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*The anomalous optical properties of some new series
of isomorphous double tartrates.*

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IN a previous paper¹ two well-known crystalline compounds, sodium-potassium tartrate, $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$, and sodium-ammonium tartrate, $\text{Na}(\text{NH}_4)\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$, were described, and it was therein shown how, in the crystals obtained by mixing these two isomorphous substances in any proportion, the dispersions of the optic axes in the freshly prepared crystals were incompatible with orthorhombic symmetry. The crystals have been frequently measured and found to be orthorhombic bisphenoidal in external symmetry and this has been further confirmed by the author's measurements. A full description of all the various dispersions to be found in the orthorhombic and monoclinic systems may be obtained from any text-book of crystallography, but in the following pages two of these are specially important. These are crossed dispersion,

¹ H. E. Buckley, Some anomalous optical properties of freshly-prepared mixed crystals of the Seignette salts. *Min. Mag.*, 1924, vol. 20, pp. 159-172.

as exemplified in borax, and belonging to monoclinic crystals; and crossed axial-plane dispersion, an example of which is given by brookite, and proper to the orthorhombic classes of symmetry.

Crystals of the mixed tartrates when freshly prepared almost invariably possessed a dispersion of the borax type, though this is only consistent with monoclinic symmetry. A description of the outward appearance of these crystals is given in the previous paper. The interference-figures are nearly always to be seen through the cleavage section parallel to (001). Only in crystals which possess less than 5% $\text{Na}(\text{NH}_4)\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ in the series described does the acute bisectrix emerge parallel to the a -axis, so that sections require to be cut parallel to (100). Only when the crystals have stood for a long time after preparation, or have been heated sufficiently long, do the interference-figures resemble that afforded by brookite or by sodium-ammonium tartrate. In the latter case, all optic axes for different colours are alined in one plane, (100), but there is a strong dispersion of the optic axes. In the former case there is one colour in the visible spectrum for which the crystal is optically uniaxial, while for colours closer to the red end of the spectrum the optic axes all lie in the (100) plane, and for colours closer to the violet end they all lie in the (010) plane.

When, however, the crystals are fresh, the dispersion is of the borax type, with the optic axial plane for deep-red nearly parallel to (100), while the remaining optic axial planes are spread out like the rays of a fan, giving as values for the total dispersions from red to violet light of from 5° to 75° . On standing, all crystals show a change of interference-figure to either the brookite type or the normal type (sodium-ammonium tartrate) of orthorhombic dispersion. When this change in optic axial plane directions is taking place a change in optic axial angles is also taking place, there being in some cases a widening, and in other cases a contraction, of optic axial angle. Measurements on any of these crystals are therefore liable to differ, according to whether they take place when the crystals are freshly prepared or after these have been allowed to stand for some time.

Fig. 1 shows a photograph of the interference-figure of a section of a crystal having the composition $50 \text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O} + 50\text{Na}(\text{NH}_4)\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$, taken in the light of the mercury-arc. An inspection will show that it appears to consist of two superimposed interference-figures. One of these is due to the 5461 line in the green and is symmetrically disposed about the eyepiece cross-wires; the other and stronger figure is that due to the 4358 line in the violet and is set at an angle of about 73°

to the other figure. The excessive actinic power of the violet light has caused the interference-figure for violet to preponderate in spite of the fact that a green filter was used at the time of the exposure. With crystals of this composition, careful measurements of the optic axial angles were made on the Hutchinson universal goniometer and the results were recorded in Table IX, p. 171, of the previous paper. They are for convenience again given in Table I *a* (p. 66) of the present paper. After three years' standing, sections of the same crystals were taken and measured, and the results are given in Table I *b*. A glance at Tables I *a* and I *b* will show that the results of this method of measuring optic axial angles support the conclusions arrived at with the more rapid, but not so accurate, method of the micrometer eyepiece used in tabling the other results given in this paper; viz. that there is a definite change in the optic axial angle for light of each wave-length as well as a re-adjustment of optic axial planes.

