

XXXV.—*Comparison of the Results of the Investigations of the Simple and Double Sulphates containing Potassium, Rubidium, and Cæsium, and general Deductions therefrom concerning the Influence of Atomic Weight on Crystal Characters.*

By ALFRED E. TUTTON, Assoc. R.C.S.

It is of considerable importance to compare the results of the detailed investigation of the crystallographical characters of the rhombic normal sulphates of potassium, rubidium, and cæsium, communicated to the Society in 1894 (Trans., 1894, **65**, 628), with those of the memoir preceding this, concerning the monoclinic double sulphates of the isomorphous series  $R_2M(SO_4)_2 \cdot 6H_2O$ , containing the same three alkali metals. The latter communication has been confined to the actual results of the experimental work. The conclusions of the former memoir are also all related to matters of fact, being the expression of the incontrovertible results of most careful measurements and determinations of physical constants, with the exception of conclusion 10 (p. 713), and more particularly the latter portion of that paragraph, in which certain speculations were indulged in relating to the problem of the nature of the crystal element. The considerations upon which those speculations were based are fully set forth in pp. 661 and 662 of the memoir, and will be discussed subsequently in the next communication, in the light of the results of the investigation of the double sulphates. It is most important in the first place, however, to review side by side the results based upon the experimentally ascertained facts in connection with the two investigations.

It has been shown that *the alkali metal R exerts a predominating*

*influence* in determining the crystallographical characters of the double sulphates. Hence the relations between the potassium, rubidium, and caesium salts of each group, that is, containing the same second metal, are fairly comparable with the relations exhibited between the simple sulphates of those metals themselves, as evidences of the effect of change in the atomic weight of the alkali metal.

The *habit* assumed by the crystals of rubidium sulphate, or of any rubidium salt of the series of double sulphates, is intermediate in character between the habits exhibited by the corresponding potassium and caesium salts.

The *morphological angles* of the rubidium salt, either simple or double, are invariably intermediate between the corresponding angles of the analogous potassium and caesium salts. Owing to the smallness of the differences in the case of the simple sulphates, no definite statement could be made regarding the relative effect of replacing potassium by rubidium, and the latter by caesium; but in the case of the larger differences presented by the double sulphates, where the symmetry is of a lower order, it was observed that as the atomic weight of the alkali metal becomes higher it exercises a relatively greater effect in modifying the morphological angles. It was interesting to find, however, that in the case of the monoclinic axial angle  $\beta$ , the angle between the two morphological axes lying in the plane of symmetry, the change of angle was approximately in direct simple proportion to the change in atomic weight.

The *morphological axial ratios* of any rubidium salt, simple or double, were also found to lie between those of the corresponding potassium and caesium salts.

The *relative density*, *molecular volume*, and *distance ratios*, that is to say, the whole of the constants connected with the extension in space, are also invariably intermediate in either the simple sulphate of rubidium or any rubidium double salt of the series under discussion, between the corresponding constants for the analogous potassium and caesium salts, and as regards the volume and the distance ratios the replacement of rubidium by caesium is always accompanied by a much larger change than when potassium is replaced by rubidium. It thus appears that extension occurs along each axial direction whenever the atomic weight of the alkali metal is raised, whatever be the nature of the symmetry, and that the amount of the extension is a function of the atomic weight, which involves higher powers of that property than the first.

It is of interest to note that the amount of increase in molecular volume on passing from a potassium to a rubidium salt in the series of double sulphates is practically constant, about 9.3 units, and similarly on passing from any rubidium salt to the corresponding caesium salt, when the larger increase is about 13 units. These

amounts of increase, however, are not quite the same as those corresponding to the replacement of potassium in the simple sulphate by rubidium, and the latter subsequently by caesium, which were observed to be somewhat less, 8·4 and 11·4. It is, doubtless, of some significance that the replacement of one alkali metal by another should be accompanied by appreciably greater change in volume in the double sulphates than in the simple salts.

