \end{array} \right.$	$\left\{ \begin{array}{l} 58 \quad 35 \\ 62 \quad 38 \\ 58 \quad 47 \end{array} \right.$	$\left\{ \begin{array}{l} 58 \quad 35 \\ 62 \quad 36 \\ 58 \quad 49 \end{array} \right.$	$\left\{ \begin{array}{l} 0 \\ 2 \\ 2 \end{array} \right.$

Total number of measurements, 820.

true single crystals of the type last described are very difficult to distinguish from them. Measurement of the angles po and bq' proves the difference, for the angular values differ by $8'$, whereas if both are po angles as in the triplets the angles are of course identical. Moreover, in the triplets the faces are not plane, but usually exhibit a line of union along the middle, and the halves on the different sides of the dividing line afford separate reflected images, well apart from each other, owing to the angle of the primary prism not being quite 60° .

The faces of the whole of the forms above enumerated, with the exception of those of the predominating brachydome $q'\{021\}$, were usually plane and bright, yielding good images of the signal. The q' faces were generally more or less striated, and yielded, when adjusted for the zone cqb , a number of images close together. Upon several of the selected crystals measured, however, plane q' faces were present, and afforded excellent single reflections of the signal; the angular values derived from these irreproachable faces coincided almost exactly with the mean of all the observed values of the angles involving the faces of this form.

The results of the measurements are recorded in the table on p. 640.

The same remarks apply to the close agreement of the mean observed and the calculated values as were made in the case of potassium sulphate.

Cæsium Sulphate, Cs₂SO₄.

There is no difficulty in obtaining apparently excellent single crystals of this salt, no tendency to form feathery aggregates being observed as is the case with rubidium sulphate. The crystals grow to large size when left undisturbed.

Spectroscopic examination as previously detailed afforded no indications of impurities, but, in order to be certain of their purity, the crystals measured were chosen from crops which had been several times fractionally recrystallised.

Eleven crystals belonging to five distinct crops were measured in the same manner as those of the sulphates of potassium and rubidium. The comparatively smaller total of measurements, 526, made in the case of cæsium sulphate is owing to the fact that the crystals of this salt are not so rich in faces as those of the other two sulphates. The number of measurements is relatively as large as regards the planes which are developed.

The ratio of the axes calculated from the measurements is—

$$a : b : c = 0.5712 : 1 : 0.7531.$$

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The ratio deduced from Von Lang's measurements (*Sitz. Ber. der Wien Akad.*, 55, 2, 415), and quoted by Topsøe (*loc. cit.*), is $a : b : c = 0.5805 : 1 : 0.7400$.

The forms observed are not so numerous as upon crystals of potassium and rubidium sulphates, the brachydomes $q''\{031\}$ and $q'''\{012\}$ and the pyramid $o''\{332\}$ not having been observed upon the 11 crystals exhaustively examined. The forms present are—

$a = \{100\} \infty \bar{P} \infty$; $b = \{010\} \infty \bar{P} \infty$; $c = \{001\} 0P$; $p = \{110\} \infty P$; $p' = \{130\} \infty \bar{P} 3$; $q = \{011\} \bar{P} \infty$; $q' = \{021\} 2\bar{P} \infty$; $o = \{111\} P$; $o' = \{112\} \frac{1}{2} P$.

The crystals of caesium sulphate usually exhibit a much larger development of the basal plane $c\{001\}$ than those of potassium and rubidium sulphates. They generally consist, as represented in Fig. 10, of stout rectangular blocks formed by the faces of the two pinacoids $a\{100\}$ and $b\{010\}$ and the basal plane $c\{001\}$, which latter, to a greater or smaller extent, predominates, the crystals thus exhibiting a tabular habit in this direction. The edges bc are, as a rule, modified by the brachydomes $q\{011\}$ and $q'\{021\}$, more or less equally developed to about the extent shown in the figure. Of the two prismatic forms $p\{110\}$ and $p'\{130\}$, the latter was most frequently present, and developed to the relatively larger, although still small, extent; the faces of the primary prism $p\{110\}$ were either very minute or failed altogether. The faces of the primary pyramid $o\{111\}$ were the largest after the pinacoids and basal plane, the corners of the rectangular block being extensively truncated by them. The crystals of the caesium salt differ from those of the other two sulphates in rarely exhibiting faces of the pyramid $o'\{112\}$. A small face of this form was, however, discovered upon one of the crystals employed in the measurements.

FIG. 10.

In certain crops, crystals were observed of which Fig. 11 is typical, in which the faces of the brachypinacoid $b\{010\}$ predominated over

those of the basal plane, thereby inducing a tabular habit in a direction at right angles to that of the ordinary type above described. The basal plane and macropinacoid were always important planes, however, the former rarely becoming reduced to such small dimensions as are exhibited by crystals of both the potassium and the caesium salt. No twins or triplet crystals of caesium sulphate were observed; numerous cases of intergrowths of crystals were examined, but none in which definite evidence of true twinning could be found.

The reflections afforded by the smaller faces of the crystals of the caesium salt were not usually of so highly perfect a character as those yielded by the crystals of the other two sulphates, being as a rule

Angle measured.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.
$\left\{ \begin{array}{l} ap = 100 : 110 \\ pp' = 110 : 130 \\ ap' = 100 : 130 \\ p'b = 130 : 010 \end{array} \right.$	$\left\{ \begin{array}{l} 6 \\ 5 \\ 15 \\ 16 \end{array} \right.$	$\left\{ \begin{array}{l} 29^{\circ} 42' - 29^{\circ} 49' \\ 29 56 - 30 3 \\ 59 39 - 59 53 \\ 30 10 - 30 18 \end{array} \right.$	$\left\{ \begin{array}{l} 29^{\circ} 45' \\ 30 0 \\ 59 45 \\ 30 15 \end{array} \right.$	$\left\{ \begin{array}{l} 29^{\circ} 44' \\ 30 0 \\ 59 44 \\ 30 16 \end{array} \right.$	$\left\{ \begin{array}{l} 1' \\ 0 \\ 1 \\ 1 \end{array} \right.$
$\left\{ \begin{array}{l} cq = 001 : 011 \\ qq' = 011 : 021 \\ cq' = 001 : 021 \\ q'b = 021 : 010 \end{array} \right.$	$\left\{ \begin{array}{l} 33 \\ 18 \\ 22 \\ 25 \end{array} \right.$	$\left\{ \begin{array}{l} 36 50 - 37 10 \\ 19 14 - 19 38 \\ 56 20 - 56 30 \\ 33 21 - 33 41 \end{array} \right.$	$\left\{ \begin{array}{l} 36 59 \\ 19 25 \\ 56 25 \\ 33 34 \end{array} \right.$	$\left\{ \begin{array}{l} 36 59 \\ 19 26 \\ 56 25 \\ 33 35 \end{array} \right.$	$\left\{ \begin{array}{l} 0 \\ 1 \\ 0 \\ 1 \end{array} \right.$
$\left\{ \begin{array}{l} ao = 100 : 111 \\ oq = 111 : 011 \end{array} \right.$	$\left\{ \begin{array}{l} 67 \\ 59 \end{array} \right.$	$\left\{ \begin{array}{l} 43 24 - 43 36 \\ 46 23 - 46 35 \end{array} \right.$	$\left\{ \begin{array}{l} 43 31 \\ 46 28 \end{array} \right.$	$\left\{ \begin{array}{l} * \\ 46 29 \end{array} \right.$	$\left\{ \begin{array}{l} \\ 1 \end{array} \right.$
$\left\{ \begin{array}{l} ao' = 100 : 112 \\ o'o' = 112 : 112 \end{array} \right.$	$\left\{ \begin{array}{l} - \\ - \end{array} \right.$	$\left\{ \begin{array}{l} - \\ - \end{array} \right.$	$\left\{ \begin{array}{l} - \\ - \end{array} \right.$	$\left\{ \begin{array}{l} 58 19 \\ 63 22 \end{array} \right.$	$\left\{ \begin{array}{l} \\ \end{array} \right.$
$\left\{ \begin{array}{l} bo = 010 : 111 \\ oo = 111 : 111 \end{array} \right.$	$\left\{ \begin{array}{l} 51 \\ 20 \end{array} \right.$	$\left\{ \begin{array}{l} 65 27 - 65 39 \\ 48 51 - 49 3 \end{array} \right.$	$\left\{ \begin{array}{l} 65 31 \\ 48 57 \end{array} \right.$	$\left\{ \begin{array}{l} 65 32 \\ 48 56 \end{array} \right.$	$\left\{ \begin{array}{l} 1 \\ 1 \end{array} \right.$
$\left\{ \begin{array}{l} bo' = 010 : 112 \\ o'o' = 112 : 112 \end{array} \right.$	$\left\{ \begin{array}{l} - \\ - \end{array} \right.$	$\left\{ \begin{array}{l} - \\ - \end{array} \right.$	$\left\{ \begin{array}{l} - \\ - \end{array} \right.$	$\left\{ \begin{array}{l} 72 33 \\ 34 54 \end{array} \right.$	$\left\{ \begin{array}{l} \\ \end{array} \right.$
$\left\{ \begin{array}{l} co' = 001 : 112 \\ o'o = 112 : 111 \\ co = 001 : 111 \\ op = 111 : 110 \\ oo = 111 : 111 \end{array} \right.$	$\left\{ \begin{array}{l} 1 \\ 1 \\ 73 \\ 20 \\ 33 \end{array} \right.$	$\left\{ \begin{array}{l} - \\ - \\ 56 27 - 56 49 \\ 33 10 - 33 28 \\ 66 34 - 66 53 \end{array} \right.$	$\left\{ \begin{array}{l} 37 10 \\ 19 20 \\ 56 38 \\ 33 21 \\ 66 44 \end{array} \right.$	$\left\{ \begin{array}{l} 37 13 \\ 19 25 \\ * \\ 33 22 \\ 66 44 \end{array} \right.$	$\left\{ \begin{array}{l} 3 \\ 5 \\ \\ 1 \\ 0 \end{array} \right.$
$\left\{ \begin{array}{l} po = 110 : 111 \\ oq' = 111 : 021 \\ q'p = 021 : 110 \end{array} \right.$	$\left\{ \begin{array}{l} 6 \\ 13 \\ 4 \end{array} \right.$	$\left\{ \begin{array}{l} 64 48 - 64 58 \\ 49 26 - 49 35 \\ 65 34 - 65 42 \end{array} \right.$	$\left\{ \begin{array}{l} 64 52 \\ 49 30 \\ 65 36 \end{array} \right.$	$\left\{ \begin{array}{l} 64 54 \\ 49 30 \\ 65 36 \end{array} \right.$	$\left\{ \begin{array}{l} 2 \\ 0 \\ 0 \end{array} \right.$
$\left\{ \begin{array}{l} po' = 110 : 112 \\ o'q = 112 : 011 \\ qp = 011 : 110 \end{array} \right.$	$\left\{ \begin{array}{l} - \\ - \\ 2 \end{array} \right.$	$\left\{ \begin{array}{l} - \\ - \\ 72 35 - 72 41 \end{array} \right.$	$\left\{ \begin{array}{l} - \\ - \\ 72 38 \end{array} \right.$	$\left\{ \begin{array}{l} 72 7 \\ 35 15 \\ 72 38 \end{array} \right.$	$\left\{ \begin{array}{l} \\ \\ 0 \end{array} \right.$
$\left\{ \begin{array}{l} po' = 130 : 111 \\ oo' = 111 : 112 \\ o'q' = 112 : 021 \\ oq' = 111 : 021 \\ q'p' = 021 : 130 \end{array} \right.$	$\left\{ \begin{array}{l} 13 \\ - \\ - \\ 8 \\ 10 \end{array} \right.$	$\left\{ \begin{array}{l} 43 32 - 43 46 \\ - \\ - \\ 92 17 - 92 26 \\ 43 55 - 44 8 \end{array} \right.$	$\left\{ \begin{array}{l} 43 39 \\ - \\ - \\ 92 22 \\ 44 1 \end{array} \right.$	$\left\{ \begin{array}{l} 43 40 \\ 45 1 \\ 46 20 \\ 92 21 \\ 43 59 \end{array} \right.$	$\left\{ \begin{array}{l} 1 \\ \\ \\ 1 \\ 2 \end{array} \right.$
$\left\{ \begin{array}{l} p'o' = 130 : 112 \\ o'q' = 112 : 011 \\ qp' = 011 : 130 \end{array} \right.$	$\left\{ \begin{array}{l} - \\ - \\ 7 \end{array} \right.$	$\left\{ \begin{array}{l} - \\ - \\ 58 40 - 58 46 \end{array} \right.$	$\left\{ \begin{array}{l} - \\ - \\ 58 43 \end{array} \right.$	$\left\{ \begin{array}{l} 58 25 \\ 62 53 \\ 58 42 \end{array} \right.$	$\left\{ \begin{array}{l} \\ \\ 1 \end{array} \right.$

Total number of measurements, 528.

much less bright and exhibiting more or less of an oleaginous surface. The number of excellent and thoroughly trustworthy values obtained for several of the angles involving these faces is therefore smaller than in the cases of potassium and rubidium sulphates. The values recorded, however, were afforded by faces on the selected well-formed specimens to which no exception could be taken, all values affected by the slightest uncertainty being rejected. The larger faces as a rule gave irreproachable reflections.

The table on the preceding page represents the results of the measurements and calculations.

The agreement between the mean observed and the calculated values again leaves nothing to be desired, and comparisons may now be made with confidence between corresponding angles of the three salts.

Comparison of the Angular Magnitudes exhibited by the three Salts.

The following table (p. 645) exhibits the magnitudes of analogous angles in the three salts side by side, so as to afford a ready means of comparison.

The following interesting facts are observed.

The magnitudes of the whole of the angles of the rubidium salt, without a single exception, lie between those of the analogous angles upon the potassium and caesium salts respectively.

The differences between the magnitudes of analogous angles in these three rhombic normal sulphates are much smaller than were observed in the case of the double sulphates of the monoclinic series $R_2M(SO_4)_2 \cdot 6H_2O$, containing respectively potassium, rubidium, and caesium. It would appear that the higher the symmetry the closer is the isomorphism, until, in the higher forms of the cubic system, perfect identity of angular magnitude is attained.

The differences are too small to enable a definite statement to be made concerning the relation between the amounts of the differences corresponding to the replacement of potassium by rubidium and rubidium by caesium respectively. There is, however, a decided tendency towards greater equality in the differences than was observed in the case of the monoclinic double sulphates, the angles for the rubidium salt being generally more nearly midway between the values for the potassium and caesium salts.

A progressive change is thus observed to be brought about in the angular magnitudes of the crystals of the normal sulphates of potassium, rubidium, and caesium corresponding to the progressive change in the atomic weight of the contained metal, when potassium is replaced by rubidium and rubidium by caesium.

Angle.	Potassium sulphate.	Difference.	Rubidium sulphate.	Difference.	Cæsium sulphate.
$\left\{ \begin{array}{l} ap = 100 : 110 \\ pp' = 110 : 130 \\ p'b = 130 : 010 \end{array} \right.$	$\begin{array}{l} 29^{\circ} 48' \\ 30 \quad 0 \\ 30 \quad 12 \end{array}$	$\begin{array}{l} - 1' \\ 0 \\ + 1 \end{array}$	$\begin{array}{l} 29^{\circ} 47' \\ 30 \quad 0 \\ 30 \quad 13 \end{array}$	$\begin{array}{l} - 3' \\ 0 \\ + 3 \end{array}$	$\begin{array}{l} 29^{\circ} 44' \\ 30 \quad 0 \\ 30 \quad 16 \end{array}$
$\left\{ \begin{array}{l} cq''' = 001 : 012 \\ q'''q = 012 : 011 \\ cq = 001 : 011 \\ qq' = 011 : 021 \\ q'q'' = 021 : 031 \\ q''b = 031 : 010 \\ q'b = 021 : 010 \end{array} \right.$	$\begin{array}{l} 20 \quad 21 \\ 16 \quad 13 \\ 36 \quad 34 \\ 19 \quad 27 \\ 9 \quad 47 \\ 24 \quad 12 \\ 33 \quad 59 \end{array}$	$\begin{array}{l} + 10 \\ + 5 \\ + 15 \\ - 1 \\ - 2 \\ - 12 \\ - 14 \end{array}$	$\begin{array}{l} 20 \quad 31 \\ 16 \quad 18 \\ 36 \quad 49 \\ 19 \quad 26 \\ 9 \quad 45 \\ 24 \quad 0 \\ 33 \quad 45 \end{array}$	$\begin{array}{l} + 7 \\ + 3 \\ + 10 \\ 0 \\ - 3 \\ - 7 \\ - 10 \end{array}$	$\begin{array}{l} 20 \quad 38 \\ 16 \quad 21 \\ 36 \quad 59 \\ 19 \quad 26 \\ 9 \quad 42 \\ 23 \quad 53 \\ 33 \quad 35 \end{array}$
$\left\{ \begin{array}{l} ao = 100 : 111 \\ oq = 111 : 011 \end{array} \right.$	$\begin{array}{l} 43 \quad 52 \\ 46 \quad 8 \end{array}$	$\begin{array}{l} - 11 \\ + 11 \end{array}$	$\begin{array}{l} 43 \quad 41 \\ 46 \quad 19 \end{array}$	$\begin{array}{l} - 10 \\ + 10 \end{array}$	$\begin{array}{l} 43 \quad 31 \\ 46 \quad 29 \end{array}$
$\left\{ \begin{array}{l} ao' = 100 : 112 \\ o'o' = 112 : 112 \end{array} \right.$	$\begin{array}{l} 58 \quad 44 \\ 62 \quad 32 \end{array}$	$\begin{array}{l} - 13 \\ + 26 \end{array}$	$\begin{array}{l} 58 \quad 31 \\ 62 \quad 58 \end{array}$	$\begin{array}{l} - 12 \\ + 24 \end{array}$	$\begin{array}{l} 58 \quad 19 \\ 63 \quad 22 \end{array}$
$\left\{ \begin{array}{l} bo = 010 : 111 \\ oo = 111 : 111 \end{array} \right.$	$\begin{array}{l} 65 \quad 37 \\ 48 \quad 46 \end{array}$	$\begin{array}{l} - 4 \\ + 8 \end{array}$	$\begin{array}{l} 65 \quad 33 \\ 48 \quad 54 \end{array}$	$\begin{array}{l} - 1 \\ + 2 \end{array}$	$\begin{array}{l} 65 \quad 32 \\ 48 \quad 56 \end{array}$
$\left\{ \begin{array}{l} bo' = 010 : 112 \\ o'o' = 112 : 112 \end{array} \right.$	$\begin{array}{l} 72 \quad 42 \\ 34 \quad 36 \end{array}$	$\begin{array}{l} - 5 \\ + 10 \end{array}$	$\begin{array}{l} 72 \quad 37 \\ 34 \quad 46 \end{array}$	$\begin{array}{l} - 4 \\ + 8 \end{array}$	$\begin{array}{l} 72 \quad 33 \\ 34 \quad 54 \end{array}$
$\left\{ \begin{array}{l} co' = 001 : 112 \\ o'o = 112 : 111 \\ co = 001 : 111 \\ oo'' = 111 : 332 \\ o''p = 332 : 110 \\ op = 111 : 110 \end{array} \right.$	$\begin{array}{l} 36 \quad 44 \\ 19 \quad 27 \\ 56 \quad 11 \\ 9 \quad 45 \\ 24 \quad 4 \\ 33 \quad 49 \end{array}$	$\begin{array}{l} + 16 \\ - 1 \\ + 15 \\ - 3 \\ - 12 \\ - 15 \end{array}$	$\begin{array}{l} 37 \quad 0 \\ 19 \quad 26 \\ 56 \quad 26 \\ 9 \quad 42 \\ 23 \quad 52 \\ 33 \quad 34 \end{array}$	$\begin{array}{l} + 13 \\ - 1 \\ + 12 \\ - 2 \\ - 10 \\ - 12 \end{array}$	$\begin{array}{l} 37 \quad 13 \\ 19 \quad 25 \\ 56 \quad 38 \\ 9 \quad 40 \\ 23 \quad 42 \\ 33 \quad 22 \end{array}$
$\left\{ \begin{array}{l} po = 110 : 111 \\ oq' = 111 : 021 \\ q'p = 021 : 110 \end{array} \right.$	$\begin{array}{l} 65 \quad 8 \\ 49 \quad 12 \\ 65 \quad 40 \end{array}$	$\begin{array}{l} - 6 \\ + 10 \\ - 4 \end{array}$	$\begin{array}{l} 65 \quad 2 \\ 49 \quad 22 \\ 65 \quad 36 \end{array}$	$\begin{array}{l} - 8 \\ + 8 \\ 0 \end{array}$	$\begin{array}{l} 64 \quad 54 \\ 49 \quad 30 \\ 65 \quad 36 \end{array}$
$\left\{ \begin{array}{l} po' = 110 : 112 \\ o'q = 112 : 011 \\ qp = 011 : 110 \end{array} \right.$	$\begin{array}{l} 72 \quad 23 \\ 34 \quad 50 \\ 72 \quad 47 \end{array}$	$\begin{array}{l} - 8 \\ + 14 \\ - 6 \end{array}$	$\begin{array}{l} 72 \quad 15 \\ 35 \quad 4 \\ 72 \quad 41 \end{array}$	$\begin{array}{l} - 8 \\ + 11 \\ - 3 \end{array}$	$\begin{array}{l} 72 \quad 7 \\ 35 \quad 15 \\ 72 \quad 38 \end{array}$
$\left\{ \begin{array}{l} p'o = 130 : 111 \\ oo' = 111 : 112 \\ o'q' = 112 : 021 \\ q'p' = 021 : 130 \end{array} \right.$	$\begin{array}{l} 43 \quad 59 \\ 45 \quad 47 \\ 46 \quad 1 \\ 44 \quad 13 \end{array}$	$\begin{array}{l} - 10 \\ + 8 \\ + 11 \\ - 9 \end{array}$	$\begin{array}{l} 43 \quad 49 \\ 45 \quad 55 \\ 46 \quad 12 \\ 44 \quad 4 \end{array}$	$\begin{array}{l} - 9 \\ + 6 \\ + 8 \\ - 5 \end{array}$	$\begin{array}{l} 43 \quad 40 \\ 46 \quad 1 \\ 46 \quad 20 \\ 43 \quad 59 \end{array}$
$\left\{ \begin{array}{l} p'o' = 130 : 112 \\ o'q' = 112 : 011 \\ qp' = 011 : 130 \end{array} \right.$	$\begin{array}{l} 58 \quad 48 \\ 62 \quad 12 \\ 59 \quad 0 \end{array}$	$\begin{array}{l} - 13 \\ + 24 \\ - 11 \end{array}$	$\begin{array}{l} 58 \quad 35 \\ 62 \quad 36 \\ 58 \quad 49 \end{array}$	$\begin{array}{l} - 10 \\ - 17 \\ - 7 \end{array}$	$\begin{array}{l} 58 \quad 25 \\ 62 \quad 55 \\ 58 \quad 42 \end{array}$

Comparison of the Axial Ratios.