The crossed dispersion shown by freshly prepared crystals is of two types:

(A) The optic axial plane for deep-red is very nearly (within 1° or 2°) parallel to (100), and the violet end of the spectrum shows greater sensitivity to change in optic axial plane (fig. 2).

(B) The optic axial plane for the extreme violet is almost parallel to (010) and there is a greater spread of the optic axial planes in the red end of the spectrum (fig. 3).

The series $\{m\text{NaK}, n\text{Na}(\text{NH}_4)\} \text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ described in the previous paper belong to both these types, mixed crystals with a greater proportion of the NaK tartrate belonging to type *B* and those with less to type *A*. Mixed crystals of the series $\{m\text{KNa}, n\text{K}(\text{NH}_4)\} \text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ all belong to type *B*, while those of the series $\{m(\text{NH}_4)\text{Na}, n(\text{NH}_4)\text{K}\}$ are all of the type *A*.

In the present paper the author has prepared for optical examination a large number of compounds obtained by the neutralization of tartaric acid with the same three bases, Na, K, and NH_4 , and has obtained results

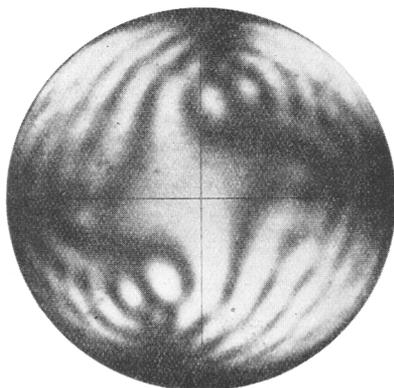


FIG. 1. Interference-figure showing crossed dispersion.

which considerably enlarge the number of mixtures which may strictly be called isomorphous with the original Seignette salt, $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$, and which form series closely resembling in form and properties the

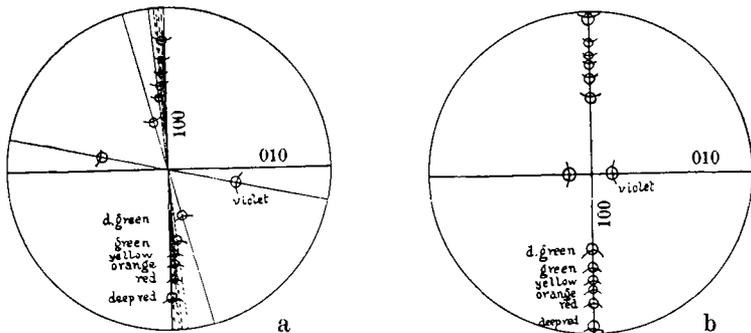


FIG. 2. Optic axes for different colours in mixed crystals
 $\{50(\text{NH}_4)\text{Na}, 50(\text{NH}_4)\text{K}\}\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$.

- (a) crossed dispersion (borax type *A*) in freshly prepared crystals;
 (b) crossed axial-plane dispersion (brookite type) in the final state.

(See Table III *b*, p. 68.)

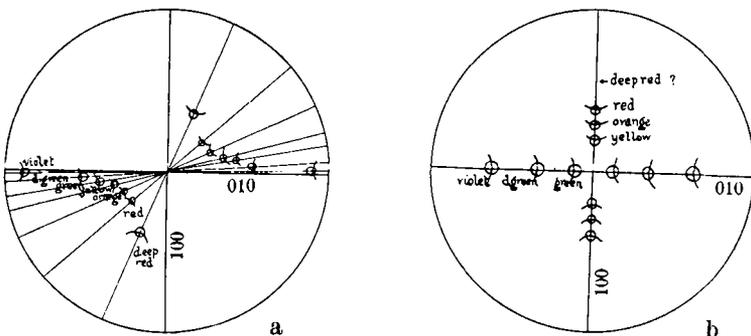


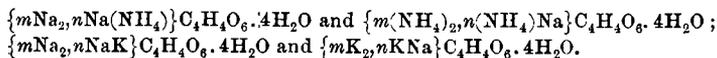
FIG. 3. Optic axes for different colours in mixed crystals
 $\{20\text{KNa}, 80\text{K}(\text{NH}_4)\}\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$.