It is next important to ascertain whether the alkaline sulphates occupy the same volume in their simple state as in the double sulphates. Fortunately there is excellent data available, as regards the volume of the M metals, in the results of the investigation of Thorpe and Watts (Trans., 1880, **37**, 102) concerning the volumes of the vitriols. In the course of that work they determined the relative densities of the anhydrous sulphates of magnesium, zinc, ferrous iron, manganese, nickel, cobalt, and copper, and the density of anhydrous nickel sulphate in the state of good crystals was also determined by Lepierre and Lachaud (*Compt. rend.*, 1892, **115**, 115), and by Klobb (*Compt. rend.*, 1892, **114**, 836). There is no data available for cadmium sulphate. Thorpe and Watts also determined the volume of the water of crystallisation in magnesium sulphate in various stages of hydration. They showed that the firmly held seventh molecule of water, the water of constitution, occupied the volume 10·7, whilst the various molecules of water of crystallisation occupied somewhat increasing volumes as their number present in the salt increased, ranging from 13·3 to 16·2, and averaging about 15. If then we take the volume of  $6\text{H}_2\text{O}$  as six times 15, or 90, and add to this the volume of the anhydrous M sulphate, and the volume of the alkaline sulphate determined by the author, we should, if the alkali sulphate occupied the same volume when crystallised alone as when present in the double salt, obtain a number practically identical with the observed molecular volume of the double salt. The following calculations will show how far this is the case.

The relative density of anhydrous magnesium sulphate is 2·709. Its molecular volume is therefore 44·3, and the volume of  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$  =  $44\cdot3 + 90 = 134\cdot3$ .

	Observed.
Mol. vol. of KMg sulphate = $65\cdot3 + 134\cdot3 = 199\cdot6$ .	198·2
„ RbMg „ = $73\cdot8 + 134\cdot3 = 208\cdot1$ .	207·6
„ CsMg „ = $85\cdot2 + 134\cdot3 = 219\cdot5$ .	220·7

The relative density of  $\text{ZnSO}_4$  is 3·623, the volume 44·4, 0·1 higher than  $\text{MgSO}_4$ . Hence

	Observed.
Mol. vol. of KZn sulphate is 199·7.	197·7
„ RbZn „ 208·2.	207·2
„ CsZn „ 219·6.	219·9

The relative density of  $\text{FeSO}_4$  is 3.346, the volume 45.4, 1.1 higher than  $\text{MgSO}_4$ .

		Observed.
Mol. vol. of KFe sulphate is	200.7.	200.1
„ RbFe „	209.2.	209.2
„ CsFe „	220.6.	222.6

The relative density of  $\text{MnSO}_4$  is 3.282, the volume 46.0, or 1.7 higher than  $\text{MgSO}_4$ .

Mol. vol. of  $\text{KMn}$  sulphate would be 201.3. Not observed.

		Observed.
„ RbMn „ is	209.8.	213.7
„ CsMn „ „	221.2.	226.6

The relative density of  $\text{NiSO}_4$  in crystals is 3.67, the volume 42.2, or 2.1 less than  $\text{MgSO}_4$ .

		Observed.
Mol. vol. of KNi sulphate is	197.5.	195.6
„ RbNi „	206.0.	204.9
„ CsNi „	217.4.	217.9

The relative density of  $\text{CoSO}_4$  in 3.472, the volume 44.8, or 0.5 greater than  $\text{MgSO}_4$ .

		Observed.
Mol. vol. of KCo sulphate is	200.1.	197.8
„ RbCo „	208.6.	207.3
„ CsCo „	220.1.	220.3

The relative density of  $\text{CuSO}_4$  is 3.606, the volume 44.1, or 0.2 less than  $\text{MgSO}_4$ .

		Observed.
Mol. vol. of KCu sulphate is	199.4.	198.3
„ RbCu „	207.9.	207.6
„ CsCu „	219.3.	220.2

Hence it is evident that *within very narrow limits the volume of the alkali sulphate is the same in the double salt as it is in the simple salt itself*. As regards these narrow limits, it will be noted that the differences between the calculated values of the potassium and caesium salts containing the same second metal is invariably 20, whilst the observed difference was 22. This, of course, is because the former smaller difference was observed between the simple sulphates of potassium and caesium, whose values are used in the calculations. There is absolutely no doubt as to the accuracy of the densities of the simple alkaline sulphates, and the results for all the several series of double salts confirm each other. The further consideration, however, of this minute difference in the amount of change of volume, accompanying replacement of one alkali metal by another, in the simple sulphates and the double salts respectively, may with advan-

tage be deferred until the completion of the work on the analogous selenates. For the present purpose, it is sufficient to observe that the volume occupied by the alkaline sulphate in the double salt is practically identical with its volume in the free state.