The axial ratios deduced from the measurements are set forth under each other below.

For K_2SO_4	$a : b : c = 0.5727 : 1 : 0.7418$
„ Rb_2SO_4	$a : b : c = 0.5723 : 1 : 0.7485$
„ Cs_2SO_4	$a : b : c = 0.5712 : 1 : 0.7531$

It will be observed that—

The axial ratios for rubidium sulphate are intermediate between those for potassium and cæsium sulphates respectively.

The ratio of the length of the axis a to that of the axis b diminishes, but the change is only very slight, upon replacing potassium by rubidium or rubidium by caesium, while the ratio of the vertical axis c to the axis b increases materially.

There is thus a true progression in the axial ratios, most marked with respect to the ratio c to b, corresponding to the progression in the atomic weight of the contained metal.

Comparison of the Predominating Habits.

It will have been gathered from the foregoing individual descriptions that the three sulphates, although so closely do they resemble each other that crystals of any one of them may be found constructed on all the types of development represented by the whole of the figures given for the three salts, are characterised by largely predominating peculiarities of structure. Thus potassium sulphate is characterised by the relatively large development of the brachypinacoid $b\{010\}$, and the comparative insignificance of the macropinacoid $a\{100\}$ and basal plane $c\{001\}$, as illustrated by a very common type represented in Fig. 3. Rubidium sulphate is peculiar in exhibiting a much larger development of the macropinacoid (which is only materially curtailed by the important pyramidal faces), a slightly increased basal plane and a very much smaller development of the brachypinacoid than in the case of potassium sulphate. The relatively small size of the basal plane and brachypinacoid causes a corresponding increase in the brachydome forms, particularly $q'\{021\}$. These characters are well shown in Fig. 7. Caesium sulphate is characterised by the exceptional development of the basal plane, as represented in Fig. 10, and likewise the large development of the macropinacoid, the crystals frequently being rectangular blocks whose largest dimensions are in the direction of the basal plane, the pair of sides formed by the brachypinacoid being the most diminished by the development of the subsidiary forms (the brachydomes).

Hence the three salts may be considered to be characterised by the relative development of the basal plane and macropinacoid. In potassium sulphate, the former is very small, in rubidium sulphate it is somewhat larger, in caesium sulphate it is the predominating form. In potassium sulphate, the macropinacoid is very narrow, in rubidium sulphate it is the characterising form, but limited somewhat by the large development of the pyramidal faces, and in caesium sulphate, where the latter faces are insignificant, the macropinacoid forms the broad flat end of the crystal. Moreover, the intermediate position of the rubidium salt is clearly indicated by the fact that while in the potassium and caesium salts a more or less tabular habit is developed, owing to the predominance of the brachypinacoid in the

former salt and the basal plane in the latter, in the rubidium salt these forms are usually rendered insignificant by the large development of the brachydome $q'\{021\}$, and a prismatic habitus is developed, which renders the crystals entirely different from those of the other two salts. With respect, therefore, to the relative development of the basal plane and brachypinacoid, it is evident that a regular progression is commonly observed from the potassium to the rubidium salt, and from the rubidium to the cæsium salt. These observations may be generalised as follows.

The habits assumed by the crystals of the rhombic sulphates of potassium, rubidium, and cæsium approach each other more closely than is the case with crystals of the monoclinic double sulphates of the series

just as do the angles. The predominating relative amounts of development of the primary faces, particularly the basal plane and brachypinacoid, indicate a progression from the potassium, through the rubidium to the cæsium salt, that is, corresponding to the progression of the atomic weight of the contained metal.

These general conclusions are based upon observations of a very large number of crystals, belonging to many different crops of each salt.

It may be here observed, for the fact will subsequently be shown to have considerable significance, that no other faces were ever discovered in the zone containing the basal plane and macropinacoid lying between those faces.

Alteration of the Angular Magnitudes with Rise of Temperature.

In order to be quite certain that the conclusions drawn from the goniometrical investigation were not dependent on the circumstance that the observations were made at the ordinary temperature, and that other relationships did not obtain at other reasonably elevated temperatures, a series of observations have been carried out successively at the ordinary temperature (18—20°) and at 120°. The large goniometer of Fuess (Model No. 1), reading directly to 10 seconds of arc, which is supplied with an admirable arrangement for heating the crystal in a small air bath furnished with plate glass windows, and in which a pair of thermometers are immersed, was employed for the purpose of these observations. Crystals of the three sulphates were selected which yielded excellent single images of the Websky slit from the faces $a\{100\}$ and $p\{110\}$, enabling the angle ap to be determined, or from the faces enabling the complementary angle bp or the angle bp' to be determined, any of these values determining the axial ratio $a:b$. Similarly the angle cq between the basal plane

$c\{001\}$ and the brachydome $q\{011\}$ was determined from excellent faces of these forms, in order to estimate the ratio $c : b$.

The changes in these angles brought about by the unequal expansion of the crystal along the three crystallographic axes are extremely small, but are distinctly larger for the angle cq than for the angle ap . The change for any angle occurs in the same direction in each salt. Both the angles ap and cq increase when a crystal of any of the three sulphates is heated, so that the ratios $a : b$ and $c : b$ both correspondingly increase. The actual amount of increase in the angle ap when the crystal is heated from 20° to 120° is less than a minute of arc, and in the neighbourhood of 45 seconds, corresponding to an increase in the value of the ratio $a : b$ of not more than 3 in the fourth place of decimals. The increase in the angle cq under the same conditions is more considerable, and is in the neighbourhood of $1\frac{1}{2}$ minutes, corresponding to an increase in the ratio $c : b$ of about 7 in the fourth place of decimals. The differences between the actual amounts of change for the potassium, rubidium, and caesium salts fall within the limits of experimental error; for they are less than the differences observed in the amount of alteration of the same angle of the same salt as determined upon different crystals.

These observations indicate that:—

The conclusions drawn from the comparison of the angular magnitudes and the axial ratios of the crystals of the normal sulphates of potassium, rubidium, and caesium are independent of the temperature, for the slight changes brought about by alteration of the latter occur in the same direction in each salt. The effect on the axial ratios of a rise of temperature of 100° is to increase the ratio $a : b$ by not more than 3 units in the fourth place of decimals, and the ratio $c : b$ by about 7 such units in each of the three salts, thus leaving the relationships of the latter the same.

Cleavage.

Potassium sulphate has long been known to possess two directions of cleavage, which, however, are not very perfect. These directions are parallel to the brachypinacoid $b\{010\}$ and basal plane $c\{001\}$. A large number of crystals of rubidium and caesium sulphates have been examined for cleavage during the course of this work, and the fact has been established that the same two directions of cleavage are common to the three salts. Under no circumstances was a plane fracture ever obtained by introducing the edge of a penknife parallel to the macropinacoid or the prismatic, domal, or pyramidal forms. The cleavage in the direction of the brachypinacoid is distinctly more perfect than that in the direction of the basal plane, but the crystals split fairly easily in both directions; whereas they offer great resistance parallel to the macropinacoid, and when they give way it is

usually with complete disruption of the crystal and production of plates parallel to the brachypinacoidal cleavage by gliding. It may, therefore, be stated that:—

The cleavage directions of the three sulphates are identical, and are parallel to the brachypinacoid and basal plane respectively. Neither cleavage is very strongly marked, but that parallel to the brachypinacoid is the better defined of the two.

INVESTIGATION OF VOLUME RELATIONSHIPS.

Relative Densities of the Three Sulphates.

Considerable trouble has been taken to obtain specific gravity determinations of the crystallised salts of a high order of accuracy, for purposes of an interesting nature which will be discussed in subsequent sections.

The specific gravity of potassium sulphate has formed the subject of frequent investigation, among the earlier determinations being those of Joule and Playfair, Schiff, Kosten, Filhol, Spring, and Schröder. Between the years 1872 and 1876, Pettersson carried out a comprehensive investigation of the molecular volumes of a number of sulphates and selenates (*Nova Acta R. Soc. Scient. Upsaliensis*, 1873, [3], 9, fasc. 1 and 1876, [3], 10, fasc. 2), among which the volumes of the sulphates of potassium, rubidium, and cæsium were determined, and the values of Pettersson are those now accepted. The main results of Pettersson's work were also contributed to the *Berichte* (1876, 9, 1559), but the detailed description is only to be found in the Upsala publication above referred to; and Arzruni, in compiling his excellent treatise on the "Physikalische Chemie der Krystalle," published last year, states that he was unable to obtain access to it, and, therefore, naturally quotes Pettersson's numbers as all of equal value. Fortunately, the library of the British Museum contains a copy, and on consulting it the author finds the following statement of Pettersson concerning the determination of the specific gravity of cæsium sulphate: "Das schwefelsaure Cäsium war nicht vollkommen rein, denn bei der spektroskopischen Prüfung zeigte sich auch eine schwache Rubidium Linie. Die ausserordentlich geringe Menge des Materials machte es unmöglich dasselbe vorher zu reinigen und gestattete nur eine Bestimmung des specifischen Gewichtes." Moreover, only two determinations of the specific gravity of rubidium sulphate were made, and with such small quantities of substance (1.9926 and 1.1628 grams) that accurate results were not very likely to have been obtained. A redetermination of the specific gravities of these two salts was therefore very necessary. The author has carried out a series of determinations, and has included potassium sulphate, in

order that the densities might be strictly comparable. Retgers has lately obtained a number, 2.666, for the latter salt, which agrees fairly well with Pettersson's numbers, 2.667, 2.669, and 2.660, but some previous observers had obtained lower numbers; thus Spring obtained 2.656, Wise 2.653, and Schröder 2.658. Spring in another determination obtained the value 2.660.

The determinations have been made with two forms of pyknometer. One was a modified form of the ordinary type, holding about 10 cubic centimetres, with well-fitting pierced stopper, which was ground into the neck until contact was perfect. The edge of the neck was then ground down to the zone of perfect contact, so that no annulus could be present capable of holding more than the extremely thin film of liquid which is drawn up by capillary attraction. The outer edge of the neck was then bevelled, and a glass cap fitted over both stopper and neck, and ground upon the bevelled edge of the latter until perfect contact was likewise obtained. In order to maintain the cap in close contact with the neck after the filling of the bottle, a small brass wire stand was constructed. The wire was first bent into a close spiral, the lower ring of which was capable of resting upon the table or balance pan, and into the upper ring of which the bulb of the pyknometer rested; the wire was then bent upright, and at a height a little less than that of the top of the cap was again bent horizontally and looped round, so as to form a small ring, which could press on the top of the cap, but was too small to allow the cap to pass through it. The wire was then bent back and downwards, and finally bent again for half an inch horizontally at the level of the table, so as to form a second support. The spiral base and the upper loop of such a stand form an excellent spring, which presses the cap firmly down upon the neck of the pyknometer when placed in position, and loss by evaporation either through the capillary bore of the stopper or from the neck is almost entirely prevented. Such a stand, if made from well-laquered brass wire, retains a constant weight for months. This form of pyknometer was employed by Chapman Jones in some determinations of specific gravity recently described by him (*J. Soc. Chem. Ind.*, 1893, 983). The determinations were made at the uniform temperature of 20°, and in duplicate, a pair of such pyknometers being used at the same time. A third larger pyknometer, of about 30 c.c. capacity, similarly fitted, was used to determine the specific gravity of the liquid employed, in addition to the determinations made by means of the small bottles themselves. The temperature of 20° was attained by immersing the bottles up to the neck in water contained in a small glass bath, surrounded in turn by water contained in a still larger bath, standing upon a metal plate; the latter was gently warmed by means of a small flame for a few

seconds from time to time, so as to cause the temperature to rise very slowly, until exactly 20° was indicated by the corrected thermometer employed. The protruding drop of liquid at the top of the stopper was then wiped off by chamois leather, leaving the liquid in the capillary flush with the top of the stopper, when the bottle was removed from the bath, well cleansed about the neck, the cap fitted over, finally cleansed completely, and placed in its stand. After treating the duplicate in the same way, both were placed under a small glass vase with ground edge fitting upon a ground glass plate, until they had attained the surface conditions under which the empty bottles, and the bottles containing the salt, were weighed.

The other form of pycnometer was one devised by Muthmann, who has recently contributed to the *Zeitschrift für Krystallographie und Mineralogie* (22, 497) an important memoir concerning the volume theory of crystallised substances. The description of his pycnometer was most generously given to the author in a letter from Dr. Muthmann, together with his entire method of carrying out the determinations. The essential point of it, which the author is enabled to communicate by the courtesy and desire of Dr. Muthmann, is that the perforated stopper is continued into a bent capillary tube, which, until the time of weighing, is allowed to dip beneath the surface of a small quantity of the liquid employed in the determinations. The results obtained by the use of it are in complete accordance with those obtained by the method above described. Dr. Muthmann will shortly fully describe his method, and therefore all further reference to it here would be out of place.

The liquid employed has been carbon tetrachloride, which Muthmann has found to dissolve or attack inorganic salts the least of all the liquids available, and is endowed with a relatively high density. The heavy methylene iodide was also tried for the two heavier salts, but a slight action was found to occur, resulting in numbers 1 per cent. too high being obtained. Turpentine was employed for one series of determinations which, as will be described in the next section, were to be afterwards repeated at a higher temperature, an impossibility with carbon tetrachloride on account of its slow boiling point. The salt was in every case employed in the state of finest powder, obtained by grinding in an agate mortar the clearest crystals. In order to be certain of the absence of traces of moisture due to inclusions of mother liquor in the crystals, the powder was heated for some hours previous to use at 110 — 120° in an air bath, a very necessary precaution. After weighing the pycnometer and its content of salt, the bottle being filled to about half its capacity with the powder, the latter was well covered with the liquid and the air bubbles entirely removed by placing the bottle under a small receiver

attached to a Sprengel pump, rapidly exhausting, and facilitating the escape of bubbles by tapping. The air was then admitted, the bottle removed, completely filled with the liquid, the stopper inserted, and the warming to 20° carried out as previously described. It is needless to say the weighings were all corrected for air displaced. The capacity of the pyknometers had been previously determined with the greatest care by repeatedly weighing them after filling with water at 20° . In the different determinations for the same salt, the specimens employed belonged to different crops of crystals.

The results of the determinations are given below. It should be mentioned that the first series of determinations by Muthmann's method were carried out at the temperature $14^{\circ}75$, a lower temperature being an advantage under the conditions of the method. The results for this series were corrected to 20° by use of the coefficients of expansion to be referred to in the next section.

Relative Density of Potassium Sulphate at 20° .

Method employed.	Liquid used.	Weight of salt employed, grams.		Sp. gr. at 20° .
Pyknometer with cap..	Carbon tetra-chloride	4.4516		2.6659
" "	" "	5.2624		2.6609
Pyknometer with cap (large size)	Turpentine....	19.1356		2.6660
Muthmann's method..	Carbon tetra-chloride	7.2834	2.6648 at $14^{\circ}75^{\circ}$	2.6630
" "	" "	6.3147	2.6640 "	2.6622
" "	" "	7.6748		2.6617
" "	" "	6.5019		2.6631

Mean of seven determinations of relative density of K_2SO_4 at $20^{\circ}/4^{\circ}$ 2.6633.

This number is about the mean of the values obtained by other workers.

Relative Density of Rubidium Sulphate at 20° .

Method employed.	Liquid used.	Weight of salt employed, grams.		Sp. gr. at 20° .
Pyknometer with cap..	Carbon tetra-chloride	6.9676		3.6150
" "	" "	7.4668		3.6094
" "	Turpentine....	10.7690		3.6128
Muthmann's method..	Carbon tetra-chloride	7.1384	3.6155 at $14^{\circ}75^{\circ}$	3.6132
" "	" "	7.2337	3.6094 "	3.6071
" "	" "	6.2758		3.6144
" "	" "	7.0490		3.6073

Mean of seven determinations of relative density of Rb_2SO_4 at $20^{\circ}/4^{\circ}$ 3.6113.

This value is considerably lower than those found by Pettersson as the result of his two determinations with 1·16 and 1·99 grams of salt respectively. Those values were 3·639 and 3·641 at 16°·8. Correcting these to 20° they are 3·638 and 3·640. The high result is either due to the very small quantities employed, or to impure salt, possibly containing cæsium sulphate.

Relative Density of Cæsium Sulphate at 20°.

Method employed.	Liquid used.	Weight of salt employed, grams.		Sp. gr. at 20°.
Pyknometer with cap..	Carbon tetra-chloride	9·5749		4·2411
" "	" "	5·5173		4·2458
" "	Turpentine....	12·4937		4·2433
Muthmann's method..	Carbon tetra-chloride	9·5117	4·2487 at 14·75°	4·2459
" "	" "	8·0768	4·2460 "	4·2432
" "	" "	4·5809		4·2412

Mean of six determinations of relative density of Cs_2SO_4 at 20°/4° **4·2434.**

This value is very considerably higher than that obtained by Pettersson, which was 4·105 at 19°·2. The weight of salt used was only 1·0925 gram, an amount far too little to give an accurate result, even if the salt had been pure, which, in the words previously quoted, he states it was not.

Coefficients of Cubical Expansion of the Three Salts.

In order to be able to calculate the specific gravities at higher temperatures, data which will be of considerable use at a later stage in this communication, and also in order to ascertain whether any differences of appreciable magnitude existed between the total amounts of thermal expansion of the salts, corresponding to the differences in atomic weight of the contained metals, a series of specific gravity determinations at 60° have been carried out. After trying methylene iodide with the two heavier salts, on account of its high boiling point, with the unfortunate result previously referred to, and as carbon tetrachloride and the only other liquids available are too volatile, and mercury is, of course, too heavy and the methods involving its use otherwise inconvenient, turpentine has at length been found to answer best. Turpentine was employed in the researches of Joule and Playfair (*Quat. J. Chem. Soc.*, 1, 121) on atomic volume and specific gravity. The results of the determinations at 20°, which were made with the pyknometers fitted with cap, using turpentine as the liquid, agree so well with the values obtained by the use of carbon tetrachloride that there would appear to be no

appreciable action on the salts under investigation. The high boiling point, 158—160°, renders it eminently suitable for the purpose in hand. After the completion of the three determinations at 20°, the stoppers were removed, more turpentine added so as to again completely fill the necks, the stoppers replaced, the pyknometers placed in the bath, and the temperature raised to 60°. After maintaining the temperature constant at 60° for some time, and finally taking off the obtruding drops, they were removed, cleansed, allowed to stand an hour in the closed vase, and weighed. A determination of the density of the turpentine at 60° had previously been made in duplicate. The results obtained were as follows, those previously determined on the same day for 20° being also given.

	Sp. gr. at 20°/4°.	Sp. gr. at 60°/4°.	Difference for 40°.	Coefficient of cubical expansion for 40°.
K ₂ SO ₄	2·6660	2·6521	0·0139	0·0053
Rb ₂ SO ₄	3·6128	3·5943	0·0185	0·0052
Cs ₂ SO ₄	4·2433	4·2218	0·0215	0·0051

The coefficients of cubical expansion thus appear to be practically identical; the intermediate number found for the rubidium salt can only be regarded as fortuitous, for the whole difference of 2 in the fourth decimal place is about the limit of experimental error. As was found with respect to the alterations of the axial ratios for a rise of 100° of temperature, the differences between the coefficients of cubical expansion for the three salts are too small to be quite certain about. Unfortunately, the admirable method of Fizeau, and its improvements at the hands of Benoît, of determining the linear expansion, are inapplicable, owing to the relatively large and thick crystal plates required. The microscopic method employed by Schrauf (*Zeitschrift für Kryst.*, 9, 433, and 12, 321), using the same type of Fues microscope, has been investigated, but the extremely small differences were found to be less than the errors of measurement when a stage heating apparatus was employed.

From the data afforded by the measurements of the angular deviations at 120°, and the determinations of the coefficient of cubical expansion, assuming the salts to expand equally as far as the expansion can be observed, it is possible to calculate the linear expansions λ_a , λ_b , λ_c along the three axial directions.

The cubical expansion e of a rhombic crystal is expressed by the formula

$$1 + e = (1 + \lambda_a)(1 + \lambda_b)(1 + \lambda_c).$$

Excluding all higher powers of the expansions than the first, the cubical expansion

$$e = \lambda_a + \lambda_b + \lambda_c.$$

The value of e for 100° , calculated from the mean value (0.0052) determined for 40° , is 0.0130. Joule and Playfair found 0.0107 for potassium sulphate, but they used small crystals, and their value for the specific gravity was much lower than the value found in this investigation, being only 2.656 at 4° .

The ratio a/b was found to increase for the potassium salt from 0.5727 at 20° to 0.5730 at 120° ; this gives for the difference of the dilatations $\lambda_a - \lambda_b = \frac{0.0003}{0.5727} = 0.00052$. Similarly the ratio c/b increased from 0.7418 to 0.7425, giving for $\lambda_c - \lambda_b = \frac{0.0007}{0.7418} = 0.00094$. Identical numbers are obtained by using the ratios of the rubidium salt, and if the caesium sulphate ratios are employed, the numbers only differ by one in the last decimal place.

From the three equations

$$\begin{aligned}\lambda_a + \lambda_b + \lambda_c &= 0.0130, \\ \lambda_a - \lambda_b &= 0.00052, \\ \lambda_c - \lambda_b &= 0.00094,\end{aligned}$$

The mean linear dilatations for the three salts are found to be as follows:—

$$\begin{aligned}\lambda_a &= 0.00437 \\ \lambda_b &= 0.00385 \\ \lambda_c &= 0.00479\end{aligned}$$

It therefore appears 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 . It is probable, however, that the dilatations along the axes a and b are more nearly equal than are represented by the above numbers, for the change in the axial ratio a/b was not greater than 0.0003, and was probably nearer 0.0002. The fact that the crystals expand so much more along the vertical axis than along the two lateral axial directions, will be subsequently shown to have an intimate connection with the alteration of optical elasticity with rise of temperature. For the greatest increase in optical elasticity occurs likewise along the vertical axis, and the lesser changes along the lateral axes are more nearly equal. From the clearly established progressive relations of the optical elasticities of the three salts, there is every probability that if the linear dilatations could be determined with precision they would exhibit a similar progression, according to the order of the atomic weights of the contained metals.