- (a) crossed dispersion (borax type *B*) in freshly prepared crystals;
 (b) crossed axial-plane dispersion (brookite type) in the final state.

(See Table II *a*, p. 66.)

series studied in the previous paper. The latter series was composed of mixtures of the type $\{m\text{NaK}, n\text{Na}(\text{NH}_4)\}\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$. Other possible variations of all three bases with tartaric acid are $\{m\text{KNa}, n\text{K}(\text{NH}_4)\}$

$C_4H_4O_6 \cdot 4H_2O$ and $\{m(NH_4)Na, n(NH_4)K\}C_4H_4O_6 \cdot 4H_2O$, and members of both these series have been prepared and their optical properties studied in a similar way to those of the first series. The results are included in the present paper. In addition, the possible variations of *two* of the three bases Na, K, and NH_4 with tartaric acid have been studied, and the following series of isomorphous mixtures, similar to the foregoing, have been found capable of preparation.



On the other hand, it was not found possible to prepare any member of the two related series $\{m(NH_4)_2, n(NH_4)K\}C_4H_4O_6 \cdot 4H_2O$ and $\{mK_2, nK(NH_4)\}C_4H_4O_6 \cdot 4H_2O$.

Observations on the new series of Seignette salts in which all three bases Na, K, and NH_4 are present.

The results obtained in the study of these mixtures are given in some detail in the following pages. It should be understood that, unless specially mentioned, the acute bisectrix is always parallel to the *c*-axis and the sign of birefringence negative.

Series $\{mKNa, nK(NH_4)\}C_4H_4O_6 \cdot 4H_2O$.—Crystals belonging to members of this series were readily obtained, but when containing a large proportion of ammonium base they showed a tendency to effloresce rather more quickly than usual on exposure to air. In the preparation, too, of the latter crystals, the solution itself had to be kept saturated with ammonia vapour; otherwise needle-like crystals of lower symmetry, and not related to these series, were obtained. Tables II *a*, II *b*, II *c*, and II *d* relate to observations made upon this series where $m=20, 33\frac{1}{3}, 50,$ and $66\frac{2}{3}$ per cent. respectively. From a perusal of these tables it will readily be seen that this series presents optically anomalous properties similar to the series described in the first paper. There is a similar rise to a maximum value of initial crossed dispersion, and the process of changing to the final state, in harmony with the orthorhombic symmetry of the crystal-angles, is similarly hastened by heating. There is, however, one striking difference. The optic axial planes in the brookite type of dispersion are always (100) for red and (010) for violet light. When the dispersion is of the normal type, i. e. when all the optic axes lie in a single plane, this is (100) in the series already described in the first paper and in most of the subsequent series, but in this particular series, $\{mKNa, nK(NH_4)\}C_4H_4O_6 \cdot 4H_2O$, the optic axial plane is (010).

Series $\{m(\text{NH}_4)\text{Na}, n(\text{NH}_4)\text{K}\}\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$.—Crystals belonging to this type of mixture are very readily prepared, and large clear crystals may be obtained more frequently than is the case with most other series. The cleavage parallel to (001) which exists to a greater or lesser degree in all members of the different series is here exceptionally good and enables sections for the study of the optical properties to be obtained readily. The results of observations on members of this series are shown in Tables III *a*, III *b*, and III *c*. From these it is seen that a precisely similar set of phenomena to those observed in the two previously described series take place. These include, (*a*) an initial crossed dispersion of the borax type which gradually settles down to an orthorhombic form of dispersion, and (*b*) a change in optic axial angle for any colour after an interval of time has elapsed.

Heating, as in all previous instances, hastens the settling-down process. It will be seen from Table III *b* that when readings of the crossed dispersion are taken in an intermediate stage in the process of settling down there is a preliminary movement of the optic axial planes. In this instance, all planes from the red end of the spectrum to Hg-green have closed up into alinement with the optic axial plane for red, but the total angle of crossed dispersion, from red to violet, has remained unchanged. There is a subsequent movement of optic axial planes for the violet end of the spectrum into a position at right angles to the optic axial plane for red. Difficulty was experienced with mixtures containing a larger proportion of $(\text{NH}_4)\text{KC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$, since, after the heating process had taken place, the sections rapidly became opaque and readings were found to be possible only in the case of the more monochromatic sources of light. This fact accounts for the shortness of Table III *c*.