Another point of importance, indicated by the agreement of the observed values with those calculated from the data specified, is that none of the molecules of water are present in the double salts in the condition of water of constitution occupying the smaller volume 10·7.

It is especially interesting to point out that the molecular volumes of the simple alkaline sulphates are very considerably less than the sum of the atomic volumes, even less than the atomic volume of the alkali metal alone. The atomic volume of potassium is 45·5, of rubidium 56·3, and of cæsium 70·7, and 2 atoms would correspond to volumes of 91, 112·6, and 141·4 respectively, whilst the molecular volume of  $K_2SO_4$  is only 65·3, of  $Rb_2SO_4$  73·8, and of  $Cs_2SO_4$  only 85·2. Hence an enormous contraction must follow the combination of the atoms of the alkali metal with the acid radicle.

In the case of the rhombic simple sulphates, the three principal optical directions, the optical elasticity axes according to the older theory, the principal axes of the *optical indicatrix* of Fletcher, and of its polar reciprocal, the optical velocity ellipsoid referred to throughout the preceding communication, are, in accordance with the nature of the symmetry, identical with the directions of the morphological axes. Consequently they suffer no change of direction when one alkali metal is replaced by another, the symmetry remaining unaltered. On the other hand, only one of these axes remains constant in direction in the double sulphates, the one which is coincident with the morphological symmetry axis, and normal to the symmetry plane. The other two principal rectangular axes of the optical ellipsoid are only subject to the conditions that they must lie in the symmetry plane, and preserve their rectangularity, being free to move together in the symmetry plane. It has been shown that the optical ellipsoid actually rotates round the fixed symmetry axis as the atomic weight of the alkali metal is raised, and that the replacement of rubidium by cæsium is accompanied by a much greater amount of rotation than when potassium is replaced by rubidium. The amount of this rotation is very considerable, reaching a maximum in the magnesium salts of 33° between the potassium and the cæsium salts. It is one of the most interesting and doubtless significant results derived from the investigation. The rotation follows in direction the movement of the inclined morphological axis, assuming the vertical axis to remain vertical; for as the atomic weight of the alkali metal increases the obtuse angle between the inclined and vertical axes widens, by about 2° between potassium and cæsium, and the two rectangular axes of the optical ellipsoid lying in the symmetry plane move round in the

same direction as the inclined morphological axis, but to a much larger extent. It would, therefore, appear that the alteration of the morphological axial angle is connected with the alteration in the orientation of the optical ellipsoid, that is to say, the alteration in the angle between lines of contiguous structural units, parallel to the two directions of the vertical and inclined morphological axes, is intimately connected with the relatively very large alteration in the directions of maximum and minimum velocity of light vibration through the crystal which is observed.

The *refractive indices* of the simple normal sulphate of rubidium, or of any rubidium salt of the series of double sulphates, are intermediate between the indices of the analogous salts containing respectively potassium and caesium, and invariably lie nearer to those of the potassium salt. It was observed, both as regards the simple sulphates and the double sulphates, that an increase in the atomic weight of the alkali metal is accompanied by an increase in the refractive power of the crystals, and that, in accordance with the latter portion of the previous statement, the increase in refraction becomes relatively greater as the atomic weight becomes higher. It is of importance to observe, however, that the actual differences between the refractive indices of corresponding potassium, rubidium, and caesium salts are much larger in the case of the simple sulphates than in any group of the double sulphates. Thus, the intermediate  $\beta$  indices for sodium light for the three simple sulphates are: for  $K_2SO_4$  1.4947, for  $Rb_2SO_4$  1.5133, and for  $Cs_2SO_4$  1.5644, a difference between K and Cs of 0.0697, whilst for the magnesium group, which exhibits the greatest difference of any group of the double sulphates, the  $\beta_{Na}$  indices are: potassium magnesium sulphate 1.4629, rubidium magnesium sulphate 1.4689, and caesium magnesium sulphate 1.4858, exhibiting a difference of 0.0229, or only one-third the difference observed for the simple sulphates. This is doubtless due to the greater magnitude and complexity of the double sulphate molecule, a change in the atomic weight of even the most important element present, the alkali metal, being naturally incapable of modifying the physical properties to so large an extent as would be the case in a simple molecule such as that of the normal sulphate.