Molecular Volumes of the Three Sulphates.

The molecular volumes M/d of the three salts, calculated from the specific gravities at 20° , are as follows.

For K_2SO_4 ..	$M/d = \frac{174}{2.6633} = 65.33$	
„ Rb_2SO_4 ..	$M/d = \frac{266.4}{3.6113} = 73.77$	Difference 8.44
„ Cs_2SO_4 ..	$M/d = \frac{361.4}{4.2434} = 85.17$	Difference 11.40

The molecular volumes given by Pettersson were 65.37, 73.27, and 88.1. The error introduced into his number for the molecular volume of caesium sulphate, owing to the small quantity and impurity of the salt employed, is seen to amount to three whole units. The fact pointed out by Pettersson, however, that the substitution of caesium for rubidium is accompanied by a much larger change of volume than that which occurs when rubidium replaces potassium, is substantially correct, but the amount of difference is not so great as stated by him, the ratio being 8.4 to 11.4 instead of 7.9 to 14.8.

The main results of the foregoing section of the investigation, concerning the volumes of the salts, may be summarised in the following terms:—

The relative densities of the crystals of the normal sulphates of potassium, rubidium, and caesium at 20° compared with water at 4° are respectively 2.6633, 3.6113, and 4.2434.

The molecular volumes of the three salts, obtained by dividing the molecular weights by these values for the densities, are respectively 65.33, 73.77, and 85.17. A greater increase of volume accompanies the replacement of rubidium by caesium than is observed when rubidium replaces potassium in the sulphate, the ratio of the respective changes being 11.4 to 8.4.

The densities of the three sulphates diminish proportionally to their numerical values, on raising the temperature. At 60°, the relative densities, compared with water at 4°, are 2.6521, 3.5943, and 4.2218, the differences in the densities for a rise of 40° of temperature being 0.0139, 0.0185, and 0.0215 for potassium, rubidium, and caesium sulphate respectively. The coefficients of cubical expansion for 100°, calculated from this data, are almost identical being 0.0133, 0.0130, and 0.0128, and the differences are about the limits of experimental error.

The coefficients of linear expansion along the three axial directions, obtained by combining the knowledge of the cubical expansion with the amount of alteration of the axial ratios for rise of temperature, are also so nearly identical that the differences between those along analogous directions in any two salts fall within the limits of error. The fact is well established, however, that in each salt the greatest amount of expansion occurs in the direction of the vertical axis c.

Relative Dimensions and Nature of the Crystal Element.

It is now generally accepted that a crystallised solid substance is not built up directly of chemical molecules, but of definite aggregates of such, to which have been applied the name "physical molecules." The theory of the internal structure of crystals is now making considerable advances, due largely to the elaboration by Sohncke of his systems of points, capable of accounting for the construction of all the known forms of crystallographic symmetry on the supposition of the existence of such crystal elements as the physical molecules may be assumed to be, and by Bravais, of the space-lattice theory of crystal structure. An important contribution to the subject has very recently been communicated by Muthmann to the *Zeitschrift für Krystallographie* (22, 497). Muthmann shows that the molecular volumes of two or more crystallised substances of similar composition can only represent the relative volumes of the chemical molecules if (1) the physical molecules of which the crystals are built up consist of equal numbers of chemical molecules, (2) the interspaces between the chemical molecules composing the physical molecules bear the same relation as the volumes of the chemical molecules themselves, and (3) if the same holds good for the interspaces between the physical molecules which build up the crystal. The first condition, equality in the number of chemical molecules which compose the physical molecule, is evidently fulfilled by strictly isomorphous substances, such as the sulphates of potassium, rubidium, and caesium, and the double sulphates containing those metals. The weights of the physical molecules in such a series of strictly isomorphous compounds must therefore bear the same relations as the molecular weights, and the molecular volumes, although they cannot be said to represent the relative volumes of the physical molecules, the crystal elements, on account of our ignorance concerning the second and third conditions, will afford relative measures of the volume of the elementary parallelepiped of Bravais and Sohncke, formed by joining the centres of adjacent crystal elements. Moreover, the sides and height of this elementary parallelepiped will be proportional to the axial ratios of the crystal element, that is, to the ordinary crystallographic axial ratios. Hence, by combining the molecular volumes with the axial ratios, the relative distances apart of the crystal elements in the three axial directions can be directly calculated. For Federow has shown that the symmetry planes of crystals are always net-planes of the spacial-lattice, and consequently in the rhombic system the points will always lie along the axial directions. A rectangular parallelepiped, therefore, whose sides are proportional to the crystallographic axes, and whose volume in the various members of the

isomorphous series is proportional to the molecular volume, will thus represent the elementary parallelopiped of the crystal structure.

Several months previous to the publication of Muthmann's memoir and shortly after the appearance of the author's paper concerning the double sulphates containing potassium, rubidium, and cæsium, the idea of combining the axial ratios with the molecular volumes, in order to obtain relative measures of the true axial ratios of the crystal element, was communicated to the author in a kindly letter from Professor Becke, of Prague. It was pointed out that if V represents the volume of the elementary parallelopiped, p the molecular weight of the salt, s its specific gravity, and a_o, b_o, c_o the lengths of the edges, then—

$$V = p/s = a_o, b_o, c_o \sin \beta,$$

if the parallelopiped is endowed with monoclinic symmetry, as in the case of the monoclinic double sulphates. Also

$$a_o : b_o : c_o = a : 1 : c \text{ (the ordinary axial ratio).}$$

Dividing the first equation by b_o^3 , we have—

$$\frac{V}{b_o^3} = \frac{a_o}{b_o} \cdot \frac{b_o}{b_o} \cdot \frac{c_o}{b_o} \cdot \sin \beta = ac \sin \beta, \text{ because } \frac{a_o}{b_o} = a, \text{ and } \frac{c_o}{b_o} = c.$$

From which we deduce—

$$\begin{aligned} b_o &= \sqrt[3]{\frac{V}{ac \sin \beta}} \\ a_o &= ab_o = \sqrt[3]{\frac{aV}{c \sin \beta}} \\ c_o &= cb_o = \sqrt[3]{\frac{c^2V}{a \sin \beta}} \end{aligned}$$

The values of a_o, b_o , and c_o , obtained for the various salts of the isomorphous series will, of course, be different, and these different values will represent the axial ratios of the crystal elements of the salts.

Adopting Professor Becke's formulæ, and adapting them to the rectangular nature of rhombic symmetry, we have—

$$a_o = \sqrt[3]{\frac{a^2V}{c}}, \quad b_o = \sqrt[3]{\frac{V}{ac}}, \quad \text{and} \quad c_o = \sqrt[3]{\frac{c^2V}{a}}.$$

These expressions for the elementary axial ratios are identical with those deduced by Muthmann by a somewhat different mode of reasoning. He assigns to the three axes the three last letters of the Greek alphabet, χ, ψ, ω , and if, instead of a_o, b_o , and c_o , we write these Greek symbols, the formulæ of Muthmann are reproduced.

Muthmann proposes to term these ratios "topic axial ratios," from $\tau\acute{o}\pi\omicron\varsigma$, space. It must not, however, as he clearly points out, be

assumed that these ratios represent the dimensions of the crystal element, the physical molecule. They certainly do not, because we are ignorant of the relations between the actual substance of the physical molecules and the amount of interspace between them. What they do represent, however, is the relative distances apart of the centres of adjacent physical molecules (crystal elements) lying along the axial directions in the different salts of the series. The word "topic" or "topical" is not, perhaps, so happy an expression of the nature of these ratios in English as is "topisch" in German, particularly as in our language the word is already current in an altogether different sense. The author, therefore, prefers to speak of them as distance ratios of the crystal elements.

On calculating the distance ratios for the normal sulphates of potassium, rubidium, and cæsium from the axial ratios and molecular volumes previously given, by means of the above formulæ, the following values are obtained.

	$x.$	:	$\psi.$	:	$w.$
K ₂ SO ₄ ..	3.0683	:	5.3575	:	3.9742
	Diff. 1157		Diff. 2061		Diff. 1901
Rb ₂ SO ₄ ..	3.1840	:	5.5636	:	4.1643
	Diff. 1452		Diff. 2648		Diff. 2251
Cs ₂ SO ₄ ..	3.3292	:	5.8284	:	4.3894

It will at once be observed that the distances of adjacent crystal elements along the axial directions of the rubidium salt are intermediate between those of adjacent physical molecules of the potassium and cæsium salts. The above numbers are somewhat similar to those obtained by Muthmann for the permanganates of the same three metals, the results of his investigation of which he next proceeds to describe in the communication (*loc. cit.*) referred to. The order of alteration of the distances is different, however, owing to the different nature of the salts. The greatest amount of alteration in the distances of the crystal elements occurs in the direction of the *b* axis, and that along the *c* axis is but little inferior, whereas there is much less increase in the amount of separation along the axis *a*.

The author can see no reason why the above ratios should not be expressed in their simplest form, taking one of the numbers as unity, because of course they do not express actual but relative distances. It is therefore proposed to divide through by the value of ψ for the potassium salt, a process which has the advantage that the ratios for the potassium salt are then identical with the crystallographical axial ratios themselves. The relations of the numbers so obtained will, of course, be the same as those expressed by the above larger numbers. The ratios thus obtained are

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	χ .		ψ .		ω .
$K_2SO_4 \dots$	0.5727	:	1	:	0.7418
	Diff. 216			Diff. 385	Diff. 355
$Rb_2SO_4 \dots$	0.5943	:	1.0385	:	0.7773
	Diff. 271			Diff. 494	Diff. 420
$Cs_2SO_4 \dots$	0.6214	:	1.0879	:	0.8193

The following statement may now be made regarding the distance ratios of the crystal elements.

It may be assumed that, in the case of the strictly isomorphous normal sulphates of potassium, rubidium, and caesium, the physical molecules or crystal elements are composed of the same number of chemical molecules. The so-called molecular volumes, more correctly equivalent volumes, will, therefore, express the relations of the volumes of the elementary parallelepiped of each salt, formed by joining the centres of adjacent crystal elements situate along the axial directions. The sides of the parallelepiped will also be proportional to the crystallographic axial ratios. Hence, by combining the molecular volumes with the axial ratios, it is possible to calculate for the three salts the relative distances apart, from centre to centre, of their physical molecules or crystal elements along the three axial directions, and thus to determine the relative dimensions for the three sulphates of the elements of the Bravais-Sohncke "Raumgitter."

The distance ratios thus calculated indicate that the replacement of potassium by rubidium and rubidium by caesium is accompanied by an increase in the separation of the crystal elements along each of the axial directions, corresponding to the increase in molecular volume, and this increase is relatively much greater when caesium replaces rubidium than when rubidium replaces potassium. The amount of increase varies in the three axial directions; it is greatest in the direction of the b axis, and least along the a axis; the amount of increase of separation along the vertical axis c is almost equal to the maximum along the axis b .

It will be subsequently shown, in comparing these changes with the changes of optical elasticity, that the increase along the axes a and b is in almost exact proportion to the lengths of those axes, while the increase along the c axis is very much greater in proportion to its length.

We may now enquire further concerning the nature of the elementary parallelepiped of the series, and concerning the structure of the crystal element itself. It is improper to assume, without considering all the evidence, that the elementary parallelepiped represented by the above distance ratios is a rectangular rhombic prism, the unit solid of the rectangular rhombic spacial-lattice system. Indeed, Muthmann shows that in the case of the permanganates this is not so, but that the ratios refer to the rectangular diagonals (axes)

of the rhombic prism, a column with a rhombic base. The question may be decided, with great probability, by reference to the cleavage of the crystals and to the relative contents of the sides of the pinacoidal and prism faces respectively. Two important rules have been established in connection with the Bravais-Sohncke theory. The first is that the planes of cleavage are those in which the "points" are most densely packed, and therefore those in which the content of the unit parallelogram formed by four adjacent points is least. The second is that faces are most readily developed upon the crystals along those planes in which the points are most densely packed. In the sulphates under consideration the opposite occurs to that which is observed in the case of the permanganates. The cleavages are, as has been shown, parallel to the brachypinacoid $b\{010\}$ and the basal plane $c\{001\}$, the cleavage in the former direction, moreover, being most perfect. Hence it would be expected that the brachypinacoid would exhibit the least area of the primary faces, and the basal plane only a little greater. This is precisely what is observed. The area of the brachypinacoid, obtained by multiplying the relative lengths of the axes a and c , is 0.57×0.74 ; that of the basal plane $= ab = 0.57 \times 1$, somewhat greater than that of the brachypinacoid, while the macropinacoid $a\{100\}$, along which no cleavage is observed, has the still greater area, 0.74×1 . Moreover, the primary prism $p\{110\}$, whose faces would be sides of the elementary parallelogram if the rhombic lattice system obtains, exhibits the largest extent of all, $\sqrt{a^2 + b^2} \times c = 1.152 \times 0.74$. Hence, in accordance with the second rule, there is far greater probability that the lattice system of the sulphates of potassium, rubidium, and cæsium is that of the rectangular rhombic prism than that of the prism with a rhombic base. It is a point worthy of note, as confirming the accuracy of this second rule, that no faces have ever been observed in the zone of the macropinacoid a and the basal plane c , the planes of greatest and medium content, other than those faces themselves.

Muthmann goes a step further in assuming that the crystal element is endowed with like symmetry to the crystal itself. It cannot but be admitted that the evidence in favour of such an assumption is almost overwhelming. If it be correct, it would naturally result in the formation of a spacial trellis structure, for the crystal elements would all be parallel to each other and arranged symmetrically according to the same axial directions. It is certainly a point of great significance that the replacement of one alkali metal by another in the sulphates under consideration invariably produces changes in the same particular directions. It has been shown that the b and c axes exhibit nearly equal changes of much greater amount than that which occurs along the a axis. It is difficult to understand why this

localised change should occur, unless it is because the metallic atoms contained in the chemical molecules are arranged in closest proximity to the two axes which exhibit most change. In the case of the permanganates, Muthmann concludes that the evidence of the changes in the distance ratios is such as can be best explained on the supposition that four chemical molecules are contained in each physical molecule, that is in each crystal element, symmetrically arranged with the four metallic atoms (considering the composition KMnO_4) in closest proximity to the single axis which exhibits large change. If there is any validity in Muthmann's supposition, for the evidence in favour of which the memoir should be consulted, then a similar interesting conclusion must follow in the case of the sulphates. In this case there are two metallic atoms in the chemical molecule, and the distance ratios for two axes show considerable change. The exact nature of these changes can be fully accounted for on the assumption that one of the two atoms of each chemical molecule behaves as if it were arranged in the plane ab and nearer to b , and the other in the plane bc and nearer to c . Such an arrangement would account for the greatest change on replacing the atoms by heavier ones occurring in the direction of the b axis, a somewhat smaller, but still relatively large, change along the c axis, and a comparatively small change, but still a very appreciable one, along the a axis. Now, if the crystal element is endowed with rhombic symmetry as regards the arrangement of the chemical molecules of which it is composed, each of these atoms must be counterbalanced by another at an equal distance at the opposite side of the centre, and this pair of atoms must be repeated upon the other side of the symmetry plane. Hence, each of the two atoms of a chemical molecule must be repeated four times, in accordance with rhombic symmetry, and therefore the physical molecule would be constructed of four chemical molecules, symmetrically arranged with regard to the three planes of symmetry.

The consideration of the volume relationships of the three salts may now be concluded with the following statement.

The directions of cleavage, the positions of the planes in which the elementary parallelograms occupy least area, together with the evidence afforded by the nature of the forms developed upon the crystals, agree in indicating that the elementary parallelepiped of the series is a rectangular rhombic prism. If it is correct that the arrangement of the chemical molecules which compose the physical molecule, the crystal element, follows the same order of symmetry as is exhibited by the crystal itself, then the order of change in the distance ratios of the crystal elements along the three axial directions can be fully accounted for on the supposition that the crystal element of the series is composed of four chemical molecules,

the atoms or groups of which are symmetrically arranged with respect to the three planes of rhombic symmetry.

OPTICAL INVESTIGATION.

The optical investigation of the three sulphates includes a comprehensive series of determinations of the refractive indices, both at the ordinary temperature and at regular temperature intervals up to 180° , a similar large number of determinations of the optic axial angles at the ordinary temperature, determinations of the sign of double refraction, and an investigation of the change in the orientation of the optic axes brought about by rise of temperature up to 100 – 120° . From the data thus acquired, together with the knowledge of the relative densities of the three salts, the axial ratios of optical elasticity have been deduced, and the specific and molecular refraction and dispersion of the three sulphates calculated.

The optical constants of potassium sulphate have been previously determined with a certain amount of completeness by Topsøe and Christiansen (*Ann. Chim. Phys.*, 1874, [5], 1, 46). Those of rubidium and caesium sulphates are entirely wanting; the only information extant being data concerning the orientation of the optic axes and the character of the double refraction, due to von Lang (*Sitz. Ber. der Wien Akad.*, 55, Abth. 2, 415), which in the case of rubidium sulphate is to some extent at variance with the results now presented.

The character of this optical investigation differs from previous investigations of the same kind, owing to the infinitely improved means of preparing the necessary section-plates and prisms afforded by the use of the accurate grinding apparatus lately described by the author to the Royal Society (*loc. cit.*). Hitherto, the section-plates and prisms of the relatively soft crystals of artificial salts have had to be prepared by hand, holding the crystal as carefully as possible in the right direction between the finger and thumb while endeavouring to grind the desired surface by movement of the crystal to and fro over a slightly convex ground glass plate lubricated with oil. The difficulty of avoiding fracture of the crystal, the practical certainty of the desired direction of the ground surface not being nearly exactly attained, and of the surface not being truly plane, together with the large expenditure of time and energy in the process, have driven crystallographers hitherto to confine their observations largely in the case of artificial salts to those obtained by the use of natural plates and prisms formed by existing faces of the crystal. It is, however, frequently impossible to obtain the theoretically desirable plates and prisms owing to the lack, malformation, or slight development of the necessary natural faces,

hence the incomplete character of much of the published optical work. Moreover, in the case of prisms, unless the natural crystal faces are remarkably perfect, the multiplication, blurring, or other distortion of the refracted images is usually sufficient to render the highest accuracy unattainable, and it is frequently necessary to cover the faces with small, cemented cover glasses. The use of cover glasses has been the rule whenever prisms have been actually ground; and it has been experimentally proved by the author that the use of them introduces errors of grave import in a comparative investigation similar to the present. Probably the work of Topsøe and Christiansen is of the highest type on record; but in the case of potassium sulphate, of the six prisms employed, two were formed by natural uncovered faces, and the other four were covered. By the use of the new instrument, which combines an accurate goniometer with a grinding and polishing apparatus, plates or prisms may be ground accurately in the theoretical directions with a possibility of error well within ten minutes of arc; the rule may therefore be invariably followed of preparing prisms which are both symmetrical to a plane of optical elasticity, and whose edges are parallel to an axis of optical elasticity, when in the case of biaxial crystals all three refractive indices are obtained by the use of two such prisms, two indices being given by each, and one being consequently determined in duplicate.

Moreover, the surfaces obtained are truly plane and so highly polished, that cover glasses are totally unnecessary, except perhaps in the case of substances which are too soft to take a polish, and such cases have not yet presented themselves to the author. The images of the goniometer or spectrometer slit afforded by these surfaces are uniformly bright and single. A delicate arrangement is also provided for varying the pressure of the crystal upon the grinding surface during the grinding, so that a crystal is rarely fractured. There is likewise provided a means of grinding a second surface truly parallel to the first ground surface, which enables a parallel-faced section-plate to be immediately obtained perfectly perpendicular to a median line (axis of optical elasticity), and such plates invariably exhibit the interference figures exactly symmetrical to the centre of the field.

The observations have been made for a larger number of wave-lengths than hitherto. This has been achieved by use of the "instrument of precision for producing monochromatic light of any desired wave-length" described on the same occasion to the Royal Society. This apparatus enables the whole field of the axial angle goniometer to be evenly and brilliantly illuminated with spectrum light confined to a very few adjacent wave-lengths;

for instance, when it is used to generate light of the wave-length of sodium light, the amount of the spectrum which emerges from the selecting slit of the apparatus, and which is diffused in order to fill the field of the polariscope by means of a diffusing screen of ground glass, need be no greater, and may even be less than that which is included between the two sodium D lines. The author has employed the lime-light as source of light during this investigation, which has enabled exceedingly fine slits to be used, ensuring the highest order of monochromatism. The facility with which the change from one wave-length to another may be made, by simply rotating the dispersing apparatus so as to set the circle carrying the latter to a known reading corresponding to the wave-length in question, enables observations for the six wave-lengths corresponding to the red lithium line, the red hydrogen C line, the sodium D lines, the green thallium line, the greenish-blue hydrogen F line, and the bluish-violet hydrogen G line to be made in a very brief space of time. This is particularly convenient in the case of temperature observations, when there is difficulty in maintaining the temperature constant for a lengthened period. The apparatus has been found to give results far superior to those obtained by the use of coloured flames which have hitherto been usually employed in crystallographical optical investigations; the illumination both of the field of the polariscope when studying the interference figures in convergent light, and of the refracted image of the Websky slit of the spectrometer when determining refractive indices by means of prisms, being immeasurably superior, enabling far more accurate approximations of the hyperbolic brushes of the former, or the narrow central portion of the latter, to the cross wires to be effected.

Full details of the construction of these instruments and of the mode of using them are given in the memoirs communicated to the Royal Society, and which will shortly appear in the *Philosophical Transactions*.

The crystals of the sulphates of potassium, rubidium, and cæsium exhibit only feeble double refraction, so that relatively thick plates are required in order to obtain well-defined interference figures in convergent polarised light. In the cases of the sulphates of potassium and cæsium, plates of at least a couple of millimetres in thickness are required to exhibit small rings around the optic axes, while in the case of rubidium sulphate a section little less than a centimetre thick is essential for the production of a similarly well-defined figure. Indeed, the optical properties of rubidium sulphate were apparently remarkably anomalous, and of quite a different nature to the normal characters of those of the sulphates of potassium and cæsium, and it was not until considerable progress had been made in

the optical investigation that the reason was discovered and the interesting fact revealed that these apparent anomalies were conditions of a true optical progression in the order of the atomic weights of the contained metals. It will be convenient to describe first the results of the detailed optical investigation of potassium and caesium sulphates, and subsequently those of rubidium sulphate.