Observations on the new series of Seignette salts in which two of the three bases NH₄, Na, and K are present.

The actual preparation of members of these series mentioned above as possible was not difficult. The crystals themselves are identical in habit and in general appearance with crystals of the three foregoing series (which contain all three bases NH₄, Na, and K). An examination of the interference-figures of sections cut from these crystals shows that although there is a strong dispersion of the optic axes for colours in the visible spectrum, no trace of the anomalous crossed dispersion of the borax type was found to be present, though subsequent movements of the optic axes themselves was traced all through the different series. The results for crystals of the series $\{m(\text{NH}_4)_2, n(\text{NH}_4)\text{Na}\}\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ are given

in Tables IV *a*, IV *b*, and IV *c*, and those for the series $\{m\text{Na}_2, n\text{Na}(\text{NH}_4)\}$ $\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ in Tables V *a*, V *b*, and V *c*. The interference-figures afforded by sections of crystals in these two series (neither of which contains potassium) are similar in that there is a very strong, though apparently normal, dispersion of the optic axes for the different colours. This may amount to as much as 50° (Table V *a*) between the optic axial angles for visible red and visible violet. It is possible, therefore, that there may be an anomalous crossed dispersion in these two series, similar to that observed in all previous series, except that it will occur in the region near the end of the visible spectrum or perhaps just beyond in the ultra-violet, so that, on settling down to the final state, the uniaxial point will be located a little beyond the point where visible observation is possible. Evidence is shown in all the tables that there is a change in optic axial angle for the different colours after a lapse of time.

The remaining two series which were found to be readily prepared are $\{m\text{K}_2, n\text{KNa}\}$ $\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ and $\{m\text{Na}_2, n\text{NaK}\}$ $\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$. The results obtained from these are shown in Tables VI *a*, VI *b*, and VI *c*. In all cases the main characteristics of the interference-figures are the wide angle of the optic axes, rendering measurements difficult, and the fact that, like the two immediately foregoing series, no trace of crossed dispersion in the initial state of the crystals was observed. The dispersion of the optic axes, in sharp contrast to all the previously described crystals, is somewhat weaker.

Effect of pressure on the rate of settling down of the crystals.

In the previous paper allusion was made to the fact that an increase of temperature has the effect of hastening considerably the process of settling down to the final state in these series of crystals. Experiments have been performed on a compound of the composition $\{80(\text{NH}_4)\text{Na}, 20(\text{NH}_4)\text{K}\}$ $\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$, already described in Table III *a*, to determine the effect of pressure on the rate of change which takes place. This particular compound was chosen because it possessed a large initial angle of crossed dispersion and is therefore more sensitive to any slight variation of the rate of settling down that might be introduced by the application of pressure on the section. The effect of pressure was observed in the following manner. Two sections were cut from freshly prepared crystals and the crossed dispersion measured at once. They were then exposed to a temperature somewhat above the ordinary, so that the whole process of settling down could be more quickly brought about. One of them was

then compressed while the other remained free, and after a suitable interval of time had elapsed measurements were again made on both sections and the differences noted. Pressure was applied normally to the section in a covering of undiluted Canada balsam, which, while keeping the section away from the air, remained fluid, so that the pressure was not interfered with. The arrangement used is shown in fig. 4. A brass box B is reinforced on one side A , and the latter is pierced by two holes H_1 and H_2 . One section S_2 is placed in a remote corner of the box and the other section S_1 is compressed between the thicker wall of the box and a flat brass strip Y connected to a second brass strip X outside the

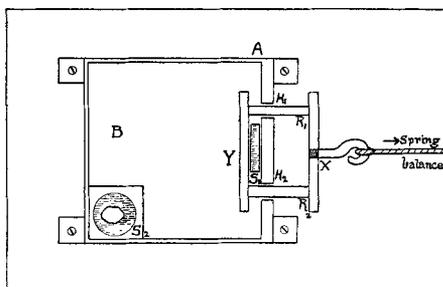


FIG. 4.