The *velocity ratios* (for light), or ratios of the refraction reciprocals, the optical elasticity ratios of the older theory, naturally follow similar laws to the refractive indices; in both simple and double sulphates the ratios for a rubidium salt are intermediate between those for the corresponding potassium and caesium salts. Increase in the atomic weight of the alkali metal is accompanied by an increase of resistance to the vibrations of light waves along each axis of the optical ellipsoid, and the resistance interposed is much greater when caesium replaces rubidium than when the latter replaces potassium,

that is to say, it becomes greatly augmented as the atomic weight rises, far more so than in proportion to the augmentation in atomic weight.

The progressive changes in the velocity ratios introduced by increasing the atomic weight of the alkali metal, graphically represented by the changes in the lengths of the axes of the optical ellipsoid, are such in both simple and double sulphates as to result in a convergence of the maximum and minimum values of these ratios towards unity. That is, as the atomic weight of the alkali metal rises the differentiation in optical behaviour in different directions in the crystals becomes less marked. In all the groups of double sulphates, except the magnesium group, the operation of this rule results in the *double refraction*, already weak in the potassium salts, becoming feebler in the rubidium salt, and feebler still in the cæsium salt. In the magnesium group it results in identity of two of the three values being actually attained when the cæsium salt is reached, and hence the remarkable optical phenomena presented by cæsium magnesium sulphate described in the preceding communication. In the simple sulphates the result is even more extraordinary, for the convergence of the two extreme values is so rapid that they are almost arrived at unity in the rubidium salt, and actually so if the temperature is slightly raised, thus causing normal rubidium sulphate to exhibit similar remarkable optical phenomena to cæsium magnesium sulphate; just beyond the rubidium salt the curves representing these same two values coincide at the ordinary temperature and cross each other, afterwards diverging until, when the cæsium salt is reached, they are further apart than they were in the potassium salt, but the sign of double refraction is completely reversed.

Hence the results as regards both the simple sulphates and the double sulphates are in perfect agreement in regard to the regularly progressive nature of the changes introduced into the optical ellipsoid by increase of the atomic weight of the alkali metal. It is doubtless significant that the striking effect, in the case of the simple sulphates, of the rule regulating these changes is most nearly reproduced in the magnesium group of the double sulphates, in which the atomic weight of the second metal magnesium is much lower than that of any other of the second metals, and hence the total relative weight of the molecule is least, and the magnesium salts are therefore more largely affected by change of the alkali metal.

The whole of the *specific and molecular optical constants* of rubidium sulphate, and of every rubidium salt of the series of double sulphates, have been shown to be intermediate between the analogous salts containing respectively potassium and cæsium. Both with respect to the simple sulphates and to the double sulphates it was observed that increase in the atomic weight of the alkali metal is accompanied by



a diminution of specific refraction and dispersion, the amount of which is much greater when potassium is replaced by rubidium than when the latter metal is replaced by caesium. The same changes are productive of an increase in the molecular refraction and dispersion, and the amount is much the greatest when caesium replaces rubidium, the opposite of the case for the specific constants. These rules were further shown to be independent of the nature of the light and of temperature.

The molecular refraction data now available for the simple sulphates and so large a number of double sulphates afford some interesting and not unimportant comparisons.

It was found that when rubidium replaced potassium in potassium sulphate a mean difference of molecular refraction for the ray C of 5.48 Gladstone and Dale or 3.11 Lorenz units was observed. In the double sulphates the like chemical change was found to be accompanied by a mean increase varying in the different groups from 5.11 to 5.32 or 2.97 to 3.09 according to the formula employed. The replacement of rubidium in rubidium sulphate by caesium was accompanied by a mean increase of 10 Gladstone and Dale units or 5.43 Lorenz units; in the double sulphates a similar replacement corresponded to a mean increase of 9.26 to 9.96 or 5.19 to 5.50 such units. It is evident, therefore, that approximately identical changes in molecular refraction accompany similar chemical changes both in the simple salts and in the double salts. The mean values from all the results, both for the simple and double sulphates, are 5.27 and 9.72 Gladstone and Dale units for the replacement respectively of potassium by rubidium, and the latter by caesium, or 3.05 and 5.41 Lorenz units.

Now, the molecular refraction equivalent of potassium has been determined with very great care by Gladstone, after taking account of recent determinations of other workers besides himself, and he ascribes the value 7.85 to it (*Trans.*, 1891, **59**, 597). Assuming this number to be correct, and adding to twice this value, 15.7, corresponding to the 2 atoms of potassium, the increment of 5.27 on replacing potassium by rubidium, we obtain, assuming no extraordinary changes occur, the value 20.97 for 2 atoms of rubidium and 10.5 as the refraction equivalent of rubidium. Adding the further increment of 9.72, for the replacement of rubidium by caesium, to 20.97 we obtain 30.69 for the value of 2 atoms of caesium, or 15.35 for the refraction equivalent of caesium.