Optical Properties of Potassium Sulphate.

The plane of the optic axes is the macropinacoid $a\{100\}$. The first median line is the crystallographic axis c . The axes and their surrounding series of rings and lemniscates are observed, symmetrical to the traces of the crystallographic symmetry planes, through a section-plate a couple of millimetres or more thick parallel to the basal plane. The double refraction is positive. Hence the crystallographic axis c (the first median line) is the axis ϵ of least optical elasticity; the axis b (the second median line) is the axis a of greatest elasticity; and the axis a is the axis b of medium elasticity, according to the scheme of Topsøe and Christiansen (*loc. cit.*), who use the symbols $a\ b\ c$ to designate the axes of optical elasticity (in the rhombic system coincident with the crystallographic axes) where $a > b > c$.

Determinations of Refractive Indices.—The three refractive indices $\alpha\ \beta\ \gamma$ (where $\alpha < \beta < \gamma$) have been directly determined by means of excellent prisms accurately ground and polished in the theoretically most desirable directions by means of the new apparatus previously referred to. Each of these prisms was formed by plane faces truly symmetrical to a plane of optical elasticity, and the intersecting edge was strictly parallel to an axis of optical elasticity. Eleven such prisms were prepared with the greatest care, and were used uncovered, the polished faces furnishing brilliant single reflected images of the slit, and a pair of bright and clearly defined refracted images corresponding to the two refractive indices afforded by the particular prism for the particular wave-length of light with which the slit was illuminated. These 11 prisms were ground upon five different well-formed crystals, from different crops, of somewhat larger size than the small crystals employed in the goniometrical investigation. It was so arranged that a pair of prisms (in one case three prisms, the third being a duplicate at the other end of the same crystallographic axis) were ground upon the same crystal in such directions that all three refractive indices were determined by use of them, one of the indices being also obtained in duplicate owing to one direction of vibration being common to the two prisms. Hence five complete independent series of indices have been obtained, the mean values of which are probably as near to the truth as is experimentally attainable. The measurements of the prism angles, which were closely approximating

to 60°, and the determinations of minimum deviation by use of the new monochromatic light apparatus, were carried out precisely as described in the communication to the Royal Society previously referred to. The measurements of minimum deviation were extended as far as G of the spectrum, the pair of images of the slit in G violet light being still sufficiently distinct with the best polished prisms to enable accurate allocation to the cross wires of the spectrometer to be made. The excellent goniometer of Fuess No. 2a was employed as spectrometer, using throughout the Websky slit. The directions of vibration of the light of the two refracted images were determined, as described in the memoir referred to, by means of a Nicol prism carried in front of the eye-piece, which was also used to extinguish one image while setting the other to the cross wire. The results of the determinations are given in the accompanying table (p. 668). Details of the determinations of minimum deviation, all of which were made in duplicate, one series with the light incident upon one face of the prism, and another series with it incident upon the other face, are omitted as more suitable for the note-book; and all values determined more than once upon the same crystal are likewise omitted, the mean only being given in each case. In all cases the duplicate values were within four units in the fourth place of decimals from the mean, and usually not more than one or two removed. In the last column, the final mean values of the refractive indices are given.

It will be understood that Li in the second column concisely expresses that the determination was made with monochromatic light from the new apparatus of the same wave-length as that of the red lithium line, C that corresponding to the red hydrogen line, Na to the sodium D lines, Tl to the green thallium line, F to the greenish-blue hydrogen line, and G that corresponding to the bluish-violet hydrogen line.

General Formula for the Refraction of Potassium Sulphate.—The refractive indices of the crystals of potassium sulphate may be represented by the following formula, obtained by combining the three equations of condition formed by placing the observed values of the indices and the corresponding wave-lengths for red hydrogen C light, light of the wave-length of the sodium lines, and light of the wave-length of the thallium flame in Cauchy's formula

$$\mu = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + \dots$$

The indices employed were the β values, those corresponding to the intermediate axis of optical elasticity. It is found that the values of the α and γ indices are equally well reproduced by the formula if

Refractive Indices of Potassium Sulphate, K₂SO₄.

Index.	Nature of light.	Crystal 1, 3 prisms.	Crystal 2, 2 prisms.	Crystal 3, 2 prisms.	Crystal 4, 2 prisms.	Crystal 5, 2 prisms.	Mean values derived from 11 prisms.
α vibrations parallel to axis <i>b</i> .	Li	1.4915	1.4910	1.4915	1.4913	1.4908	1.4912
	C	1.4917	1.4914	1.4919	1.4917	1.4912	1.4916
	Na	1.4936	1.4933	1.4938	1.4937	1.4931	1.4935
	Tl	1.4956	1.4954	1.4957	1.4956	1.4953	1.4955
	F	1.4982	1.4979	1.4985	1.4984	1.4978	1.4982
	G	1.5010	1.5010	1.5010	1.5012	1.5016	1.5012
β vibrations parallel to axis <i>a</i> .	Li	1.4924	1.4922	1.4923	1.4921	1.4925	1.4924
	C	1.4928	1.4926	1.4927	1.4928	1.4929	1.4928
	Na	1.4947	1.4945	1.4947	1.4948	1.4948	1.4947
	Tl	1.4967	1.4966	1.4967	1.4967	1.4970	1.4967
	F	1.4994	1.4993	1.4994	1.4996	1.5000	1.4995
	G	1.5023	1.5022	1.5023	1.5025	1.5029	1.5024
γ vibrations parallel to axis <i>c</i> .	Li	1.4949	1.4952	1.4949	1.4952	1.4948	1.4950
	C	1.4953	1.4956	1.4953	1.4955	1.4952	1.4954
	Na	1.4973	1.4975	1.4973	1.4974	1.4972	1.4973
	Tl	1.4994	1.4996	1.4993	1.4994	1.4994	1.4994
	F	1.5021	1.5024	1.5021	1.5024	1.5023	1.5023
	G	1.5050	1.5049	1.5050	1.5052	1.5057	1.5052

the constant A is diminished by 0.0012, and increased by 0.0026 respectively. In calculating the constants, the mean values given in the table have been corrected for the atmospheric refraction by adding to the mean observed values 0.0004, so that the formula expresses the true refractive indices *in vacuo*. In the calculations also, only the significant figures of the wave-lengths 6562, 5892, and 5348 have been used as whole numbers.

$$\mu_{K_2SO_4} = \left. \begin{array}{l} \alpha \ 1.4831 \\ \beta \ 1.4843 \\ \gamma \ 1.4869 \end{array} \right\} + \frac{417 \ 458}{\lambda^2} - \frac{1 \ 474 \ 690 \ 000 \ 000}{\lambda^4} + \dots$$

The formula reproduces the values with great precision, the calculated values for G light being only 4—6 units in the fourth place of decimals removed from the observed values (+ the reduction to *vacuo* constant 0.0004), while the values for the more brilliantly illuminating portions of the spectrum are exactly reproduced.

Observations of Refractive Index at Higher Temperatures.—It was considered important, in order that any deductions drawn from a comparison of the refractive indices of the three salts should be independent of temperature, that a series of observations should be made at regular temperature intervals up to a reasonably elevated limit. A series of such determinations have therefore been made at intervals of 40° up to 180°. The large goniometer, Model No. 1, was employed, with its accompanying heating apparatus. Such investigations are much facilitated by the new monochromatic light apparatus, for a whole series of observations with five wave-lengths, together with the measurement of the angle of the prism, can be made in a very few minutes, during which time it is not difficult to maintain the temperature constant. The determinations were obtained with two of the best of the prisms.

In the following table are given the results for the different temperatures, the mean values for the ordinary temperature taken from the previous table being also given for the sake of comparison. The values for G light were not observed owing to the relative weakness of the G images after passing through the plate-glass windows of the heating apparatus, the setting of such images requiring much longer time.

It will be observed (1) that there is a steady decrease of refractive power as the temperature rises; (2) that the change is greatest in the γ indices corresponding to rays vibrating parallel to the vertical axis c , the difference for a rise of 160° amounting to about 0.0067; and (3) the change in the α and β indices corresponding to the axes a and b is about equal, amounting to approximately 0.0057. It will be interesting to observe subsequently whether the same rules hold in the cases of the other two salts.

Refraction of Potassium Sulphate at Different Temperatures.

Index.	Nature of light.	At ordinary temperature (18—20°).	At 60°.	At 100°.	At 140°.	At 180°.
α Vibs. par. to axis <i>b</i> .	Li	1·4912	1·4902	1·4890	1·4876	1·4855
	C	1·4916	1·4906	1·4894	1·4880	1·4859
	Na	1·4935	1·4925	1·4911	1·4896	1·4878
	Tl	1·4955	1·4945	1·4931	1·4917	1·4899
	F	1·4982	1·4972	1·4960	1·4946	1·4926
β Vibs. par. to axis <i>a</i> .	Li	1·4924	1·4914	1·4901	1·4886	1·4869
	C	1·4928	1·4918	1·4905	1·4890	1·4873
	Na	1·4947	1·4936	1·4921	1·4909	1·4890
	Tl	1·4967	1·4955	1·4944	1·4928	1·4910
	F	1·4995	1·4984	1·4972	1·4956	1·4936
γ Vibs. par. to axis <i>c</i> .	Li	1·4950	1·4938	1·4924	1·4905	1·4883
	C	1·4954	1·4942	1·4928	1·4909	1·4887
	Na	1·4973	1·4963	1·4948	1·4929	1·4906
	Tl	1·4994	1·4983	1·4968	1·4949	1·4927
	F	1·5023	1·5010	1·4995	1·4978	1·4954

Optical Elasticity Axes of Potassium Sulphate.—The relative optical elasticities at the ordinary temperature along the directions of the three crystallographic axes, determined by comparing the reciprocals of the refractive indices corresponding to the crystallographic axes *a* and *c* with the reciprocal of that for *b*, and for the same wave-length, are as follows.

$$a : b : c = 0.9992 : 1 : 0.9975.$$

The values were calculated for the wave-lengths of the C hydrogen line, the D sodium lines, and the thallium line, and are identical for these three wave-lengths.

The refractive indices of potassium sulphate were determined by Topsoe and Christiansen (*loc. cit.*) for the rays C, D, and F of the spectrum, the sources of light being a hydrogen Geissler tube and a spirit lamp whose flame was impregnated with salt. Six prisms were employed; two were formed by natural faces, and the remaining four were ground by hand and covered with glass plates. Five of these six prisms, however, were only such as afforded one refractive index, not being symmetrical to a plane of optical elasticity. The values arrived at for the indices are fairly close to those given in this communication, the greatest difference for any index being 7 in the fourth place of decimals. The ratios of the elasticity axes derived from their values are 0.9991 : 1 : 0.9968.

Adopting the scheme of orientation of elasticity axes employed by Topsoe and Christiansen, where $a > b > c$, the order for potassium

sulphate corresponding to the order of the crystallographic axes is $b a c$, the cross under the last symbol indicating that the crystallographic axis c , the axis of least optical elasticity, is the first median line and that the sign of double refraction is positive. The sign of double refraction was confirmed by observation of the distortion of the interference figure, exhibited by a plate perpendicular to the first median line, produced by the introduction of a quarter undulation mica plate in the ordinary manner; its positive character is, of course, determined by the fact that the intermediate indices β are nearer to the α than to the γ values.

The elasticity ratios calculated from the refractive indices at 180° are: $a : b : c = 0.9992 : 1 : 0.9981$, the former being identical with, and the latter not far removed from, the value at the ordinary temperature, and the order being the same.

Determinations of Optic Axial Angle.—Experimental determinations of the optic axial angle are of much greater value, particularly in the case of low doubly refracting substances like those under consideration, than values calculated from the refractive indices by the formula

$$\cos V = \sqrt{\frac{1 - \frac{1}{\beta^2}}{1 - \frac{1}{\alpha^2}}}.$$

For the differences between the reciprocals of the squares of the refractive indices are so small that a change of one unit in the fourth place of decimals in the refractive indices is sufficient to alter the calculated value of the optic axial angle by as much as from one to two whole degrees. Even in the case of the refractive indices determined with so much care in the present determination it is quite possible that the error may even attain to two such units, hence measurements of the optic axial angle are alone to be regarded as worthy of acceptance.

Three pairs of section-plates were ground by means of the new grinding instrument, perpendicular to the first (axis c) and second (axis b) median lines respectively. The sections require to be relatively very thick in order to exhibit well-defined interference figures, owing to the low double refraction. The three sections parallel to the basal plane employed for the determination of $2E$, the apparent angle in air, and $2Ha$, the apparent acute angle in the highly refractive liquid employed (α -monobromonaphthalene) varied from 2 to over 3 mm. in thickness, the latter dimension being well adapted for the purpose. Somewhat large crystals are required to furnish such sections, for usually the crystals are narrow in this direction. Particular care was therefore bestowed on the choice of the most perfect

large crystals. The greater development of the crystals in the direction of the brachypinacoid b enabled three excellent large and sufficiently thick sections to be prepared perpendicular to the second median line, through which the obtuse angle of the axes, $2H_0$, was well observed in monobromonaphthalene. The excellent polish which the surfaces presented after five minutes' use of the polishing apparatus of the instrument enabled the whole of the measurements to be carried out without the use of cemented glass cover-plates. The larger axial angle goniometer of Fuess was employed, illuminated by the new monochromatic light apparatus, the operations being conducted as described in the communication to the *Phil. Trans.* of the Royal Society previously referred to. Three settings of each hyperbolic brush were made to the cross wires for each wave-length, and the mean of the goniometer circle readings taken as the true position.

The interference figure of potassium sulphate in air $2E$ is much less well-defined than in bromonaphthalene, and owing to the large angle by which the hyperbolic brushes are separated, fairly wide as well as thick sections are required in order that well-defined brushes may be brought to the cross wires. No trace of colour could be detected about the brushes when viewed in white light, indicating the absence or minuteness of dispersion of the axes. In bromonaphthalene there is over a degree of dispersion. Upon proceeding to measure the angle $2E$ in air, although the thick sections employed furnished fairly fine brushes, no difference greater than the error of setting of the brushes to the cross wires could be detected between the values of the angles for the extreme ends of the spectrum. Topsøe and Christiansen give the angle in air $2E$ as $111^\circ 19'$. Des Cloizeaux had previously found $2E$ 107 — 109° , and in a later memoir (*Memoires des Savants Étrangers*, t. xviii, p. 608) gave the values for the red and blue of the spectrum as $110^\circ 15'$ and $110^\circ 26'$ respectively.

A large number of measurements of $2E$ were made for light of the wave-lengths of the red lithium line and the greenish-blue hydrogen F line, with the three sections, but the numbers obtained exhibit differences for the same wave-length greater than the limits of Des Cloizeaux's values. The author therefore prefers to give the mean of all the values obtained and to record the fact that the dispersion of the axes is extremely small. The mean value of the apparent angle in air thus obtained is

$$2E = 111^\circ 0'.$$

The limits of the individual observations lie about $30'$ on each side of this mean value.

The determinations of the apparent acute and obtuse angles in bromonaphthalene presented no difficulties, the brushes being admirably defined and the dispersion unmistakable. The new monochromatic light apparatus enables small amounts of dispersion to be particularly easily recognised; by rapid rotation of the prism circle and consequent rapid change in the colour with which the whole field is illuminated the brushes can be seen to move from one position to another with respect to the horizontal pair of cross wires. The following are the results of the observations with the six sections:—

Determination of True Optic Axial Angle 2Va of K₂SO₄.

Nature of light.	No. of section perp. 1st median line.	Observed values of 2Ha.	No. of section perp. 2nd median line.	Observed values of 2Ho.	Calculated value of 2Va.	Mean values of 2Va.
Li.....	{ 1	60° 5'	1a	97° 16	67° 25'	67° 25'
	{ 2	60 30	2a	97 48	67 32	
	{ 3	60 3	3a	97 28	67 18	
C.....	{ 1	60 2	1a	97 12	67 24	67 24
	{ 2	60 23	2a	97 36	67 31	
	{ 3	59 57	3a	97 23	67 16	
Na.....	{ 1	59 53	1a	97 2	67 21	67 20
	{ 2	59 59	2a	96 58	67 27	
	{ 3	59 44	3a	97 6	67 12	
Tl.....	{ 1	59 30	1a	96 28	67 16	67 15
	{ 2	59 33	2a	96 18	67 23	
	{ 3	59 12	3a	96 17	67 6	
F.....	{ 1	59 0	1a	95 44	67 10	67 7
	{ 2	58 54	2a	95 35	67 9	
	{ 3	58 49	3a	95 42	67 2	

The measurements of 2Ha and 2Ho with each pair of sections arranged in the same horizontal line in the table, which together enabled the true angle 2Va to be calculated from the formula

$\tan Va = \frac{\sin Ha}{\sin Ho}$, were carried out in immediate succession on the same evening, so that no change in the refraction of the bromonaphthalene was possible. Observations with G light are not very trustworthy, on account of loss of light by the absorption of the bromonaphthalene.

The value of 2Va for sodium light calculated from the observed refractive indices is 67° 38'. This excellent agreement, however, is purely fortuitous, for a difference of 0.0001 in any of the refractive indices would make a very large difference. For instance, if the value of the index α were taken as 1.4936 instead of 1.4935, the calculated 2Va becomes 66° 6', a difference of a degree and a half. As the possible error of the refractive index determinations may even attain 0.0002, it is purely accidental that the agreement between the observed and calculated optic axial angle is so close.

The optic axial angle $2Va$ for sodium light was found by Topsøe and Christiansen in two determinations to be $66^\circ 40'$ and $67^\circ 28'$ respectively, values very much further apart than those now presented.

Effect of Rise of Temperature on the Separation of the Optic Axes.—Observations at higher temperatures than the ordinary have previously been carried out for potassium sulphate by Des Cloizeaux (*Nouv. Rech.*) and Mallard (*Zeitschrift für Kryst.*, 9, 402). The former found that upon raising the temperature by 140° the apparent angle in air increased by about 10° . This observation has been confirmed by the author, and is in agreement with the indications of the changes in the refractive indices for rise of temperature. At 116° , the brushes were observed to be distinctly tinted with red inside and blue outside, indicating that the angle for red was larger than that for blue. Measurements conducted at this temperature, using the heating apparatus constructed by Fuess for the large axial angle goniometer, gave the following results:—

2E at 116° for Li light	= $118^\circ 55'$
„ Na „	= $118^\circ 40'$
„ F „	= $118^\circ 30'$

Hence for 100° of rise of temperature, 2E increases by nearly 7° , and a perceptible amount of dispersion of the axes is produced. The author did not pursue the heating further, in order to avoid risk of injuring the delicate instrument employed; moreover, for the purpose of comparing the three sulphates under investigation, it will subsequently be shown that this is ample. Mallard, who has followed the phenomena to very high temperatures in the case of potassium sulphate, employing a less valuable instrument, has shown that the widening of the angle occurs until at about 380° the axes unite in the crystallographic axis b , and then pass out in the plane $\{001\}$ at right angles to their former plane, and at still higher temperatures further similar changes occur until between 600° and 650° a sudden change into a truly hexagonal dimorphous form with negative double refraction occurs. These observations of Mallard are of considerable interest for the purposes of this communication, as it will be subsequently shown that rubidium sulphate is remarkable, and for a reason of prime importance, in exhibiting similar, but still more complicated, phenomena at temperatures but slightly elevated above the ordinary.

Optical Properties of Cæsium Sulphate.

Cæsium sulphate resembles potassium sulphate in its low double refraction, similar thick plates, not, however, quite so thick, being required to exhibit interference figures with small rings round the

axes. It differs, however, in being endowed with negative double refraction, and the dispersion of the axes for light of different wave-lengths is greater. The first median line is the vertical axis c , and the interference figure is well seen in convergent polarised light through the broadly developed basal plane, a crystal 2—3 mm. thick exhibiting it admirably. The plane of the optic axes is that containing the axes a and c parallel to the brachypinacoid $b\{010\}$. The orientation of the axes of optical elasticity is therefore cba , as given

by von Lang, who made a cursory examination of the salt (*Sitz. Ber. Wien. Akad.*, 55, ii, 415).

Refractive Indices of Cs_2SO_4 .—Fourteen prisms were prepared in like manner to those of K_2SO_4 , belonging to five different crystals. The faces of all these prisms were ground and polished symmetrically to known symmetry planes of the crystals, and their intersecting edges were all parallel to axes of optical elasticity. Hence each prism, as in the case of potassium sulphate, furnished the values of two refractive indices. In the cases of crystals 1 and 2, no less than four prisms were successfully ground and polished upon each, a pair of similar ones at the ends of each of two of the crystallographic axes. With a good crystal of 4 or 5 mm. diameter, there is no difficulty in accomplishing this by means of the new instrument, and two of the indices are thus obtained twice and the other four times repeated from the same crystal.

The mean values obtained from each crystal, together with the final mean values, are given in the table (p. 676). The individual values were all very close to the mean numbers.

The refraction of cæsium sulphate for any wave-length, corrected to a vacuum, may be accurately expressed by the following general formula, the constants of which have been calculated by combining the equations of condition formed by inserting the observed values for C, Na, and Tl light, plus the vacuum correction (0.0004) in Cauchy's formula.

$$\mu_{\text{Cs}_2\text{SO}_4} = \left. \begin{array}{l} \alpha \ 1.5478 \\ \beta \ 1.5524 \\ \gamma \ 1.5542 \end{array} \right\} + \frac{409 \ 782}{\lambda^2} + \frac{716 \ 952 \ 000 \ 600}{\lambda^4} + \dots$$

The values calculated from the formula, after subtracting the vacuum correction (0.0004), are in nearly all cases identical, or only one unit in the fourth place of decimals removed from the mean observed values above given.

It will be observed that the β indices approach more closely to the γ than to the α values, proving the negative sign of double refraction, which was also independently confirmed by the use of a quarter undulation mica plate. The value of the constant A in the

Refractive Indices of Cæsium Sulphate, Cs₂SO₄.