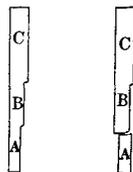


FIG. 5 a. FIG. 5 b.

FIG. 4. Apparatus for applying pressure to crystal-sections.

FIG. 5. Side-view of crystal-section (Table VII b, p. 71).

box by means of two brass rods R_1 and R_2 , which pass through the holes H_1 and H_2 in the box. A hook attached to the outer brass strip X connects the arrangement to a spring-balance, by means of which the pressure may be regulated. The whole arrangement is mounted on a board which can be moved into an asbestos-lined wooden box provided with air outlet-holes and heated to the required temperature by a set of filaments.

No results were obtained for pressures of from 1 to 5 lb. With pressures of from 10 to 15 lb. definite effects were recorded. These are included in Tables VII a and VII b, and show that pressure has a *retarding* effect on the rate of settling down of these crystals. The section used in the experiment recorded in Table VII b is shown in side-elevation in figs. 5 a and 5 b. Fig. 5 a shows the original outline of the section as cleaved. It was step-like in shape and consisted of three portions A , B ,

and *C*. Each portion gave identical values of initial crossed-dispersion, &c., and the interference-figures observed were exceptionally clear and sharp, so that re-grinding of the lower surface was not resorted to. On the application of pressure the thinnest portion *A* broke off and was shielded from the compressing influence by the thick portion *C*, while the middle portion *B* only received part of the pressure. Table VII *b* shows that the uncompressed section S_2 on re-examination after heating to 42° C. for one day has still a crossed dispersion of 5°. The shielded part of the compressed section, shown in fig. 5 *b*, has also a crossed dispersion of 5°, while the fully compressed part *C* has been retarded to 12° of crossed dispersion and the intermediate portion *B* to 7½°. There is no doubt, therefore, that pressure has a definite influence on the rate of settling down of these crystals and that this is a retardation, as opposed to the accelerating influence of an increase in temperature. Neither pressure nor temperature has any effect on the final state when this is arrived at, for then all crystals of the same composition, no matter in what way the final state has been reached, possess identical optical properties.

Homogeneity of crystals exhibiting anomalous optical properties.

In order to ascertain whether the crystals used in these experiments suffered any change in composition while growing in solution or whether they remained homogeneous throughout, a special experiment was made, using the mixed crystals of the same composition as in the pressure experiment, viz. $\{80(\text{NH}_4)\text{Na}, 20(\text{NH}_4)\text{K}\}\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$. All results previously recorded were obtained from sections which actually included the basal planes (001) of the crystals. No observations have been so far recorded of sections drawn from the central portions of the crystals. The author, however, has made many observations on sections taken from the middle of crystals and has invariably found that the crossed dispersion, when this occurred, and also the optic axial angles in freshly prepared crystals differed appreciably from those in a terminal (001) section (Table VIII *a*). From this it might at first be supposed that the composition of the mixture was varying with the crystal-growth. When, however, the sections from the middle portion of a crystal were heated until the final state was reached, it was found that the optical properties were then absolutely identical with those of the terminal sections. This makes it reasonable to suppose that there is homogeneity of composition throughout the growth of these crystals. The interior portion was in

contact with the warm solution in the earlier stages of growth and then probably exhibited the same crossed dispersion as is found in the terminal sections of the same crystal when growth has finished. In the meantime, while further growth is taking place, the earlier terminal section is now inside the crystal and has suffered a partial change towards the final state through being heated for some hours longer than that which is the terminal section of the crystal when growth has finished. Further heating brings interior and exterior portions of the crystal to the same final state.

Location of the seat of change in the molecule.