The values for rubidium and caesium previously given by Gladstone (*Phil. Trans.*, **159**, 13: *Proc. Roy. Soc.*, **18**, 49) are 12.1 and 19.1 respectively, and by Kanonnikoff 12.04 and 19.55 (*J. pr. Chem.*, 1885, **31**, 321, 497).



It is evident that either these latter values of the two metals are incorrect, or that some extraordinary diminution of molecular refraction occurs in both simple and double sulphates.

A most valuable confirmation of the author's values for the molecular refraction of the simple sulphates has recently been published by Gladstone (*Trans.*, 1895, **67**, 840), who has determined the refractive indices in solution. The numbers thus obtained for the refraction equivalents are: for  $K_2SO_4$  32.15, practically the same as the 1891 value, for  $Rb_2SO_4$  38.39, and for  $Cs_2SO_4$  47.57. The mean values corresponding to the three crystal indices obtained by the author for the three respective salts were 32.30, 37.79, and 47.77. Hence it is clear that solution merely gets rid of the differential refraction in different directions, the value for the dissolved salt being practically identical with the mean of the three values along the principal optical directions of the crystal. Gladstone has also determined the molecular refraction of potassium zinc sulphate, and obtained the number 95.94, a value almost absolutely identical with the author's mean value for the crystal 95.90.

Before proceeding further it will afford some guide if the values of the radicle  $SO_4$  are deduced from the refraction equivalents of the simple sulphates, assuming 7.85, 10.5, and 15.35 to be the equivalents of potassium, rubidium, and caesium respectively. Deducting twice these values, for the 2 atoms of each respective alkali metal, from the above quoted mean values for crystals of  $K_2SO_4$ ,  $Rb_2SO_4$ , and  $Cs_2SO_4$ , the numbers 16.6, 16.79, and 17.07 are obtained for  $SO_4$ . Now, even the highest of these is appreciably lower than the value previously found by Gladstone for this radicle, 17.5 (*Trans.*, 1891, **59**, 597), and if the previously accepted values of Gladstone and of Kanonnikoff for rubidium and caesium were adopted the numbers for  $SO_4$  derived from the two corresponding salts would be much lower still, namely, 13.59 and 9.57, numbers which are absurdly low. Hence one of two things occurs. Either the refraction equivalents hitherto accepted for rubidium and caesium are incorrect, at any rate in these salts, or, being correct, there is some disturbing cause in operation which results in a considerable absorption of refractive energy, and which becomes more powerful as the atomic weight of the alkali metal rises. For it is evident that if the molecular refractions of  $K_2SO_4$ ,  $Rb_2SO_4$ , and  $Cs_2SO_4$  are calculated, assuming Gladstone's 1891 values for  $SO_4$  and potassium, and the older values of Gladstone and of Kanonnikoff for rubidium and caesium, the number obtained for  $K_2SO_4$  will be practically identical (33.2) with that derived from actual observation, while the numbers for  $Rb_2SO_4$  (41.7) and  $Cs_2SO_4$  (55.7) will be considerably larger than those calculated from the observed refraction, the latter number exhibiting the greatest discrepancy.

It is also possible to calculate with especial accuracy the molecular refraction of two of the groups of double sulphates, those containing magnesium and zinc; for Gladstone has recently determined the values of  $\text{MgSO}_4$  and of  $\text{ZnSO}_4$  (Trans., 1895, **67**, 838), and in the same memoir publishes the results of a most careful re-determination of the value for water. Assuming these values,  $\text{MgSO}_4 = 24.1$ ,  $\text{ZnSO}_4 = 26.32$ ,  $\text{H}_2\text{O} = 6.01$ , and taking first the author's determined values for  $\text{K}_2\text{SO}_4$ ,  $\text{Rb}_2\text{SO}_4$ , and  $\text{Cs}_2\text{SO}_4$ , and afterwards the values calculated for these salts, on the assumption that  $\text{K} = 7.85$ ,  $\text{Rb} = 12.1$ , and  $\text{Cs} = 19.1$ , the following results are obtained.