Index.	Wave-length for which determined.	Crystal 1, 4 prisms.	Crystal 2, 4 prisms.	Crystal 3, 1 prism.	Crystal 4, 3 prisms.	Crystal 5, 2 prisms.	Mean values from 14 prisms.
α vibrations parallel to axis <i>c</i> .	Li	1.5571	1.5503	1.5571	1.5576	1.5565	1.5569
	C	1.5574	1.5567	1.5575	1.5580	1.5568	1.5573
	Na	1.5600	1.5592	1.5599	1.5606	1.5594	1.5598
	Tl	1.5627	1.5618	1.5624	1.5632	1.5620	1.5624
	F	1.5662	1.5652	1.5660	1.5669	1.5655	1.5660
	G	—	1.5703	—	—	1.5707	1.5705
β vibrations parallel to axis <i>b</i> .	Li	1.5614	1.5614	1.5616	1.5619	1.5613	1.5615
	C	1.5618	1.5619	1.5620	1.5623	1.5617	1.5619
	Na	1.5644	1.5644	1.5644	1.5649	1.5642	1.5644
	Tl	1.5672	1.5671	1.5680	1.5676	1.5670	1.5672
	F	1.5708	1.5706	1.5704	1.5711	1.5703	1.5706
	G	—	1.5752	—	1.5752	1.5753	1.5756
γ vibrations parallel to axis <i>a</i> .	Li	1.5629	1.5629	—	1.5639	1.5634	1.5633
	C	1.5633	1.5633	—	1.5643	1.5638	1.5637
	Na	1.5660	1.5659	—	1.5667	1.5663	1.5662
	Tl	1.5687	1.5686	—	1.5695	1.5692	1.5690
	F	1.5724	1.5721	—	1.5730	1.5725	1.5725
	G	—	1.5770	—	1.5780	—	1.5775

above formula for α is obtained by subtracting 0.0046 from the constant for β actually calculated, and that for γ by adding 0.0018.

Refraction of Cæsium Sulphate at Higher Temperatures.—A series of observations of refractive index with a pair of prisms at regular intervals of temperature was carried out as in the case of potassium sulphate. The results are as follows:—

Refraction of Cæsium Sulphate at Different Temperatures.

Index.	Nature of light.	At ordinary temperature (18–20°).	At 60°.	At 100°.	At 140°.	At 180°.
α Vibs. par. to axis c .	Li	1.5569	1.5559	1.5544	1.5527	1.5508
	C	1.5573	1.5563	1.5548	1.5531	1.5512
	Na	1.5598	1.5584	1.5568	1.5554	1.5534
	Tl	1.5624	1.5609	1.5590	1.5576	1.5558
	F	1.5660	1.5641	1.5622	1.5608	1.5590
β Vibs. par. to axis b .	Li	1.5615	1.5607	1.5595	1.5581	1.5566
	C	1.5619	1.5611	1.5599	1.5585	1.5570
	Na	1.5644	1.5634	1.5622	1.5609	1.5594
	Tl	1.5672	1.5658	1.5645	1.5632	1.5619
	F	1.5706	1.5690	1.5677	1.5664	1.5651
γ Vibs. par. to axis a .	Li	1.5633	1.5625	1.5611	1.5599	1.5587
	C	1.5637	1.5629	1.5615	1.5603	1.5591
	Na	1.5662	1.5651	1.5640	1.5626	1.5614
	Tl	1.5690	1.5674	1.5664	1.5649	1.5639
	F	1.5725	1.5706	1.5696	1.5681	1.5671

It is interesting to observe, as in the case of potassium sulphate, (1), that there is a steady decrease in refractive power as the temperature rises; (2), that the greatest amount of change occurs in the indices corresponding to the axis c , where the difference for 160° amounts to about 0.0065; and (3), that the changes of the indices corresponding to the axes a and b are approximately equal, amounting to about 0.0049. It would also appear in the case of cæsium sulphate that there is a perceptible diminution in the dispersion as the temperature rises, the difference between the indices for the two extreme wave-lengths being 0.0091–92 at the ordinary temperature, while at 180° it is 0.0082–85, the diminution in refractive power for rise of temperature being apparently greater at the blue end of the spectrum than at the red end.

Optical Elasticity Axes of Cæsium Sulphate.—The ratios of the optical elasticity along the three crystallographic axes at the ordinary temperature are:—

$$a : b : c = 0.9989 : 1 : 1.0029.$$

These correspond to the orientation cba .

The ratios calculated from the refractive indices at 180° are:— $a:b:c = 0.9987:1:1.0039$, not far removed from, and of the same order as, their values at the ordinary temperature.

Measurements of the Optic Axial Angle of Cæsium Sulphate.—These measurements were carried out with six excellent section-plates about $2\frac{1}{2}$ mm. thick, three perpendicular to the first and three perpendicular to the second median line. Sections Nos. 1 and 2 were formed by beautifully perfect natural faces of the basal plane, largely developed upon crystals half an inch long. The remaining sections were ground and polished by means of the new instrument, and all were employed uncovered by glass plates. The interference figures of cæsium sulphate are admirably defined, and with sections of the thickness used the values of $2E$ may be very accurately determined. In bromonaphthalene, the figures are even better defined, and although it curiously happens that the dispersion of the axes, which amounts to over 3° for $2E$ between the red and blue, is reduced almost to zero in the highly refractive liquid, still by use of the new monochromatic illuminator the difference of only five or six minutes is clearly discernible, and is confirmed by the slight tints upon the margins of the brushes. The results are presented in the accompanying tables.

Determination of apparent Optic Axial Angle in Air $2E$ of Cs_2SO_4 .

Nature of light.	Section 1.	Section 2.	Section 3.	Mean values of $2E$.
Li.....	$114^\circ 47'$	$114^\circ 33'$	$114^\circ 20'$	$114^\circ 33'$
C.....	$114 53$	$114 45$	$114 40$	$114 46$
Na.....	$115 39$	$115 43$	$115 39$	$115 40$
Tl.....	$116 50$	$116 47$	$116 41$	$116 46$
F.....	$117 55$	$117 52$	$117 34$	$117 47$

Determination of true Optic Axial Angle $2Va$ of Cs_2SO_4 .

Nature of light.	No. of section perp. 1st median line.	Observed values of $2Ha$.	No. of section perp. 2nd median line.	Observed values of $2Ho$.	Calculated value of $2Va$.	Mean values of $2Va$.
Li.....	{ 1	$61^\circ 14'$	1a	$106^\circ 9'$	$65^\circ 0'$	{ $65^\circ 5'$
	{ 2	$61 11$	2a	$105 36$	$65 9$	
	{ 3	$61 11$	3a	$105 47$	$65 6$	
C.....	{ 1	$61 13$	1a	$106 4$	$65 1$	{ $65 8$
	{ 2	$61 10$	2a	$105 25$	$65 12$	
	{ 3	$61 10$	3a	$105 45$	$65 6$	
Na.....	{ 1	$61 12$	1a	$105 15$	$65 17$	{ $65 20$
	{ 2	$61 8$	2a	$104 54$	$65 22$	
	{ 3	$61 8$	3a	$104 59$	$65 20$	
Tl....	{ 1	$61 11$	1a	$104 10$	$65 40$	{ $65 39$
	{ 2	$61 7$	2a	$104 6$	$65 38$	
	{ 3	$61 7$	3a	$104 3$	$65 38$	
F.....	{ 1	$61 10$	1a	$103 12$	$65 59$	{ $66 0$
	{ 2	$61 5$	2a	$103 3$	$65 58$	
	{ 3	$61 6$	3a	$102 56$	$66 2$	

In each case, as with potassium sulphate, the pairs of sections 1 and 1a, 2 and 2a, 3 and 3a, were measured in immediate succession, for 2E, 2Ha, and 2Ho, on the same evening, in order to ensure that no change in the refractive index of the bromonaphthalene should occur.

Von Lang (*loc. cit.*) states that the apparent angle of the optic axes is 114° , and for red is smaller than for violet, $\rho < v$.

Effect of Rise of Temperature on the Separation of the Optic Axes of Cæsium Sulphate.—Measurements of 2E were carried out at temperatures of 60° and 100° , employing the same arrangement as in the case of potassium sulphate. The results are as follows, the values at the ordinary temperature being also given for the sake of comparison:—

	2E at $18-20^\circ$.	2E at 60° .	2E at 100° .
Li	$114^\circ 33'$	$110^\circ 50'$	$108^\circ 30'$
C	114 46	111 15	108 42
Na	115 40	112 27	109 10
Tl	116 46	113 30	110 56
F	117 47	115 25	112 35

The axes are thus observed to approach each other by about 6° for a rise of temperature of 80° , corresponding to an approach of $7\frac{1}{2}^\circ$ for 100° of rise of temperature. This is about the same amount, but in the inverse order, corresponding to the negative sign of double refraction, as was observed in the case of the positive crystals of potassium sulphate. The amount and direction of change agree with those indicated by the determinations of refractive index at the higher temperatures. For a reason previously discussed, the true optic axial angle is only afforded by the formula

$$\cos V = \sqrt{\frac{1 - \frac{1}{\beta^2}}{1 - \frac{1}{\gamma^2}}}$$

very roughly indeed, the possible error being quite two degrees. Yet the order of the change for a considerable interval of temperature is clearly indicated. The approximate value of the true optic axial angle (the supplement of V , the crystal being negative) thus calculated from the refractive indices for sodium light at the ordinary temperature, is $63^\circ 52'$, and that calculated from the indices obtained at 180° is $59^\circ 28'$, indicating a decrease in the true angle of about $4\frac{1}{2}^\circ$ for 160° of rise of temperature. The actual amount thus indicated is of little value, but its order and direction indicate the agreement of the phenomena observed with regard to the changes of refractive index and of the apparent angle of the optic axes in air brought about by rise of temperature.

Optical properties of Rubidium Sulphate.

It will have been gathered from the foregoing that potassium sulphate and caesium sulphate are normally behaved, low doubly refracting substances of positive and negative characters respectively. The optical characters of rubidium sulphate are apparently quite different and unusual. Upon examining a crystal in convergent polarised white light through a pair of the well developed macropinacoid faces $a\{100\}$, the plate thus formed being about the thickness (two to three millimetres) which was sufficient in the cases of the two other salts to afford well defined interference figures, when the axial directions coincide with the planes of the nicols a broad dark cross deeply fringed with colour is observed; this breaks up on rotating the plate through 45° into two brilliant rainbow-coloured hyperbolic curves, containing no dark central core, or a mere trace of such. The broad blue fringe is inside and the red outside. These curves indeed more resemble portions of rings than hyperbolic brushes. There may, if the section is sufficiently thick, be one ellipse or a portion of one surrounding the loci of the axes. The crystals are evidently endowed with very feeble double refraction and exhibit very high dispersion of the optic axes. If a similar plate about a quarter of an inch thick is procured, a most beautiful figure is observed in white light, reminding one of the figures given by substances endowed with such high dispersion that the axes for one end of the spectrum lie in a plane at right angles to the one containing them for light of the other end of the spectrum, the only difference being that the axes appear to be just contained in one plane, the plane $a\ b$ parallel to the basal plane $c\{001\}$. With a beautiful section which the author has succeeded in grinding parallel to the $a\{100\}$ faces out of the largest perfect crystal obtained, and which is 8 mm. thick, the cross is seen, when the crystallographic axes are parallel to the nicols, surrounded by four complete curves, the outer simulating ellipses surrounding both axes and symmetrical to the crystallographic axial directions, and the inner one just coming in towards the centre so as to nearly form a pair of lemniscate loops. These curves are distinguished by having a very long diameter in the direction of the optic axial plane $c\{001\}$ and a very short one at right angles to this direction. Near the ends of the longest diameter, the curves become dark but still fringed deeply with colour. The whole space between each end of the largest diameter of the inner curve and the central dark cross bar is filled with a single broad spectrum very similar to that shown by crystals of the type mentioned, such as brookite and the triple tartrate of potassium, sodium, and ammonium. Upon rotating the section for 45° , no dark brushes or rings are observed, but an

exquisite pair of spectrum hyperbolæ enveloped by three spectrum ellipse-like curves and an inner pair of similar rainbow-tinted lemniscate loops. When the monochromatic light apparatus is employed to illuminate the polariscope, and the prism circle of the former is rotated so as to review the figures in all the colours of the spectrum in succession, it is observed that the optic axial brushes are very well defined and are but slightly separated for the extreme red, whilst for the violet their separation is very wide, indicating very high dispersion; moreover, several complete rings become in turn visible round the brushes as the violet is approached. If a quarter undulation mica plate is used with the section again arranged with the axial directions parallel to the nicols and illuminated by blue light, the double refraction is distinctly seen to be positive. The phenomena will be more fully described when the measurements are considered. With thinner sections, the brushes are very much diffused, rendering accurate measurement impossible.

Von Lang (*loc. cit.*) states concerning rubidium sulphate that the double refraction is very small, and that the sign of the double refraction can only be determined with thick plates, and is negative. He is scarcely likely, however, to have obtained a section so thick as the one used by the author, for he further states that the optic axial angle could only be measured approximately owing to the small double refraction, while the author had no difficulty in obtaining accurate measurements from the 8 mm. section. It will be conclusively proved from the refractive index determinations and the detailed study of the orientation of the optic axes, that the pure rubidium sulphate employed exhibits positive double refraction.

The orientation of the optic axes is therefore $\pm$ ab.

The reason for this remarkable sensitiveness of the axial angle of rubidium sulphate to change in the wave-length of the illuminating light is of the most interesting character, and will be fully explained when the refractive index determinations and the calculations of the elasticity ratios have been discussed.

Refractive Indices of Rubidium Sulphate.—Ten excellent prisms were ground and polished by means of the new instrument in the same manner as those of the sulphates of potassium and cesium, upon five different crystals; each prism was symmetrical to a plane, and its refracting edge parallel to an axis, of optical elasticity so as to afford two indices for each wave-length. The angles were all in the neighbourhood of 60° , and their faces so well polished as to require no cover-glasses.

Three of these prisms were ground in such directions in the crystal that the vibrations of the two polarised refracted rays were parallel

to the crystallographic axes b and c , which are identical with the axes of optical elasticity ab , and should furnish the two indices α and β . The remarkable observation was made with each of these prisms that they gave only one refracted image of the Websky slit of the spectrometer with all the colours of light employed. This image, moreover, remained permanent for all positions of the nicol placed in front of the eyepiece of the telescope, although there was a slight difference in the illumination of the image for the positions 0° and 90° , not nearly so great, however, as would be the case with a single refracted image obtained from an isotropic or glass prism. There were, consequently, two images occupying the same position, one of which was extinguished by the nicol at 0° and the other at 90° . With the magnifying power usually employed, and with the slit arranged so that its central narrow portion was extremely fine, no distinction could be observed between the positions of these images. Indeed it would appear at first sight as if the light transmitted along the axis a (the direction in which the light travels at minimum deviation in these prisms) suffers no double refraction, and as if this were the direction of the single optic axis of an uniaxial crystal. This is not, however, the case, for when the higher power eyepiece provided with the Fuess instrument was employed two distinct, partially overlapping images could be detected when the brilliant light from the monochromatic light apparatus corresponding to sodium light was used to illuminate the slit; the image corresponding to the α -index (vibrating parallel to the axis b) being distinctly nearer at minimum deviation to the direct reading of the slit, than the β -image (vibrating parallel to the axis c) by about one minute of arc. There is not sufficient light to employ this high power eyepiece satisfactorily for the end rays of the spectrum, but sufficient evidence was obtained with the lower power that no separation amounting to $2'$ (an amount easily detected) occurred for other wave-lengths as far as F of the spectrum, although it may have been and probably was (as will subsequently be shown) less than $1'$ for the red end of the spectrum.

The results of the measurements of refractive index, conducted precisely as in the case of the potassium and caesium salts, employing the same ordinary eyepiece, are given in the table, p. 683.

As the three prisms which afforded the indices α and β indicated, with the ordinary eyepiece employed in all the observations of refractive index, no perceptible difference between the two images, the mean of the whole of the closely agreeing values for these indices obtained from the ten prisms has been taken as representing the two values as nearly as the limits of accuracy of such determinations, which are probably about 0.0002, will admit. A difference of one

Refractive Indices of Rubidium Sulphate, Rb₂SO₄, as determined by use of ordinary Egyptian.

Index.	Wave-length for which determined.	Crystal 1, 2 prisms.	Crystal 2, 2 prisms.	Crystal 3, 2 prisms.	Crystal 4, 2 prisms.	Crystal 5, 2 prisms.	Mean values from 10 prisms.
α and β vibrations parallel to axes b and c respectively.	Li	1.5106	1.5109	1.5108	1.5110	1.5113	1.5109
	C	1.5110	1.5113	1.5112	1.5114	1.5117	1.5113
	Na	1.5132	1.5133	1.5132	1.5134	1.5136	1.5133
	Tl	1.5153	1.5155	1.5153	1.5155	1.5158	1.5155
	F	1.5182	1.5183	1.5182	1.5183	1.5186	1.5183
	G	1.5222	1.5224	—	1.5226	—	1.5224
γ vibrations parallel to axis a .	Li	1.5117	1.5119	1.5118	1.5123	1.5124	1.5120
	C	1.5121	1.5123	1.5123	1.5127	1.5128	1.5124
	Na	1.5141	1.5143	1.5143	1.5146	1.5149	1.5144
	Tl	1.5162	1.5165	1.5164	1.5168	1.5171	1.5166
	F	1.5191	1.5193	1.5191	1.5196	1.5199	1.5194
	G	1.5232	—	—	1.5237	—	1.5235

minute in the angle of minimum deviation makes a difference of 0.00017 in the refractive index. Such a difference can just be perceived with the eyepiece in question when a single image is being observed, but when two such images are present and each has to be extinguished by the nicol while the other is examined, it is difficult to be quite certain of such a small difference. From the evidence afforded by the high power eyepiece, however, and conclusively from the optic axial angle measurements presently to be recorded, it is certain that the α - and β -indices ought not to be expressed by identical numbers, but that the α -indices would be more accurately represented by numbers 0.0001 to 0.0002 less than those of the β -indices. Such numbers will then accurately represent the refractive indices of rubidium sulphate at the ordinary temperature, within the limits of error previously laid down, the order of the three indices will be in full accordance with the optic axial angle phenomena, and the actual values of the α -indices will correspond exactly with those calculated from the measurements of the optic axial angle.

The refractive indices of rubidium sulphate may therefore be finally recorded as given below, with the reservation, which will subsequently be fully proved, that the difference between the α - and β -indices for red light is somewhat less than 0.0001, while that for blue light may just exceed 0.0002. Such differences might perhaps be represented by figures in the fifth decimal place, but the author does not feel justified in introducing a fifth decimal place, which in view of the possible error can have no real although it might have relative significance.

Refractive Indices of Rubidium Sulphate from Evidence of High Power Eyepiece and Optic Axial Angle Phenomena.

	α .	β .	γ .
Li	1.5108	1.5109	1.5120
C	1.5112	1.5113	1.5124
Na	1.5131	1.5133	1.5144
Tl	1.5153	1.5155	1.5166
F	1.5181	1.5183	1.5194
G	1.5222	1.5224	1.5235

The refraction of rubidium sulphate for any wave-length may be expressed by the following general formula, the constants of which were calculated, as in the cases of the other two salts, by introducing the β values for C, Na and Tl light in Cauchy's formula, and combining the three equations of condition thus obtained.

$$\mu_{\text{Rb}_2\text{SO}_4} = \frac{\alpha}{\gamma} \frac{1.5032 \text{ or } 1}{1.5044} + \frac{364}{\lambda^2} - \frac{217}{\lambda^2} - \frac{111}{\lambda^4} - \frac{239}{\lambda^4} - \frac{000}{\lambda^4} - \frac{000}{\lambda^4} + \dots$$

The constant A for the α -index is most accurately taken as 1.5032 for wave-lengths from the red as far as the sodium lines, and 1.5031 beyond this. The formula then reproduces the above indices with great accuracy, the calculated values being identical as far as thallium light, the differences for F light are only 0.0002, and for G light 0.0005.

The fact that the β -indices are nearer to the α than to the γ -indices, of course, proves the positive nature of the double refraction.

Refraction of Rubidium Sulphate at Higher Temperatures.—Particular interest attached to these observations, as it was to be expected that a difference between the indices α and β , appreciable by the ordinary eyepiece, might be developed on raising the temperature. One of the three prisms previously referred to as affording both these indices, whose vibration directions were parallel to the axes b and c , was therefore first examined at the same intervals of temperature as in the cases of the other two salts. At 60° , there was no apparent difference, the images being perfectly coincident. As the temperature approached 100° , however, the images commenced to separate, and at 100° they were distinctly apart, the difference in the reading of the minimum deviation being $2'$. At 140° , the difference had increased to $3'$, and at 180° to $5'$. Moreover, it was observed from the positions of the nicol for the two images, and knowing the orientation of the prism, that the image nearest to the direct reading of the slit, and therefore affording the lowest refractive index α , was produced by light vibrating parallel to the axis c , while the direction of vibration for the other image corresponding to the index β was parallel to the axis b . This is just the reverse of the case at the ordinary temperature. In addition to the separation, both images moved towards the direct reading, showing that there is a gradual diminution in refraction as the temperature rises. On examining a second prism whose vibration directions were parallel to the axes a and b respectively, at the same intervals of temperature, the two images corresponding to these two directions of vibration were observed to retain their distance ($6-7'$) from each other while both approached the direct reading, indicating as before diminution of refraction with rise of temperature. It is evident, therefore, that the greatest amount of change for rise of temperature occurs in the optical elasticity of the axis c , and that the changes in the elasticities along the other two axes a and b are approximately equal. The alteration in the refractive indices corresponding to the axis c occurs, moreover, in a remarkable manner. At the ordinary temperature, the c -axis is the axis of medium optical elasticity, and corresponds to the medium refractive index β ; the elasticity, however, is so very little less than the greater elasticity a along the axis b , which affords

the least refractive index α , that the two indices for any wave-length only differ by an amount varying from less than one unit to two units in the fourth place of decimals. On warming the crystal, the elasticity along the axis c increases, and inversely the refractive indices diminish relatively more than those corresponding to the other axes, and thus approach the values along the axis b still more closely until for some temperature between 20° and 100° , and this temperature will be different for each wave-length of light employed, the values along the two axes c and b are identical, and the crystal is apparently uniaxial, the optic axis lying in the crystallographic axis a . As the greater movement along the axis c relatively to the slower and simultaneous movements along the axes a and b continues, the elasticity along the c -axis passes that of the axis b , and becomes the greatest, and its corresponding refractive index the least α , the b -axis being then endowed with the medium elasticity; the change goes on until at 180° the values of the two series of refractive indices α and β corresponding to these two axes are about as far removed from each other as those corresponding to the simultaneously moving axes c and b . For temperatures beyond that for which for any particular wave-length the elasticities along the b and c axes are equal, and up to about 180° , the orientation of the axes is therefore cba , while at ordinary temperatures it has been shown to be cab , that is, there is an interchange between the elasticities along the axes b and c , the c value rapidly overstepping the b value as the temperature of the crystal is raised. Beyond 180° , it is probable that the crystal will become negative, owing to the medium elasticity becoming nearer to the minimum elasticity, the axis c then becoming first instead of second median line.