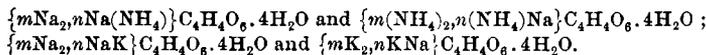
The above results simply indicate that somewhere in the packing together of the crystal-units there is an initial disturbance or strain, possibly due to some spatial difficulty of fitting in, in so short a time, the complex molecules of two or more different shapes and sizes. Since no observable variation in crystal-angles has been observed in any of these cases, the seat of the strain is most probably in some region of minor importance. To obtain the complete set of anomalous phenomena, viz. crossed dispersion and change in optic axial angle on standing, it appears necessary that all three bases, NH_4 , Na, and K, must be present, though the data do not rule out the possibility of the complete set of phenomena taking place in the ultra-violet region in those crystals that contain NH_4 and Na only. The alteration of optic axial angle on standing is a phenomenon which is characteristic of the whole series. To penetrate further into the structure X-ray examination of the crystals will be necessary, both before and after the changes have taken place.

The directions in which the strains may be set up are, from the changes studied in these papers, limited to those which are proper to the monoclinic system; and more probably to those space-groups which can be arrived at by taking the orthorhombic holoaxial space-groups, on which the structure of the crystals in the final state must depend, and eliminating two of the axes of symmetry but leaving the third. Three possible space-groups are then involved, viz. C_2^1 , C_2^2 , and C_2^3 . Further than this it is not at present possible to speculate.

Summary.

I. In addition to the isomorphous series of mixed crystals studied in the first paper, and having the general composition $\{m \text{NaK}, n \text{Na}(\text{NH}_4)\}$ $\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$, the same three bases can unite to form the series

$\{m \text{KNa}, n\text{K}(\text{NH}_4)\} \text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ and $\{m(\text{NH}_4)\text{Na}, n(\text{NH}_4)\text{K}\} \text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$. Further, there are four other series found to be possible, in which only *two* of the bases NH_4 , Na , and K are united with the acid. These are of the general type



All these series are isomorphous with each other, and are similar in habit and cleavage.

II. In the series which contain all three substituents NH_4 , Na , and K the following effects are to be observed :

(a) Initial crossed dispersion of the optic axial planes, with subsequent changes to a normal orthorhombic dispersion or to a crossed axial-plane dispersion of the brookite type.

(b) A change in optic axial angles for different colours of the spectrum as the crystals settle down to the final state. In crystals which contain only two of the substituent bases NH_4 , Na , and K only the second (b) of these effects is invariably present.

III. In basal sections of the freshly prepared crystals, the greatest optical anomalies are exhibited by the terminal sections, and as the distance from the surface increases the anomalous effects fall off in magnitude. All sections, whether terminal or otherwise, ultimately possess the same optical properties when the crystals have reached the final state. This may be considered as evidence in favour of the homogeneity of these crystals.

IV. A rise in temperature hastens considerably in these crystals the process of settling down to the final state. Application of pressure, normal to the section, has a contrary effect. In neither case is there any effect on the final state when this is ultimately reached.

V. The strains involved degrade the symmetry of the freshly prepared crystals to that of a monoclinic class. Externally, however, judging from a large number of angular measurements, the crystals appear to be still orthorhombic holoaxial, and there is no corresponding readjustment of angular values as the settling down process in the interior takes place.

The author desires to take this opportunity of thanking Sir Henry Miers for his kind interest throughout this work and for helpful advice on many occasions.

TABLE I a. $\{50\text{NaK}, 50\text{Na}(\text{NH}_4)\}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$.

Colour	Red (6,500 Å.U. ca.).	Hg-yellow.	Hg-green.	Hg-violet. ¹
2E of freshly prepared crystals ...	69° 10'	56° 2'	45° 4'	54° 40'
Angle of crossed dispersion ...	4°		8°	61°
	Total = 73°			

TABLE I b. $\{50\text{NaK}, 50\text{Na}(\text{NH}_4)\}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$.

Colour	Red (6,500 Å.U. ca.).	Hg-yellow.	Hg-green.	Hg-violet.
2E in final state ...	73° 29'	62° 49'	55° 35'	40° 32'
Optic axial plane ...	(100)			(010)

TABLE II a. $\{80\text{K}(\text{NH}_4), 20\text{KNa}\}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$. (See fig. 3.)