Salt.	Mean values derived from direct observation.	Value calculated on first assumption.	Value calculated on second assumption.
$\text{K}_2\text{Mg}(\text{SO}_4)_2, 6\text{H}_2\text{O} \dots$	92.41	92.46	93.36
$\text{Rb}_2\text{Mg}(\text{SO}_4)_2, 6\text{H}_2\text{O} \dots$	97.73	97.95	101.86
$\text{Cs}_2\text{Mg}(\text{SO}_4)_2, 6\text{H}_2\text{O} \dots$	107.42	107.93	115.86
$\text{K}_2\text{Zn}(\text{SO}_4)_2, 6\text{H}_2\text{O} \dots$	95.90	94.68	95.58
$\text{Rb}_2\text{Zn}(\text{SO}_4)_2, 6\text{H}_2\text{O} \dots$	101.22	100.17	104.08
$\text{Cs}_2\text{Zn}(\text{SO}_4)_2, 6\text{H}_2\text{O} \dots$	110.75	110.15	118.08

It is evident that the numbers calculated on the first assumption agree very closely with the values derived from the actual measurements, while those based upon the second assumption are much too high for the rubidium and caesium salts, and particularly the latter. The first series of numbers for the zinc salts agree still more closely if Kanonnikoff's value for Zn (9.8) be taken, along with Gladstone's recent value for  $\text{SO}_4$ , when  $\text{ZnSO}_4$  becomes 27.3, one unit more than Gladstone's value for  $\text{ZnSO}_4$ .

Hence the same fact is as clearly demonstrated in the double sulphates as in the simple sulphates, that either the hitherto accepted values for Rb and Cs are too high, and the latter to the greatest extent, or there is some internal source of loss of refractive energy which is more effective as the atomic weight of the alkali metal rises. Which of the two possibilities is correct had perhaps better be left undiscussed until further observations on other compounds of these metals are available. Doubtless the investigation of the selenates and double selenates on which the author is now engaged will afford additional information on this point.

The refraction equivalents of the remaining double salts of the series, derived from direct observation, will now be compared with the values calculated by use of the author's observed values for  $\text{K}_2\text{SO}_4$ ,  $\text{Rb}_2\text{SO}_4$ , and  $\text{Cs}_2\text{SO}_4$ , and Gladstone's older values for ferrous Fe (12), Ni (10.4), Co (10.8), Cu (11.6), Mn (12.2), Cd (13.6), and his more recent values for  $\text{SO}_4$  (17.5), and  $\text{H}_2\text{O}$  (6.01), in order to ascertain

whether a similar agreement occurs to that shown between the values in the first two columns in the preceding table for the magnesium and zinc salts.

Salt.	Mean value derived from direct observation.	Calculated value.
$K_2Fe(SO_4)_2 \cdot 6H_2O$ . . . . .	96.92	97.86
$Rb_2Fe(SO_4)_2 \cdot 6H_2O$ . . . . .	102.03	103.35
$Cs_2Fe(SO_4)_2 \cdot 6H_2O$ . . . . .	112.00	113.33
$K_2Ni(SO_4)_2 \cdot 6H_2O$ . . . . .	96.33	96.26
$Rb_2Ni(SO_4)_2 \cdot 6H_2O$ . . . . .	101.50	101.75
$Cs_2Ni(SO_4)_2 \cdot 6H_2O$ . . . . .	111.25	111.73
$K_2Co(SO_4)_2 \cdot 6H_2O$ . . . . .	96.63	96.66
$Rb_2Co(SO_4)_2 \cdot 6H_2O$ . . . . .	101.91	102.15
$Cs_2Co(SO_4)_2 \cdot 6H_2O$ . . . . .	111.76	112.13
$K_2Cu(SO_4)_2 \cdot 6H_2O$ . . . . .	97.29	97.46
$Rb_2Cu(SO_4)_2 \cdot 6H_2O$ . . . . .	102.54	102.95
$Cs_2Cu(SO_4)_2 \cdot 6H_2O$ . . . . .	111.80	112.93
$Rb_2Mn(SO_4)_2 \cdot 6H_2O$ . . . . .	102.95	103.55
$Cs_2Mn(SO_4)_2 \cdot 6H_2O$ . . . . .	112.49	113.53
$Rb_2Cd(SO_4)_2 \cdot 6H_2O$ . . . . .	105.80	104.95
$Cs_2Cd(SO_4)_2 \cdot 6H_2O$ . . . . .	114.58	114.93

It will be observed that the agreement is fairly close throughout. If, however, instead of the observed values of  $Rb_2SO_4$  and  $Cs_2SO_4$ , corresponding to the values for Rb and Cs of 10.5 and 15.35 respectively, being used in the calculations, the usually accepted values for Rb and Cs, 12.1 and 19.1 are employed, the calculated values for the rubidium double salts will be 3—4 units higher than the observed values, and for the caesium double salts 7—8 units higher, as in the cases of the magnesium and zinc salts.