The results of the temperature measurements are recorded in the accompanying table (next page), the figures given for the refractive indices at the ordinary temperatures being the values actually obtained from the two prisms employed in the temperature determinations.

The two rules pointed out in the cases of potassium and caesium sulphates, that the greatest amount of change in optical elasticity for rise of temperature occurs along the c -axis, and that the change in the direction of the two other axes is approximately equal, have already been shown to hold in the case of rubidium sulphate and to lead to interesting conclusions. The amount of the difference for 160° between the refractive indices corresponding to the c -axis is $0.0059-61$, while that along the a and b axes respectively is $0.0050-54$ and $0.0049-51$.

Optical Elasticity Axes of Rubidium Sulphate.—On calculating the ratios of the optical elasticities along the crystallographic axes from

Refraction of Rubidium Sulphate at Different Temperatures.

Index.	Nature of light.	At ordinary temperature (18—20°).	At 60°.	At 100°.	At 140°.	At 180°.
<i>a</i> Vibrations par. axis <i>b</i> at low temps., and par. axis <i>c</i> at higher temps.	Li	1·5111	1·5104	1·5084	1·5069	1·5050
	C	1·5115	1·5108	1·5088	1·5073	1·5054
	Na	1·5135	1·5126	1·5108	1·5091	1·5075
	Tl	1·5158	1·5149	1·5130	1·5114	1·5098
	F	1·5184	1·5176	1·5158	1·5144	1·5125
<i>β</i> Vibrations par. axis <i>c</i> at low temps., and par. axis <i>b</i> at higher temps.	Li	identical with the <i>a</i> values	identical with the <i>a</i> values	1·5088	1·5077	1·5060
	C			1·5092	1·5081	1·5064
	Na			1·5112	1·5099	1·5085
	Tl			1·5134	1·5122	1·5108
	F			1·5162	1·5152	1·5135
<i>γ</i> Vibrations par. axis <i>a</i> .	Li	1·5124	1·5115	1·5098	1·5086	1·5070
	C	1·5128	1·5119	1·5102	1·5090	1·5074
	Na	1·5149	1·5137	1·5124	1·5110	1·5096
	Tl	1·5170	1·5160	1·5146	1·5132	1·5117
	F	1·5195	1·5187	1·5174	1·5160	1·5145

the refractive indices given in the table, in which the evidence of the high power eyepiece and the optic axial angle phenomena are taken into account, the following numbers are obtained.

$$a : b : c = 0.9991 : 1 : 0.9999.$$

These correspond to the orientation *cab*.

+

The ratios calculated from the refractive indices at 180° are

$$a : b : c = 0.9993 : 1 : 1.0006.$$

These correspond to the orientation *cba*.

The remarkable nearness to equality of elasticity along the three axes is admirably expressed by these ratios, the differences being only nine in 10,000 and one in 10,000 respectively.

Measurements of the Optic Axial Angle of Rubidium Sulphate.—The extraordinary thickness of section plate perpendicular to the first median line necessary to exhibit a well-defined interference figure, and the unusual amount of dispersion of the optic axes indicated by the beautiful figure in white light, and demonstrated by the great sensitiveness of the optic axial angle viewed in monochromatic light to change of wave-length, are fully accounted for by the optical elasticity relationships along the three axial directions above revealed. For the angle of separation of the optic axes depends essentially on the relation of the medium elasticity (in the rhombic system, the elasticity

along that one of the three crystallographic axes for which it is intermediate in value) to the greatest and least elasticity values. If it is nearer to the greatest, the crystal is positive, the conventional term for expressing that the first median line bisecting the acute angle between the optic axes is the axis of least optical elasticity; if it approximates more closely to the least, the crystal is negative, that is to say, the first median line is the axis of greatest elasticity. The relative amounts of the differences between the medium elasticity and maximum and minimum values determines the separation of the optic axes; in the special case when the medium elasticity is the exact mean of the two others, the optic axes are inclined at 90° , symmetrically 45° on each side of the axes of greatest and least elasticity, and the nearer it approaches to either of the extreme values the less becomes the acute angle of the optic axes, which is bisected by the elasticity axis whose value is furthest removed from the medium value. If the approach continues until the medium elasticity becomes identical with the extreme value, it has been approaching, the optic axes coincide in the other elasticity axis, which thus becomes the one optic axis of an apparently uniaxial substance.

From these theoretical considerations it is clear that a substance possessing such elasticity relations as do the crystals of rubidium sulphate, must exhibit remarkable optic axial angle phenomena at the ordinary temperature, and still more interesting phenomena when the temperature is raised.

On calculating the optic axial angle for sodium light by means of

the formula $\cos V = \sqrt{\frac{1 - \frac{1}{\beta^2}}{1 - \frac{1}{\alpha^2}}}$ from the refractive indices of rubidium

sulphate, taking the values of β and γ from the first table of results obtained with the ordinary eye-piece, and assuming a difference of 0.0001 between the values for the α - and β -indices, it is found to amount to 34° , while of course the angle is 0° if they are assumed to be identical. It is somewhat astonishing at first sight to find that so small a difference in the refractive index, barely perceptible experimentally, should produce so great a change in the optic axial angle. If the α value is taken as 0.0002 less than the β -index, the calculated optic axial angle is 47° . Rubidium sulphate affords an extreme case illustrating the fact pointed out earlier in this communication, that the above formula can only afford approximate values of the optic axial angle, and that actual measurements of the latter are always to be preferred. In the particular case in question, the angle for sodium light corresponding to the same value of refractive index expressed with four decimal places, may vary by as much as 12° (from midway between 34° and 47° to 5° or 6° beyond the latter

value). It will be evident, however, that an experimental determination of the optic axial angle will afford a means of fixing the difference between the refractive indices α and β to four places of decimals with accuracy.

It has now been shown that the difference between the α - and β -indices for light as far as the blue of the spectrum cannot appreciably exceed 0.0002, for if it did two distinct images of the slit of the spectrometer would be observed; also that a minute difference of this extent corresponds to a separation of the optic axes of about 50° while the angle would be about 35° if the difference were 0.0001, and 0° if the indices were identical. Now the two indices are scarcely likely to be precisely equally removed from each other for all wave-lengths of light, small differences of an order which could only be represented by a fifth place of decimals probably occurring, corresponding to minute differences in the elasticity of the substance along the two axes c and b for different wave-lengths of light. Such minute differences must, however, from the considerations contained in the previous sentence, call forth relatively very large changes in the optic axial angle. In other words, rubidium sulphate is likely to exhibit very considerable dispersion of the optic axes for different wave-lengths of light.

It is also to be expected that different crystals may exhibit somewhat different axial angles. For the differences in the fourth place of decimals between the various individual determinations of the same refractive index afforded by different crystals, cannot be entirely due to experimental error; it is much more probable that slight differences in optical elasticity, and of different extent in the directions of the three axes, may occur just as apparently perfect crystals usually exhibit differences of a few minutes (formational error) in the crystallographical angles. These small variations, which are of no consequence in ordinary cases where the elasticity ratios are widely different, will also produce relatively large differences of optic axial angle.

Measurements of the Angle in Air 2E.—Five section-plates of rubidium sulphate perpendicular to the first median line, the axis a , and therefore parallel to the macropinacoid $a\{100\}$, were employed in the measurements. Three of these were ground and polished by means of the new instrument, and two were formed by crystals of the type represented in Fig. 8, exhibiting excellent predominating macropinacoid faces. They were all of considerable thickness, the first four from $3-4\frac{1}{2}$ mm., and No. 5 was the section plate 8 mm. in thickness previously referred to. The possible error in the determination of 2E for any wave-length is quite 2° with the first four sections, owing to the diffusion of the brushes. The very thick section

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afforded very much more certain results, the brushes being sharply defined. The following values were obtained from the five sections, all of which were used uncovered.

Determinations of the apparent Optic Axial Angle in Air 2E of Rb_2SO_4 .

Nature of light.	Section 1.	Section 2.	Section 3.	Section 4.	Section 5.
Li.....	63° 40'	35° 20'	52° 40'	36° 45'	36° 25'
C.....	65 35	37 10	55 0	38 45	38 35
Na.....	70 50	44 45	79 40	46 0	46 20
Tl.....	76 35	50 0	65 0	53 10	52 10
F.....	83 35	58 10	70 30	58 40	61 50
G.....	91 5		79 10		

The above results fully agree with the expectations derived from the study of the axial elasticity relationships. There are very considerable differences between the values of the apparent angle in air, and therefore, also, of the true angle within the crystal, exhibited by different crystals; indeed, each crystal of rubidium sulphate may be said to possess its own axial angle, dependent on the extremely minute differences of structure, owing to correspondingly slight disturbances during its formation, or possibly to very minute traces of impurities, especially if they consist of isomorphous salts such as either potassium or caesium sulphate. Indeed it is quite conceivable that von Lang really had a negative crystal of rubidium sulphate, owing to its containing a small quantity of caesium sulphate. He gives the value of 2E as approximately 64°.

It is also observed that there is a very considerable amount of dispersion of the optic axes, varying between Li and F light from 18° to 25° in the different crystals examined.

The whole axial angle phenomena of rubidium sulphate are so exceptional, and so interesting from the cause which produces them, that a series of photographs of the interference figures in monochromatic light afforded by the thick section No. 5 have been obtained. The new monochromatic light apparatus lends itself admirably to the photography of interference figures, it being only necessary to place the camera immediately in front of the polariscope of the axial angle goniometer and to employ as powerful a source of light as possible in order to reduce the exposure. The wide-angle polariscope of the Groth universal apparatus was employed in order to include as wide an angle as possible, the nearest lens of each convergent system being removed in order to permit of the introduction of so thick a section-plate without constricting the field. The actual instrument employed was one recently made by Fuess for the author, and its lens systems are better adapted for this kind of work than the older form. An electric arc light of 3000 to 4000 candle power was employed as the

INTERFERENCE FIGURES OF RUBIDIUM SULPHATE.

source of light, in order that the slit of the monochromatic light producer should be sufficiently fine to permit of a high order of monochromatism being attained. In the accompanying reproduction of these photographs, the first four figures are those observed at the ordinary temperature. No. 1 is the figure obtained with the greenish-blue F light, when the angle of separation of the axes is $61^{\circ} 50'$. No. 2 is the figure for light of the wave-length of the green thallium line, the axes being separated at $52^{\circ} 10'$. No. 3 was produced by yellow light of the wave-length of the sodium D lines, the separation having now diminished to $46^{\circ} 20'$; and No. 4 was given by red light of the wave-length of the C hydrogen line, when the axes had closed up to $38^{\circ} 35'$. The photographic plate employed in this latter case was sensitised for red by means of cyanine, and a much longer exposure given. These photographs will afford some idea of the beautiful changes which occur when the dispersing apparatus of the monochromatic light producer is slowly rotated so as to cause the field to be illuminated by light of every wave-length in turn. How the inner single curve wrapping round the two axes for red light, and which is just commencing to contract in the centre, breaks up into lemniscate loops as the yellow is approached, which recede from each other more and more until they form distinct, small rings for green light, during which time the second ellipse-like curve has been contracting, and eventually for the greenish-blue light breaks up into a second pair of rings surrounding the axes.

Measurements of the True Angle $2Va$.

Owing to the great thickness of section necessary to obtain interference figures of sufficient definition for measuring purposes, and also to the usual somewhat small angle of separation of the axes, it is not generally possible to observe the obtuse angle of separation in oil, or even in bromonaphthalene. Moreover, owing to the variation in the amount of separation of the axes, unless the measurements of $2Ha$ and $2Ho$ are carried out with a pair of sections ground from the same crystal, the value of $2Va$ calculated from the formula

$$\tan Va = \frac{\sin Ha}{\sin Ho},$$

cannot be regarded as more than an average value, and certainly does not represent the true value of the optic axial angle for either of the two crystals from which the sections were prepared. In the case of the crystal from which Section 2 in the last table was ground, a second pair of faces were also ground upon it perpendicular to the second median line (the axis b), the crystal being thus ground down to a rectangular prismatic block. It may be of interest here to remark that crystal 4 in the table of refractive index determinations is identical with this crystal, the two prisms

being ground at the ends of the rectangular block with their edges at right angles. A single crystal thus treated is capable of affording the whole of the optical constants of a substance, and there is no difficulty in grinding this number of faces upon a crystal 4 mm. in diameter by means of the new instrument. In the case of this crystal, however, the obtuse angle in bromonaphthalene was too large to permit of the emergence of the axes, only portions of rings being visible.

The true angle between the optic axes of rubidium sulphate has been determined, however, upon four crystals, by measurement of the separation exhibited by four of the five sections perpendicular to the first median line when immersed successively in two liquids whose refractive indices are almost, and the mean exactly, identical with the medium refractive index β of rubidium sulphate. The liquids in question were benzene ($\mu_D = 1.507$), and cedar oil ($\mu_D = 1.520$). The angles observed by use of these two liquids were practically identical, so that there can be no question that the values of $2Va$ recorded in the accompanying table are accurate for each of the crystals employed.

Determinations of true Axial Angle of Rubidium Sulphate $2Va$, by immersion in Benzene and Cedar Oil.

Nature of light.	Section 1.	Section 2.	Section 3.	Section 5.
Li.....	40° 25'	22° 55'	38° 40'	28° 30'
C.....	41 40	23 50	39 25	29 5
Na.....	44 10	28 25	41 55	33 0
Tl.....	47 35	33 5	43 35	37 40
F.....	51 15	38 0	48 45	41 35
G.....	55 50	44 35	52 30	47 30

It will be observed that a considerable variation in the magnitude of the true optic axial angle occurs, just as in the apparent angle in air, and this must therefore be considered as a fully demonstrated property of the substance, and fulfils the expectations based upon the closeness of the elasticity ratios. The possible error in setting the brushes to the cross wires is much greater than in the cases of potassium and cesium sulphates, except in the case of the very thick Section 5, owing to the greater diffusion of the brushes. It probably does not exceed 1° however, and the variations observed are therefore widely removed from experimental error.

The above determinations of the real inclination of the optic axes within the crystal afford a delicate means of calculating the differences for the various wave-lengths between the refractive indices α

and β ; it is only necessary to insert in the formula $\cos^2 V = \frac{\frac{1}{\beta^2} - \frac{1}{\gamma^2}}{\frac{1}{\alpha^2} - \frac{1}{\gamma^2}}$

the values of V , β , and γ obtained by direct measurement, when α is at once obtained. On thus calculating the values of α for the Li and F rays corresponding to the highest and lowest observed values of the optic axial angle, taking the corresponding values of β and γ from the first of the two tables previously given, the following values are obtained.

For the maximum values of the optic axial angle (Section 1),
 $\alpha = 1.51078_{\text{Li}}$ and 1.51806_{F} .

For the minimum values of the optic axial angle (Section 2),
 $\alpha = 1.51088_{\text{Li}}$ and 1.51820_{F} .

The values of β given in the table and used in the calculations
 are $\beta = 1.5109_{\text{Li}}$ and 1.5183_{F} .

These numbers indicate that the α -index for Li light differs from the β -index by 0.00002—0.00012, on the average about 6 in the fifth place of decimals, and that it may therefore be represented, as in the second table of refractive indices, by one unit in the fourth place of decimals less than the β -index; and that the α -index for F light differs from the β -index by 0.00010—0.00024, on the average 0.00017, and may consequently be represented as differing by two in the fourth place of decimals when only four-place numbers are used. The values of the α -indices given in the second table therefore accurately represent the relations of the three refractive indices, and the actual numbers themselves are of the same high order of accuracy as those determined for potassium and caesium sulphates, the possible error being within 0.0002.

Effect of Rise of Temperature on the Separation of the Optic Axes of Rubidium Sulphate.—In addition to great sensitiveness to change of wave-length of the monochromatic light with which the section-plate is illuminated, and to minute changes of structure of the crystal brought about by corresponding minute disturbances during deposition or by the introduction of traces of the isomorphous potassium or caesium salts, the axial angle of rubidium sulphate exhibits remarkable sensitiveness to change of temperature. At the conclusion of the optical investigation at the ordinary temperature, and after the determinations of refractive index for temperatures superior to the ordinary had been carried out, the relative changes in elasticity along the three crystallographic axial directions were worked out and the interesting results obtained which have been recorded at the conclusion of the section referring to the temperature observations. It was shown that as the temperature rises, the elasticity along the c axis increases most, the elasticity along the axes b and a increasing at a slower rate but almost equally. This relative movement of the medium elasticity corresponding to the axis c was shown to result, for

some temperature between 20° and 100° , and varying with the wave-length, in its overtaking the previously greater elasticity along the axis b (the second median line), and thus causing the crystal to simulate a uniaxial one, the single optic axis being the axis a , at right angles to the plane of equal elasticity containing the axes c and b . Further heating would result in the elasticity along the axis c passing that corresponding to the axis b and becoming the greatest elasticity, that is to say, biaxial properties would again be resumed, with the axis c as the second median line instead of the axis b , the plane of the optic axes being now that containing the axes a and c at right angles to that (ab) which contains them at the ordinary temperature. It was therefore to be expected that on warming a section plate cut perpendicular to what at the ordinary temperature is the first median line, the axis a , arranged at 45° to the planes of the crossed nicols and illuminated with monochromatic light, the optic axial brushes would be observed to approach the centre of the field along the trace of the optic axial plane ab (the basal plane $c\{001\}$), until they united in the centre to form a cross surrounded by uniaxial circular rings; further, that on continued heating the cross would again break up into hyperbolic brushes, but their centres would lie in the plane ac at right angles to that which formerly contained them, and that the separation of the axes in this plane would more and more increase as the temperature rose, until they passed out of sight altogether, and the axis c would become first instead of second median line. Moreover, the temperature at which the uniaxial figure would be produced would necessarily be different for every different wave-length, being lowest for the red and highest for the blue, owing to the large dispersion of the optic axes for different wave-lengths.

On proceeding to experimentally test these predictions, the phenomena were observed to fulfil them precisely. Employing the 8-mm. thick section No. 5, illuminating by red light of the wave-length of the lithium line, and very slowly raising the temperature of the air bath in which the section was enclosed, the brushes, separated along the horizontal diameter, were observed to rapidly approach each other, until at 36° they united in the centre of the field and a perfect uniaxial figure was produced. They then opened out and separated in the vertical diameter. On immediately changing to yellow light of the wave-length of the sodium lines, the axes were found still just separated in the horizontal plane for this colour, but almost immediately coalesced to form the uniaxial figure, the temperature being 38° , and then passed out in the vertical plane. Following up the changes for other wave-lengths, the uniaxial figure was produced for green light of the wave-length of the thallium line at 44° , for F light at 51° , and for G light at about 60° .

The section was then rotated 90° , and a series of measurements of the separation of the axes in the plane ac carried out while the temperature was maintained in the neighbourhood of 60° . The results are as follows.

				Measurements of 2E for Rb_2SO_4 at 60° , plane of axes $b\{010\}$.	
For light of Li wave-length				2E = 59°	0'
"	C	"		57	40
"	Na	"		52	0
"	Tl	"		45	15
"	F	"		32	45
"	G	"		Just separated.	

Another series of observations of 2E, recorded below, were carried out with Section 3, which exhibits a larger axial angle than Section 5.

	Plane of axes $c\{001\}$.				Plane of axes $b\{010\}$.			
	At $18-20^\circ$		At 40°		At 60°		At 100°	
Li.	52°	40'	20°	0'	55°	45'	94°	5'
C	55	0	22	0	53	40	91	15
Na	59	40	27	45	49	35	87	45
Tl	65	0	36	20	36	10	83	15
F	70	30	49	0	10	0	76	55
G	79	10	62	50	Just separated in the plane at right angles.		68	0

For Li light, the figure was uniaxial at 42° , for C light at 44° , for Na light at 48° , for Tl light at 52° , for F light at 58° , and for G light at about 67° . In the neighbourhood of the crossing, as will be gathered from the above table, the change of angle appears to be relatively greater for the same change of wave-length than when the axes are well separated. Hence the amount of dispersion of the axes as seen in air between Li and G appears correspondingly larger for temperatures near that of the average crossing point, which is in the neighbourhood of 50° .

In order to give some idea of the whole of the beautiful phenomena presented by this exceptional case of sensitiveness, both to change of wave-length and to temperature, two additional series of photographs of the interference figures in monochromatic light were taken at higher temperatures, immediately after the four photographs for the ordinary temperature previously described. The section was enclosed in the air bath provided with the "Groth" axial angle apparatus, but in order to be able to approach the lens systems (whose nearest lenses were removed), sufficiently near to the faces of the section to avoid constricting the field, the adjustable windows of the

air bath were entirely removed and replaced by discs of much thinner glass (thinnest lantern slide glass) mounted in suitable carriers. The air bath thus arranged was in position while the first series of photographs Nos. 1, 2, 3, and 4 were taken at the temperature of the room, 18° . The bath was then carefully warmed by means of the very small flames of two miniature Bunsen burners, the temperature being allowed to rise very slowly. By judiciously regulating the size of the flames, the temperature was eventually brought to constancy at 44° , for which temperature the uniaxial figure is produced for thallium light, and maintained at such while the exposures were made for a second series of four photographs. No. 5 was illuminated by greenish-blue F light, and shows the axes still separated by a small angle in their original plane. No. 6 is the uniaxial figure for bright green light of the wave-length of the thallium line, circular rings, and a rectangular cross. Half a degree of change in the temperature is sufficient to spoil this figure, the cross breaking up into separate hyperbolæ, and two were attempted and lost in this manner before the temperature could be kept sufficiently constant. No. 7 was taken with yellow light of sodium wave-length, and exhibits the axes passed well out in the vertical plane. No. 8 is the figure for red C light, for which the axes are still further separated in the vertical plane.

The third series were taken at a temperature of 60° , for which the uniaxial figure is obtained with bluish-violet G light. No. 9 represents it, the circular rings being closer together and more numerous than in the uniaxial figure for thallium light, No. 6. No. 10 is the figure for greenish-blue F light, the axes well separated in the vertical plane. No. 11 shows them further separated for green thallium light; and No. 12 further still for yellow sodium light.

It will, of course, be understood that the section remained fixed in the same position while the whole of the twelve plates were exposed, so that the horizontal diameter of each is parallel to the axis b and the vertical diameter to the axis c , while the axis a is perpendicular to the plane of the paper.

On rotating the nicols 45° so as to bring their directions of vibration parallel to the crystallographic axes and thus produce the black cross instead of hyperbolic brushes, while the temperature was still 60° and the light any colour between blue and red, and inserting the quarter undulation mica plate diagonally in the usual manner, the sign of double refraction was observed to be still positive.

The changes of optic axial angle have only been followed as high as 100° of temperature, in order not to risk injuring the valuable observing instrument. There can be no doubt, however, from the precise manner in which the deductions from the refraction observa-

tions have been verified as high as 100° , that beyond this temperature the optic axial angle would continue to increase until, as 180° was approached and passed, the axis c would become, for the various wavelengths in succession, the first median line, and the sign of double refraction would change to negative.

Comparison of the Optical Properties of the three Sulphates.

Having now described in detail the optical properties of the three salts, we are in a position to compare them in order to ascertain whether any progression in the order of the atomic weight of the contained metals exists.

The following table exhibits the refractive indices of the three salts arranged so that those corresponding to analogous crystallographic axes are placed alongside.

Comparative Table of Refractive Indices of K_2SO_4 , Rb_2SO_4 , and Cs_2SO_4 .

Axial direction for which determined.	Nature of light.	K_2SO_4 .	Rb_2SO_4 .	Cs_2SO_4 .
a	Li	β 1.4924	γ 1.5120	γ 1.5633
	C	1.4928	1.5124	1.5637
	Na	1.4947	1.5144	1.5662
	Tl	1.4967	1.5166	1.5690
	F	1.4995	1.5194	1.5725
	G	1.5024	1.5235	1.5775
b	Li	α 1.4912	α 1.5108	β 1.5615
	C	1.4916	1.5112	1.5619
	Na	1.4935	1.5131	1.5644
	Tl	1.4955	1.5153	1.5672
	F	1.4982	1.5181	1.5706
	G	1.5012	1.5222	1.5756
c	Li	γ 1.4950	β 1.5109	α 1.5569
	C	1.4954	1.5113	1.5573
	Na	1.4973	1.5133	1.5598
	Tl	1.4994	1.5155	1.5624
	F	1.5023	1.5183	1.5660
	G	1.5052	1.5224	1.5705

It will be observed that the refractive indices of rubidium sulphate fall between those of potassium and cæsium sulphates. The actual numbers, however, are considerably nearer to those of the potassium salt than to those of cæsium sulphate. A concise idea of the relation may be obtained from a comparison of the A constants for the intermediate β indices in the general formulæ, these values, the so-called

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indices for a ray of infinite wave-length, being independent of the nature of the light.

For K_2SO_4	$A_\beta = 1.4843$	
		Difference 0.0190
„ Rb_2SO_4	$A_\beta = 1.5033$	
		Difference 0.0491
„ Cs_2SO_4	$A_\beta = 1.5524$	

The differences are approximately in the ratio 2 : 5. The first important conclusion concerning the optical properties, therefore, may be stated in the following terms.

The refractive indices of rubidium sulphate are intermediate in value between those of the sulphates of potassium and caesium, and lie nearest to those of the potassium salt; the average differences between the indices of the potassium and rubidium salts on the one hand and those of the rubidium and caesium salts on the other, are in the ratio of 2 : 5. An increase of refractive power accompanies an increase in the atomic weight of the contained metal, and the increase becomes relatively greater as the atomic weight becomes higher.

As the refractive index represents the ratio of the velocity of light in air (or in a vacuum if the correction for the refraction of air is applied) to that in the crystal, its value varies inversely as the velocity with which light is transmitted through the crystal; the ratio of the reciprocals of corresponding indices of the three salts will consequently afford relative measures of the velocity of light along those directions in the crystals for which the indices were determined. Such velocity ratios or axial ratios of optical elasticity as they are termed by Topsøe and Christiansen, will exhibit in the clearest light the nature of the changes in optical characters brought about by replacing the potassium in potassium sulphate by rubidium and the rubidium in turn by caesium.

The change in optical elasticity must be regarded from two points of view, first, with respect to the average alteration of elasticity on passing from the potassium to the rubidium salt and from the rubidium to the caesium salt; and, secondly, with regard to the effect of the different amounts of alteration along the three axial directions in bringing about different relations between the three elasticities of any one salt. For it must be remembered that these latter relations entirely determine the amount and sign of the double refraction, the distance apart of the three refractive indices, and the positions of the optic axes. The elasticity ratios given in the description of the optical properties of each salt were calculated for sodium light in the same manner as those of Topsøe and Christiansen, taking the elasticity for that particular salt along the *b* axis as unity. Thus the ratio *a* : *b* was

obtained by taking the ratio of the reciprocals of the refractive indices for the a and b axes, and $c : b$ in like manner from the indices along the c and b axes. These ratios are placed under each other for comparison below.

For K_2SO_4	$a : b : c = 0.9992 : 1 : 0.9975$
„ Rb_2SO_4	$a : b : c = 0.9991 : 1 : 0.9999$
„ Cs_2SO_4	$a : b : c = 0.9989 : 1 : 1.0029$

Before directing attention to the interesting relationships which these ratios exhibit, it will be convenient to consider a mode of expression in which not only the relative elasticities along the axial directions of any one salt are shown, but also the actual changes of elasticity along all three axes on passing from one salt to another. This may be most advantageously accomplished by taking the medium elasticity of potassium sulphate as unit, and expressing all the other elasticities proportionally; the ratios for potassium sulphate are then those above given. The other ratios are similarly obtained in each case by dividing the refractive index for sodium light corresponding to the axis in question in that particular salt into the β_{Na} index of potassium sulphate. The ratios thus obtained are given below, and completely represent the changes in optical elasticity. They were calculated for sodium light, and it was also found that practically identical values are afforded if the calculations are made for C or for Tl light.

For K_2SO_4 . .	$a : b : c = 0.9992 : 1$	$: 0.9975$
	130	129
„ Rb_2SO_4 . .	$a : b : c = 0.9862 : 0.9871 : 0.9869$	or $0.9991 : 1 : 0.9999$
	326	324
„ Cs_2SO_4 . .	$a : b : c = 0.9536 : 0.9547 : 0.9575$	„ $0.9989 : 1 : 1.0029$
	326	294

The following important deductions may be drawn from these relationships.

The optical elasticity of the crystals of rubidium sulphate is intermediate between the greater value exhibited by the crystals of potassium sulphate and the lesser value of those of caesium sulphate, whatever directions in the crystals are chosen for comparison, whether analogous or not, the differences between the maximum and minimum values of the elasticity of any one salt being very small compared with the differences between different salts. If the same direction is chosen for comparison, the value for the rubidium salt is nearer to that of the potassium salt than to that of the caesium salt in the proportion approximately of 2 : 5.

This may be expressed in a more striking and comprehensive manner as follows.

The ellipsoidal wave-surface, of rays emanating from a common central point, for rubidium sulphate lies between the wave-surfaces of potassium

and caesium sulphates respectively, and nearer to the outer enveloping wave-surface of the potassium salt than to the inner one of caesium sulphate approximately in the proportion of 2 : 5.

It will be further observed that—

The amount of diminution of optical elasticity on passing from one salt to another is almost identical in the directions of the axes *a* and *b*, so that the ratio of the elasticities in these two directions to each other remains practically constant for the three salts. The change of elasticity along the axis *c*, however, proceeds at a slower rate, and thus causes a considerable alteration in the relations between the elasticity along this axis and that corresponding to the other two axial directions.

This alteration in the relations between the three elasticities for any one salt, brought about by the difference between the amounts of alteration along the equally changing *a* and *b* axes on the one hand and the *c* axis on the other, is clearly exhibited by the elasticity ratios in which *b* is taken as unity in each salt. The values of the *a* : *b* ratios for the potassium, rubidium, and caesium salts respectively, 0.9992, 0.9991, and 0.9989, are practically identical, while the *c* : *b* ratios change considerably from 0.9975 to 1.0029. It will be observed with interest, however, that rubidium preserves its intermediate position. These relations may be graphically expressed by three curves representing the elasticities along the axial directions, drawn as in Fig. 12 by taking the atomic weights of the contained metals as ordinates and optical elasticity as abscissæ. Two series of such curves are given; the dotted ones lying close together represent the

FIG. 12.

actual elasticities, as given in the above table of ratios, in which the elasticity of potassium sulphate along the b axis is taken as unity, and the continuous curves the ratios in which the elasticities of each individual salt along the a and c axes are compared with that along the b axis considered as unity. The same facts are indicated by both series of curves, but the dotted series affords an excellent indication of the closeness of all three values of the elasticity in each salt, while the continuous series exhibits the relations of the three values for each salt more clearly.

The nature of these altered relations of the three elasticities in each salt must next be considered, together with the important alterations in the optical characters to which they give rise.

The practically equal diminution in optical elasticity along the a and b axes is represented by nearly parallel curves; in the continuous series, the unit optical elasticity along the axis b is, of course, represented by a vertical line, and the curve of elasticity for the axis a is almost a straight line, very slightly diverging at an accelerated rate from the b line as the atomic weight increases, the distance of the two curves apart being least for the potassium salt, greatest for the cæsium salt, and intermediate in amount for the rubidium salt. On the other hand, the relatively very much smaller diminishing effect on the optical elasticity along the c axis (represented by greater steepness in the dotted curve for c), which is produced by the replacement of the lighter potassium atom by the heavier rubidium, or still heavier cæsium, atom, results in completely reversing the character of the double refraction. In Fig. 12 this is graphically expressed by the c curve in each series crossing the others. In the potassium salt, the optical elasticity is at its minimum along the c axis, while in the cæsium salt it is at its maximum along this axis. Not only so, but the value of the minimum elasticity along the c axis in the potassium salt is further removed from the intermediate value along the a axis than is the maximum value along the b axis, and hence this axis c is the first median line bisecting the acute angle of separation of the optic axes, and as the value of the elasticity is here at its minimum, the double refraction, according to the usual convention, is positive; again, in the cæsium salt the value of the elasticity along the c axis is furthest removed of the two extreme values from the intermediate value along the b axis, so that this axis is again the first median line, but as the elasticity along the c axis is now the maximum value, the sign of the double refraction is reversed, namely, negative. Hence it is that potassium and cæsium sulphates are observed to form normally behaving positive and negative doubly refracting crystals respectively. On account, however, of the closeness of all three values of the elasticity in each salt, compared with the elasticity differences exhibited

by the majority of substances forming biaxial crystals, a trait which is well brought out by the dotted curves representing the actual elasticities, the double refraction is unusually small, and sections 2 or 3 mm. thick are consequently required to exhibit well-defined interference figures in convergent light.

Now, if the crystallographical properties of these three salts are functions of the atomic weight of the metals which they contain, the optical elasticity along the c axis of rubidium sulphate, the atomic weight of whose metal is practically the mean of the atomic weights of the metals in the other two salts, must be intermediate in value to the values observed for it in potassium and caesium sulphate respectively, precisely as occurs with respect to the elasticities along the two other axes. It has been shown that this is the case. The effect, however, on the optical properties, brought about by the optical elasticity along the c axis taking its proper intermediate value in the rubidium salt, is extraordinary, for it causes the value of the elasticity along this axis, relatively so widely removed from the others in the potassium and caesium salts, to become in the rubidium salt almost identical with the value along the b axis, and to lie between the already closely approximating values of the optical elasticity along the a and b axes. Hence, rubidium sulphate is a substance of very remarkably low double refraction, the differences between the maximum and minimum values of the optical elasticity along the b and a axes respectively being so unusually small that sections perpendicular to the first median line, which is now the axis a , almost a centimetre thick, are required to furnish sharp interference figures. Moreover, the extreme closeness, all but identity, of the medium elasticity along the c axis and the maximum along the b axis, renders the optic axial angle of rubidium sulphate extraordinarily sensitive to change of wave-length, to temperature, and to the presence of traces of the other two salts.

Hence the interesting conclusion is arrived at that the abnormal optical properties of rubidium sulphate are entirely such as would be brought about by the operation of a rule to the effect that the crystallographical characters of strictly isomorphous salts are functions of the atomic weight of the metals which they contain.

These facts may be summarised in the following terms.

The lesser diminution of optical elasticity along the axis c , compared with that along the a and b axes, which accompanies the replacement of potassium by rubidium and rubidium by caesium, causes a complete reversal of the nature of the double refraction. The elasticity along the c axis is the minimum of the three values along the axial directions in the potassium salt, and the maximum in the caesium salt, and in both cases

these values for the *c* axis are furthest removed from the values of the medium elasticity in the same salt. Hence potassium sulphate is endowed with positive, and caesium sulphate with negative, double refraction, in both cases of weak order, owing to the comparative closeness of the maximum and minimum values. The intermediate value which the elasticity along the axis *c* assumes in the rubidium salt falls between the values of the elasticity along the *a* and *b* axes, and is almost identical with that along the axis *b*. As the values of the optical elasticity along the *a* and *b* axes, now the minimum and maximum values, are very close together, the crystals of rubidium sulphate exhibit extraordinarily low double refraction, a section-plate almost a centimetre thick being required for the production of well-defined interference figures in convergent polarised light. Moreover, the extreme closeness, almost identity, of the elasticity values for the *b* and *c* axes renders the optic axial angle exceptionally sensitive to change of wave-length in the illuminating light, to change of temperature, and to the presence of traces of isomorphous impurities. The dispersion of the optic axes of rubidium sulphate at the ordinary temperature between the wave-lengths of the red lithium line and the bluish-violet hydrogen line *G* amounts for 2E to about 35°, and for 2Va to about 20°; and the closeness of the two elasticity values along the *b* and *c* axes, which causes this sensitiveness to change of wave-length, is strikingly shown by the fact that a prism ground in the theoretical direction to afford the two indices of refraction corresponding to these axes of optical elasticity exhibits in an ordinary spectrometer the two refracted images of the slit exactly coincident, appearing as a single image, a very high power eye-piece being requisite to separate them. The whole of these exceptional optical properties of rubidium sulphate are thus found to be entirely due to the fact that the three values of the optical elasticity for this salt are intermediate between those of the oppositely doubly-refractive potassium and caesium salts. Hence the optical properties of the crystals of the three salts, in common with their geometrical form, are functions of the atomic weights of the metals which they contain.

Comparison of the Optical Properties at Higher Temperatures.—It will be interesting to ascertain next whether the relationships established between the optical properties of the three salts continue to obtain at temperatures other than the ordinary.

The following rules have been observed with regard to the refraction of all three salts at temperatures up to 180°.

A regular decrease in the refractive power of the crystals of each of the three sulphates, corresponding to an increase in the optical elasticity, is observed as the temperature rises. The diminution in refractive index is greatest for rays vibrating parallel to the vertical axis *c*, the elasticity along this direction accelerating at a more rapid rate than along the other

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two axes *a* and *b*, in which latter directions the changes are approximately equal. It is significant that a greater rate of thermal expansion was also observed in the direction of the vertical axis *c*.

The effect of this difference in the alteration of the elasticity along the *c* axis, compared with that along the other two axes, will be most readily explained by means of elasticity ratios, calculated from the refractive indices for 180°, in the same manner as those previously given for the ordinary temperature. The elasticity ratios for 180° are:

$$\begin{array}{lll} \text{For } K_2SO_4 \dots & a:b:c = 0.9992:1 & :0.9981 \\ & \quad \quad \quad 136 \quad \quad 137 \quad \quad 112 \\ \text{,, } Rb_2SO_4 \dots & a:b:c = 0.9856:0.9863:0.9869 & \text{or } 0.9993:1:1.0007 \\ & \quad \quad \quad 327 \quad \quad 322 \quad \quad 291 \\ \text{,, } Cs_2SO_4 \dots & a:b:c = 0.9529:0.9541:0.9578 & \text{,, } 0.9987:1:1.0039 \end{array}$$

On comparing these ratios with those for the ordinary temperature, it will at once be seen that the relation of the optical elasticities along any one axis in the three salts remains precisely the same within the limits of error, which are, of course, somewhat wider in the case of observations at a temperature so elevated, and may amount to 0.0003. The same lesser amount of diminution of elasticity along the *c* axis, on passing from one salt to another containing a metal of higher atomic weight, is observed, while the greater amounts of diminution along the *a* and *b* axes are approximately equal. The effect of rise of temperature, however, in causing an increase in the actual value of the optical elasticity is not, of course, shown in the ratios, because the new value of the elasticity along the *b* axis of potassium sulphate at 180° is taken as unity. It might, however, be expressed if the ratios were calculated taking the value at the ordinary temperature as unity, that is, using the same unit as in the ratios for the ordinary temperature, in which case the *b* elasticity of potassium sulphate at 180° becomes 1.0039 instead of 1, and all the other ratios would be increased in the same proportion. Bearing this fact in mind, it is perhaps simplest to retain the above ratios, which show the relations of the three elasticities in each salt and the changes upon passing from one salt to another equally well.

The greater increase in the optical elasticity along the *c* axis of any one salt as the temperature rises, compared with that along the other two axes, must be regarded quite distinctly from the lesser diminution observed on passing from one salt to another, which has just been shown to be similar to that which occurs at the ordinary temperature. The effect of this altered relationship of the *c* elasticity to the elasticities along the two other axes, which retain their original distance apart, is to move the curve representing the elasticity along the axis *c* in the continuous series of Fig. 12 (p. 700) almost parallel with

itself for some distance to the right, so as to pass through the three points indicated by crosses. In the potassium salt, the minimum c elasticity now approaches more closely to the medium value along the a axis, but is still slightly further removed from it than is the maximum elasticity along the b axis. Hence the optic axial angle of potassium sulphate should increase with the temperature, as is found by direct experiment to be the case. In the caesium salt, however, rise of temperature causes the c elasticity to become still further removed from the medium value along the b axis, and the optic axial angle ought consequently to diminish on warming the crystal, a deduction likewise in accordance with the experimentally determined fact. Finally, in the interesting case of the rubidium salt, the new relative position occupied by the c axis lies upon the other side of the b elasticity to that upon which it lies at the ordinary temperature, and so far upon the other (the maximum) side at 180° that it is almost as far removed from the now medium value along the b axis as is the minimum elasticity along the a axis. Hence, at this elevated temperature, the order of the b and c axes is reversed, and the plane of the optic axes changed from ab to ac ; the double refraction is still positive, and the axis a the first median line, but a very little further heating would cause the sign of double refraction to change to negative, and the axis c to be endowed with the elasticity furthest removed from the others, and therefore to become the first median line. Hence this over-stepping of the elasticity b by that along the c axis is the cause of the beautiful optic axial angle phenomena of rubidium sulphate, observed on warming a section perpendicular to the first median line a , the nature of which has been fully explained. It may, however, be now with propriety further remarked, having the curves before us, that it can readily be understood why so slight a rise of temperature should cause a crossing of the plane of the optic axes. For the elasticity c at the ordinary temperature is so near to the b value that a comparatively few degrees of heating are sufficient to cause the c value to become coincident with the b value, and so for the optic axes to rapidly approach until the uniaxial interference figure is produced, after which further heating as rapidly separates them in the plane at right angles; and of course, owing to the strong dispersion of the axes for different wave-lengths, the uniaxial figure will be produced first for the red rays, and at slightly higher temperatures for the other rays in succession.

There is one further point in connection with this greater relative increase of optical elasticity along the axis c worthy of notice. The distance of the curve for this axis at 180° from that for the ordinary temperature is not equal throughout, that is, the curves are not parallel; they diverge with increase of atomic weight of the metal

contained in the salt, and their distance apart for the rubidium salt is intermediate between the distances for the potassium and caesium salts. The differences between the c ratios of the potassium salt at the ordinary temperature and at 180° is 0.0006, for the rubidium salt 0.0008, and for the caesium salt 0.0010. One cannot help being struck with the perfect manner in which, even in the minutest details of the crystallographic properties, rubidium sulphate maintains its intermediate position.

These facts may now be concisely summarised in the following terms.

The relations established between the optical elasticities of the three sulphates at the ordinary temperature are still maintained on raising the temperature, rubidium sulphate preserving its intermediate position along all three axial directions. Moreover, the difference introduced into the relations of the three elasticity values of any one salt by the greater rate of acceleration of the elasticity along the axis c as the temperature rises, compared with the acceleration along the a and b axes, is intermediate in amount in the case of the rubidium salt, compared with its magnitude in the potassium and caesium salts respectively. Hence the elasticity values of rubidium sulphate remain, at higher temperatures, intermediate between those of potassium and caesium sulphates, whether the comparison is made between the actual values along the same axis for the three salts, or whether the ratios of the three elasticities for each of the three salts in succession are compared. The conclusion drawn from the observations at the ordinary temperature, that "the optical properties of the crystals of the three salts are functions of the atomic weights of the metals which they contain," is, therefore, independent of the temperature.

The greater rate of acceleration of the elasticity along the axis c as the temperature is increased, produces a remarkable change in the optical characters of rubidium sulphate. In potassium sulphate, it merely has the effect of causing the minimum elasticity along the c axis to approach a little nearer to the medium value, and so to increase the optic axial angle by a slight amount. In caesium sulphate, the value along the c axis, in this salt the maximum elasticity, is removed still further from the medium value, and consequently the optic axial angle is slightly diminished by warming the crystal. In the rubidium salt, however, the effect of heating the crystal is to cause the elasticity along the c axis, at the ordinary temperature the medium elasticity and but very slightly less than the maximum value along the b axis, to approach, and for a rise of a very few degrees of temperature to become identical with, the value of the elasticity along the b axis, when the crystal possesses uniaxial optical properties. Further heating causes the c elasticity to overstep the b value and to become the maximum elasticity. This rapid change in the relations of the optical elasticity along the b and c axes is translated in a most

interesting manner in the optic axial angle phenomena. On warming a section-plate cut perpendicular to the first median line, the optic axes rapidly approach each other in their plane $a b$, and eventually unite in the centre of the field to form the uniaxial cross surrounded by circular rings; on continuing the heating, the axes separate again in the plane $a c$ at right angles to the plane which previously contained them, and the separation becomes greater and greater until the axial brushes pass out of the field, the axis c becomes first median line instead of the axis a , and the positive nature of the double refraction changes to negative. Owing to the great amount of dispersion of the optic axes for different wave-lengths (over 30°), these changes happen in succession at different temperatures for the different wave-lengths, the uniaxial figure being produced first for red light, and last for violet light, the differences of temperature for red lithium and violet G light being about 25° ; the mean temperature of the production of the uniaxial figure is about 50° . These unique optical properties of rubidium sulphate are thus the direct natural consequence of the mutual relations of the three elasticity values for this salt, brought about by the operation of the rule above established connecting the optical properties with the atomic weight of the metal contained in the salt.