*It is, therefore, undoubtedly a fact that the same refraction equivalents which were observed in the case of the simple sulphates apply also to those salts when combined with the sulphates of magnesium, zinc, iron, nickel, cobalt, copper, manganese, and cadmium to form the double sulphates crystallising with 6 mols. of water.*

It is interesting to note that the greater difference which is observed in molecular refraction between the caesium and rubidium salts than between the potassium and rubidium salts, whether simple or double, is entirely in accordance with the relations of the difference between the atomic refractions of the alkali metals themselves. If the author's values, as derived from the sulphates and

double sulphates, are taken, the differences between the refraction equivalents of potassium and rubidium and caesium and rubidium respectively are 2.7 and 4.8. If Gladstone's values are taken, the differences are 4.3 and 7.0 respectively. In either case the ratio is of the same order as in the salts.

*The optic axial angle phenomena* of both simple and double sulphates were shown to be precisely in accordance with the requirements of the rule regarding the progressive change in the velocity ratios or the relationships of the axes of the optical ellipsoid. With regard to the double sulphates, in every group except that containing magnesium, where extraordinary relationships of those ratios are exhibited in the case of caesium magnesium sulphate, the optic axial angle of any rubidium salt is intermediate between that of the potassium and that of the caesium salt of the same group. In the case of the magnesium group the remarkable crossed axial plane dispersion of the optic axes of the caesium salt, and the great sensitiveness of the optic axial angle to change of temperature, were shown to be the direct effect of the operation of the rule of convergence of the velocity ratios towards unity, which resulted in two of the axial values of the optical ellipsoid actually attaining unity, but at any one temperature only for a particular wave-length, hence the crossing of the optic axial plane and the simulation for that particular wave-length of uniaxial optical properties. In the simple sulphates the result of the operation of the same rule regarding the convergence of the maximum and minimum axes of the optical ellipsoid towards equality has been shown to lead to an even more extreme result, namely, that unity is almost attained at the ordinary temperature in the case of the rubidium salt, and actually so on slightly raising the temperature, causing the optic axial angle of that salt to be likewise extremely sensitive to change of wave-length and of temperature, and to exhibit the phenomenon of crossed axial plane dispersion at temperatures slightly elevated above the ordinary; further, that in caesium sulphate those axial values are again separated, but in the contrary direction, as would be expected after the meeting if the change were continuous; and hence this salt exhibits negative double refraction, and the plane of the optic axes is perpendicular to that in the potassium salt. The whole of these complicated and very beautiful, as well as unusual, phenomena are thus immediately explained on the assumption of progressive changes corresponding to the progressive change in the atomic weight of the alkali metal.

It has now been conclusively shown that *the whole of the morphological and physical characters of the crystals of the rhombic normal sulphates of potassium, rubidium, and caesium, and of any group of the*

*monoclinic double sulphates of the series  $R_2M(SO_4)_2 \cdot 6H_2O$ , in which those simple salts of the three alkali metals are combined with the sulphate of either magnesium, zinc, iron, manganese, nickel, cobalt, copper, or cadmium, whilst conforming to the same symmetry and exhibiting the general similarities proper to isomorphous series, present well-defined differences which are functions of the atomic weight of the alkali metal which those salts contain, and usually functions which involve higher powers of the atomic weight than the first.*

The completion of the work on the potassium, rubidium, and caesium salts of sulphuric acid, therefore, establishes beyond doubt, as regards these three definitely related metals and this particular acid, that *The characters of the crystals of isomorphous series of salts are functions of the atomic weight, that is to say of the energy of which atomic weight is the expression, of the interchangeable dominant elements belonging to the same family group of the periodic system which give rise to the series.* There is strong presumptive evidence that this will eventually prove to be a general law of Nature. The investigation of the analogous selenates and double selenates which the author is now undertaking, will afford a substantial addition to the information already accumulated.

---