Before taking leave of the consideration of the optical elasticity relationships, it will be of considerable interest and importance to enquire whether any connection is to be traced between them and the volume relationships of the three salts.

Considering first the volume changes on replacing potassium by rubidium, and the latter metal by cæsium, it was shown that the distance ratios along the axial directions increased as the weight of the metallic atom was increased, and that the b axis elongated most, the c axis nearly as much, and the a axis least. If the actual values of the distance ratios are referred to (p. 660), it will be seen that the elongation along the b axis is nearly twice as great as that along the a axis, the amounts being as 385 to 216. But the lengths of these axes are, to start with, that is to say in the potassium salt, almost in this proportion, being as 1 to 0.5727. Now if unit length expands 385 on the introduction of rubidium, a length of 0.5727 would, if it expanded in exact proportion, elongate 220; it actually expands 216, that is to say, almost exactly proportionally to the length. Consequently the relative lengths of the axes a and b in the rubidium salt are almost exactly what they were in the potassium salt, the a axis being just a little shorter, as expressed by the crystallographic axial ratio; and the net effect of the introduction of rubidium instead of potassium, as regards these axial directions, is to cause an imaginary line joining the ends of the two axes to be pushed outwards

almost parallel with itself. On the other hand, on considering the relations of the axes b and c , it is observed that the amount of extension is nearly the same in each direction, while the original proportion is as 1 to 0.7418. It is easy to see that this means that the line joining the ends of the axes after the introduction of rubidium remains no longer parallel to its direction in the potassium salt, but that the extension is so much greater, proportionally to the original lengths, along the c axis, that the line is not only pushed outwards, but its inclination is considerably altered, so that the lines diverge as the end of the c axis is approached. This is represented by an increase in the crystallographical axial ratio $c : b$. The changes are, of course, of similar nature, as there is a true progression in the order of atomic weight, on the replacement of rubidium by caesium, the only material difference being that the amount by which the lines joining the ends of the axes are actually moved further away from the centre is greater.

It has been shown as regards the optical elasticity, that the changes ensuing on the introduction of a heavier metal are also such as result in the relations of the a and b axes remaining almost the same, the ratio $a : b$ decreasing very slightly; while the ratio $c : b$ increases relatively very considerably. Hence it is clear that the relations of the optical elasticity values along the three axial directions, in the case of the three sulphates under consideration, vary similarly to the variations in the *relative* lengths of these axes, although there is apparently no relation between their numerical values. Thus both show very little change on passing from one salt to another with respect to the relations of the axes $a : b$, while the ratio $c : b$ changes materially, and the changes are also of like sign; but the actual values of the ratios are of different order, for while the axis b is the longest axis in all three salts, and the a axis the shortest, the order of the optical elasticities is different. Moreover, the actual increase in the lengths of all the axes as the atomic weight of the metal is increased, is accompanied by a decrease along all the axial directions in optical elasticity, while an increase in the *ratio* of the length of any one axis to that of any other is accompanied by an increase in the optical elasticity. Hence it may be concluded that :

The only connection which is apparent between the changes in the lengths of the crystallographic axes and the alterations in optical elasticity, brought about by replacing potassium by rubidium and rubidium by caesium, is exhibited between the relations of the values of these constants along the three axes towards each other, a very slight change being in both cases apparent in the ratio $a : b$, and a much larger one in the ratio $c : b$. These changes occur in the same direction for both properties. The actual values appear to bear no relationship, except that the values for the rubidium salt are always intermediate. From these

considerations it may be concluded that the actual value of the optical elasticity is not a function of the crystal element, the physical molecule, but of the chemical molecule. The fact that it is modified in a manner analogous to the modification of the axial ratios, would appear to confirm the supposition that the crystal element is endowed with like symmetry to the crystal itself in regard to the internal arrangement of the chemical molecules of which it is composed.

Molecular Optical Constants.

As it may be accepted that in a strictly isomorphous series of salts, such as those under consideration, the crystal elements are composed of the same number of molecules, it is probable that the molecular refractions and dispersions, calculated from the formulæ of Lorenz and of Gladstone and Dale, will be strictly comparable quantities, whether they are functions of the crystal element, the chemical molecule, or both combined.

The specific and molecular refractions have, therefore, been calculated for the wave-lengths of the two hydrogen lines C and G, the

Refraction Constants.

$$\text{Specific refraction } \frac{n^2 - 1}{(n^2 + 2)d} = \mathfrak{R}.$$

	a.	Diff.	b.	Diff.	c.	Diff.
For ray $\left\{ \begin{array}{l} \text{K}_2\text{SO}_4 \dots \\ \text{Rb}_2\text{SO}_4 \dots \\ \text{Cs}_2\text{SO}_4 \dots \end{array} \right.$	0.1092	260	0.1089	259	0.1096	265
C(H α)	0.0832	65	0.0830	65	0.0831	72
	0.0767		0.0765		0.0759	

$$\text{Molecular refraction } \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = \mathfrak{M}.$$

	a.	Diff.	b.	Diff.	c.	Diff.
For ray $\left\{ \begin{array}{l} \text{K}_2\text{SO}_4 \dots \\ \text{Rb}_2\text{SO}_4 \dots \\ \text{Cs}_2\text{SO}_4 \dots \end{array} \right.$	18.99	3.17	18.96	3.16	19.08	3.05
C(H α)	22.16	5.55	22.12	5.51	22.13	5.32
	27.71		27.63		27.45	

$$\text{Specific refraction } \frac{n^2 - 1}{(n^2 + 2)d} = \mathfrak{R}.$$

	a.	Diff.	b.	Diff.	c.	Diff.
For ray $\left\{ \begin{array}{l} \text{K}_2\text{SO}_4 \dots \\ \text{Rb}_2\text{SO}_4 \dots \\ \text{Cs}_2\text{SO}_4 \dots \end{array} \right.$	0.1110	263	0.1107	262	0.1115	269
G(H γ)	0.0847	65	0.0845	65	0.0846	72
	0.0782		0.0780		0.0774	

$$\text{Molecular refraction } \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = \mathfrak{M}.$$

	a.	Diff.	b.	Diff.	c.	Diff.
For ray $\left\{ \begin{array}{l} \text{K}_2\text{SO}_4 \dots \\ \text{Rb}_2\text{SO}_4 \dots \\ \text{Cs}_2\text{SO}_4 \dots \end{array} \right.$	19.31	3.26	19.27	3.25	19.40	3.13
G(H γ)	22.57	5.69	22.52	5.66	22.53	5.45
	28.26		28.18		27.98	

Dispersion Constants.

Axes . . .	Specific dispersion $\mu_G - \mu_C$.			Molecular dispersion $M_G - M_C$.		
	a.	b.	c.	a.	b.	c.
K ₂ SO ₄ . . .	0.0018	0.0018	0.0019	0.32	0.31	0.32
Rb ₂ SO ₄ . .	0.0015	0.0015	0.0015	0.41	0.40	0.40
Cs ₂ SO ₄ . .	0.0015	0.0015	0.0015	0.55	0.55	0.53

same two rays as are preferred by Brühl. The difference of the values for the two rays is taken to represent the dispersion. The constants are arranged according to analogous axial directions in the crystals of the three salts.

The following relations are observed between the values for the three salts.

The molecular refraction and dispersion of the crystals of the normal sulphates of potassium, rubidium, and caesium, calculated from the formula of Lorenz, increase with the atomic weight of the contained metal, so that the values for the rubidium salt are intermediate between those for the potassium and caesium salts. The increase becomes greater as the atomic weight rises, so that the differences between the constants for the caesium and rubidium salts are greater than those between the values for the rubidium and potassium salts. These statements are equally true whatever direction in the crystals is chosen for comparison, and as regards the refraction for whatever wave-length the comparison is made. It is observed, however, that the increase along the direction of the vertical axis c proceeds at a somewhat slower rate than along the directions of the two lateral axes, in which two latter directions the rate of increase is almost identical.

It is of interest to note that the above relations are in perfect accordance with those exhibited by the elasticity values of the three salts. It may next be enquired whether similar relationships are exhibited by the molecular refractions calculated from the formula of Gladstone and Dale. The following are the values of $\frac{n-1}{d}M$ for the wave-length of the red hydrogen line C.

	a.	Diff.	b.	Diff.	c.	Diff.
K ₂ SO ₄ . . .	32.22		32.14		32.39	
Rb ₂ SO ₄ . .	37.83	5.61	37.74	5.60	37.75	5.36
Cs ₂ SO ₄ . .	48.05	10.22	47.89	10.15	47.50	9.75

It will at once be perceived that precisely similar relationships are indicated with regard to all the points above enumerated, as by use of the Lorenz formula.

We may now further enquire whether these relationships are merely fortuitous ones for the ordinary temperature, or are valid for

all reasonable temperatures. As the alteration of the density and the refraction for rise of temperature has been determined, the molecular refraction for a higher temperature can at once be calculated. The highest temperature, 180° , at which refraction observations were carried out has been chosen for the comparison. From the data afforded by the determination of the cubical expansion of the salts, their specific gravities at $180^{\circ}/4^{\circ}$ are found by calculation to be:

$$\text{K}_2\text{SO}_4, 2.6080; \text{Rb}_2\text{SO}_4, 3.5377; \text{Cs}_2\text{SO}_4, 4.1585.$$

The specific and molecular refraction have been calculated, by use of the Lorenz formula, from the above densities and the refractive indices for the temperature 180° , and for the intermediate wavelength of the sodium D lines. The values are as follows.

	Specific refraction.					
	<i>a.</i>	Diff.	<i>b.</i>	Diff.	<i>c.</i>	Diff.
K ₂ SO ₄ . . .	0.1107	262	0.1105	261	0.1111	269
Rb ₂ SO ₄ . . .	0.0845	65	0.0844	67	0.0842	72
Cs ₂ SO ₄ . . .	0.0780		0.0777		0.0770	

	Molecular refraction.					
	<i>a.</i>	Diff.	<i>b.</i>	Diff.	<i>c.</i>	Diff.
K ₂ SO ₄ ...	19.27	3.25	19.23	3.25	19.32	3.12
Rb ₂ SO ₄ ...	22.52	5.66	22.48	5.61	22.44	5.40
Cs ₂ SO ₄ ...	28.18		28.09		27.84	

The molecular refractions for 180° and the ray C calculated by the formula of Gladstone and Dale are as under.

	<i>a.</i>	Diff.	<i>b.</i>	Diff.	<i>c.</i>	Diff.
$\text{K}_2\text{SO}_4 \dots$	32.54	5.70	32.44	5.72	32.63	5.46
$\text{Rb}_2\text{SO}_4 \dots$	38.24	10.38	38.16	10.28	38.09	9.85
$\text{Cs}_2\text{SO}_4 \dots$	48.62		48.44		47.94	

The values for the molecular refraction at 180° calculated from both formulæ, are thus seen to be almost identical with those for the ordinary temperature ($18-20^{\circ}$), and the relationships are precisely the same. The following further statements concerning the molecular refraction may now therefore be made.

The values for the molecular refraction obtained by use of the formula of Gladstone and Dale, exhibit precisely similar relationships to those derived by use of the Lorenz formula. Moreover, the values of the specific and molecular dispersion at the temperature of 180° , calculated by use of either formula, are practically identical with those for the ordinary temperature, and exhibit exactly the same relationships. The relationships exhibited by the refraction constants of the three salts are therefore independent of the temperature.

SUMMARY OF CONCLUSIONS.

The main results of this investigation may be summarised in the following terms.

1. The normal sulphates of potassium, rubidium, and caesium differ widely with regard to their *solubility in water*—potassium sulphate being very sparingly soluble and caesium sulphate extremely soluble at whatever temperature the comparison is made, the solubility of rubidium sulphate is intermediate between that of potassium and caesium sulphates.

2. The *habits* assumed by the strictly isomorphous rhombic crystals of these salts approach each other more closely than was observed in the case of the monoclinic double sulphates of the series

containing the same three alkali metals. The predominating relative amounts of development of the primary faces, however, indicate a progression corresponding to the order of the atomic weights of the three metals.

3. The magnitudes of the whole of the *angles* of the rubidium salt lie between those of the analogous angles upon the potassium and caesium salts respectively. The angular differences are much smaller than was observed in the case of the double sulphates, indicating that the difference of angle decreases as the symmetry becomes higher. They are too small to enable a definite statement to be made with regard to the relation between the differences corresponding to the replacement of potassium by rubidium and rubidium by caesium respectively.

4. The *axial ratios* for rubidium sulphate are intermediate between those for potassium and caesium sulphates respectively. The ratio $a : b$ diminishes, but only very slightly, upon replacing potassium by rubidium or the latter metal by caesium, while the ratio $c : b$ increases materially.

5. Goniometrical observations at higher temperatures indicate that *conclusions 3 and 4 are independent of the temperature*.

6. The directions of *cleavage* in the crystals of the three salts are identical, being parallel to the brachypinacoid and basal plane respectively; that along the former direction is the more perfect in each case.

7. The *relative density* and *molecular volume* of rubidium sulphate are intermediate between the values of those constants for potassium and caesium sulphates respectively. A greater increase of volume accompanies the replacement of rubidium by caesium than is observed when rubidium replaces potassium, the ratio of the respective changes being 11.4 to 8.4.

8. The densities of the three sulphates diminish proportionally to their numerical values on raising the temperature, so that the *coefficients of cubical expansion* are almost identical, the differences being about the limits of experimental error. Determinations of the *coefficients of linear expansion* along the three axial directions indicate that in each salt the greatest amount of expansion occurs in the direction of the vertical axis c , the expansion along the other two axial directions being more nearly equal.

9. It may be assumed that in the case of the strictly isomorphous normal sulphates of potassium, rubidium, and cæsium, the physical molecules or crystal elements are composed of the same number of chemical molecules. The molecular volumes, more correctly termed equivalent volumes, will therefore express the relations of the volumes of the elementary parallelopiped of each salt, formed by joining the centres of adjacent crystal elements situate along the axial directions. The sides of the parallelopipeda will also be proportional to the crystallographic axial ratios. Hence, by combining the molecular volumes with the axial ratios, it is possible to calculate for the three salts the relative distances apart, from centre to centre of their crystal elements along the axial directions. The *distance ratios* (Muthmann's topic axes) thus calculated indicate that the replacement of potassium by rubidium and rubidium by cæsium is accompanied by an increase in the separation of the crystal elements along each of the axial directions, and this increase is relatively much greater when cæsium replaces rubidium than when the latter metal replaces potassium. The amount of increase varies in the three axial directions; it is greatest along the b axis and least along the a axis, and the increase of separation in the direction of the vertical c axis is almost equal to the maximum along the axis b . Considered proportionally to the lengths of the axes the change along the a and b axes is almost in exact proportion to their lengths, while that along the vertical axis c is much greater proportionately to its length.

10. The directions of cleavage, the positions of the planes in which the elementary parallelograms occupy least area, and the evidence afforded by the nature of the forms developed upon the crystals, agree in indicating that *the elementary parallelopiped of the series is a rectangular rhombic prism*. The order of change in the distance ratios can be fully accounted for on the supposition that the crystal element of the series is composed of four chemical molecules, symmetrically arranged with respect to the three planes of rhombic symmetry.

11. The *refractive indices* of rubidium sulphate are intermediate in value between those of the sulphates of potassium and cæsium, and lie nearest to those of the potassium salt; the average differences

between the indices of the potassium and rubidium salts on the one hand, and those of the rubidium and caesium salts on the other, are in the ratio of 2:5. An increase of refractive power accompanies an increase in the atomic weight of the contained metal, and the increase becomes relatively greater as the atomic weight becomes higher.

12. The *optical elasticity* of rubidium sulphate is consequently intermediate between the greater value of potassium sulphate and the lesser value of caesium sulphate. This is true whatever directions in the crystals are chosen for comparison, and whether analogous or not, the differences between the maximum and minimum values of the elasticity of any one salt being very small compared with the differences between different salts. If the same direction is chosen for comparison, the value for the rubidium salt is nearer to that of the potassium salt than to that of the caesium salt in the proportion of 2:5.

This may be more strikingly expressed as follows. The *ellipsoidal wave-surface*, of rays emanating from a common central point, for rubidium sulphate lies between the wave-surfaces of potassium and caesium sulphates respectively, and nearer to the outer enveloping wave-surface of the potassium salt than to the inner one of caesium sulphate in the proportion of 2:5.

13. The amount of diminution of optical elasticity on passing from one salt to another is almost identical in the directions of the axes *a* and *b*, so that the ratio of the elasticities in these two directions to each other remains practically constant for the three salts. The change of elasticity along the axis *c*, however, proceeds at a slower rate as the atomic weight of the contained metal is increased, and thus a considerable alteration in the relations between the elasticity along this axis and that corresponding to the other two axial directions is brought about. So considerable is this alteration that a complete reversal of the *nature of the double refraction* is produced. The elasticity along the *c* axis is the minimum of the three values along the axial directions in the potassium salt, and the maximum in the caesium salt, and in both cases these values for the *c* axis are furthest removed from the value of the medium elasticity in the same salt. Hence potassium sulphate is endowed with positive and caesium sulphate with negative double refraction, in both cases of weak order owing to the comparative closeness of the maximum and minimum values. The intermediate value which the elasticity along the axis *c* assumes in the rubidium salt falls between the values along the *a* and *b* axes, and is almost identical with that along the *b* axis. As the values along the *a* and *b* axes, now the minimum and maximum values, are very close together, the crystals of rubidium sulphate exhibit extraordinarily low double refraction, a section-plate almost a

centimetre thick being required to exhibit well-defined interference figures in convergent polarised light. Moreover, the extreme closeness, almost identity, of the values for the b and c axes renders the optic axial angle of rubidium sulphate exceptionally sensitive to change of wave-length in the illuminating light, to change of temperature, and to the presence of traces of isomorphous impurities. The dispersion of the optic axes at the ordinary temperature between the wave-lengths of the red lithium line and the bluish-violet G hydrogen line is about 35° for 2E and 20° for 2Va.

These exceptional optical properties of rubidium sulphate are entirely due to the fact that the three values of the optical elasticity for this salt are intermediate between those of the oppositely doubly-refractive potassium and caesium salts. Hence the optical properties of the crystals of the three salts are functions of the atomic weights of the metals which they contain.

14. A regular decrease in refractive power, corresponding to an increase of optical elasticity, is observed as the temperature of the crystals of each of the three sulphates is raised. The change is greatest for rays vibrating parallel to the vertical axis c , and the lesser changes in the directions of the axes a and b are approximately equal. The relations, however, established for the ordinary temperature are still maintained at higher temperatures, rubidium sulphate preserving its intermediate position along all three axial directions. The important conclusion, therefore, stated at the end of paragraph 13 is independent of the temperature.

15. The greater rate of acceleration of the elasticity along the axis c as the temperature is increased, while only slightly altering the optic axial angles of potassium and caesium sulphates, produces a remarkable change in the optic axial angle of rubidium sulphate. On heating a crystal of this salt, the elasticity along the c axis, the medium value at the ordinary temperature but very close to the maximum value along the b axis, rapidly approaches the latter value, and for a few degrees of rise of temperature becomes identical with it, when the crystal apparently possesses uniaxial properties. Further heating causes the c value to overstep that along the b axis and to become the maximum value. Hence, on warming a section-plate cut perpendicular to the first median line, the optic axes rapidly approach the centre of the field, and unite to form a uniaxial figure; they then separate again along the plane at right angles to that which previously contained them. Owing to the great dispersion, these changes occur in succession at different temperatures for the different wave-lengths, the uniaxial figure being produced first for red light, at about 40° for light of the wave-length of the red lithium line, and last for violet light, the temperature for G light being about 65° .

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16. The only connection which is apparent between the changes in the lengths of the crystallographic axes and the optical elasticity, brought about by replacing potassium by rubidium and rubidium by caesium, is exhibited between the relations of the values of these constants along the three axes towards each other. A very slight change in both cases is apparent in the ratio $a : b$, and a much larger one in the ratio $c : b$, and these changes occur in the same direction for both properties. The actual values appear to bear no relationship, except that the values for the rubidium salt are always intermediate. It may therefore be concluded that the actual value of the optical elasticity is not a function of the crystal element, the physical molecule, but of the chemical molecule. The fact that it is modified in a manner analogous to the modification of the axial ratios would appear to confirm the supposition that the crystal element is endowed with like symmetry to the crystal itself in regard to the internal arrangement of the chemical molecules of which it is composed.

17. The molecular refraction and dispersion of the crystals of the three salts, whether calculated by the formulæ of Lorenz or Gladstone and Dale, increase with the atomic weight of the contained metal, rubidium sulphate being again intermediate in this respect. The increase becomes greater as the atomic weight rises, so that the differences between the constants for the caesium and rubidium salts are greater than those between the constants for the rubidium and potassium salts. These statements are equally true whatever direction in the crystal is chosen for comparison, and as regards the refraction for whatever wave-length the comparison is made. It is observed, however, that the increase along the direction of the vertical axis c proceeds at a somewhat slower rate than along the directions of the two lateral axes, in which two latter directions the rate of increase is almost identical. These relationships are independent of the temperature.

18. It has now been shown that a regular progression is observed in the crystallographical characters of the three sulphates under consideration, corresponding to the progression in the atomic weight of the metal which they contain. With regard to every property, whether morphological or physical, the rubidium salt stands intermediate between the potassium and the caesium salt. The replacement of rubidium by caesium, however, is generally accompanied by a greater modification of the crystallographical characters than when potassium is replaced by rubidium, the heavier atom exerting an influence greater than in mere simple proportion to the increase in atomic weight. The comparative results for the different properties are all in line with each other, the relations of the amounts of change along the directions of the three crystallographic axes being similar with

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respect to all. Moreover, the progression according to the atomic weight of the alkali metal is perceptible with regard to the minutest details of the physical phenomena presented by the crystal, and is entirely independent of the temperature. It may therefore be finally stated that—

The whole of the crystallographical properties of the strictly isomorphous, rhombic, normal sulphates of potassium, rubidium, and cæsium, are functions of the atomic weight of the metal which they contain.

The author is now engaged on the physical section of the investigation of the double sulphates. The research is also being extended to the corresponding simple and double selenates of the same three alkali metals, the salts for this purpose being now in course of preparation. It is also hoped eventually to include in the scope of this investigation the analogous simple and double salts, of both sulphuric and selenic acids, containing ammonium and thallium.