	Crossed dispersion of freshly prepared crystals.	2E of freshly prepared crystals.
Deep-red to red ² ...	25½°	Deep-red ... 43°
Red to orange ...	16½	Red ... 30½
Orange to Hg-yellow ...	10	Orange ... 32
Hg-yellow to Hg-green	5	Hg-yellow ... 38
Hg-green to deep-green	5½	Hg-green ... 46
Deep-green to Hg-violet	3½	Deep-green ... 56
	} Total, 66°	Hg-violet ... 84

Equilibrium was reached after heating the sections for 4 days to 37° C., and the following readings were then obtained :

	2E in final state.	Optic axial plane.
Deep-red ...	{ good reading } { not obtained }	
Red	42½° (100)
Orange	33	
Hg-yellow	23	
Hg-green	14	
Deep-green	38 (010)
Hg-violet	64	

¹ The mercury-arc spectrum consists of lines of the following wave-lengths :

Red	6,152 and 6,232 Å.U. (weak).
Yellow	5,770 and 5,791 ,, (intense).
Green	5,461 ,, (intense).
Blue	4,916 ,, (weak).
Violet	4,358 ,, (intense).
Deep-violet	4,047 and 4,078 ,, (weak).

The three lines of sufficient intensity to be of use in this work and which can be isolated by means of suitable filters are the yellow, green, and violet (indicated above as intense).

² In addition to the colours obtained from the mercury-arc shown in Table I, the following approximate colour-filters were used: deep-red ($\lambda = 7,000$ Å.U. ca.),

TABLE II b. $\{66\frac{2}{3}\text{K}(\text{NH}_4), 33\frac{1}{3}\text{KNa}\}\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$.

Crossed dispersion of freshly prepared crystals.			2E of freshly prepared crystals.		
Deep-red to red	25°	Deep-red	...	32°
Red to orange	10	Red	...	35
Orange to Hg-yellow	3	Orange	...	41
Hg-yellow to Hg-green	...	5	Hg-yellow	...	45
Hg-green to deep-green	...	5	Hg-green	...	54
Deep-green to Hg-violet	...	2	Deep-green	...	57
		} Total, 50°	Hg-violet	...	74

After heating the sections for 4 days at 37° C., equilibrium was obtained, with the following results:

2E in final state.			Optic axial plane.		
Deep-red	...	} good reading not obtained	(100)
Red	
Orange	
Hg-yellow	
Hg-green	...	} 25	(010)
Deep-green	
Hg-violet	

TABLE II c. $\{50\text{K}(\text{NH}_4), 50\text{KNa}\}\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$.

Crossed dispersion of freshly prepared crystals.			2E of freshly prepared crystals.		
Deep-red to red	...	11°	Deep-red	...	43°
Red to orange	...	1½	Red	...	52
Orange to Hg-yellow	...	1	Orange	...	59
Hg-yellow to Hg-green	...	1	Hg-yellow	...	62
Hg-green to deep-green	...	1½	Hg-green	...	66
Deep-green to Hg-violet	...	1	Deep-green	...	74
		} Total, 17°	Hg-violet	...	104

After heating the sections for 4 days at 35°C., the following equilibrium readings were obtained:

2E in final state.			Optic axial plane.		
Deep-red	...	10°	(100)
Red	...	34	} ...	} ...	(010)
Orange	...	44			
Hg-yellow	...	50			
Hg green	...	58			
Deep-green	...	66			
Hg-violet	...	82			

red ($\lambda = 6,500 \text{ \AA.U. ca.}$), orange ($\lambda = 6,000 \text{ \AA.U. ca.}$), deep-green ($\lambda = 5,000 \text{ \AA.U. ca.}$).

TABLE II *d.* $\{33\frac{1}{3}\text{K}(\text{NH}_4), 66\frac{2}{3}\text{KNa}\}\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$.

Crossed dispersion of freshly prepared crystals: Deep-red to Hg-violet (total) = 5° . This was found to disappear in about a week even at ordinary temperatures. The optic axial angles were then found to have the following values:

	2E in final state.			Optic axial plane.
Deep-red	} ... (101)
Red	
Orange	
Hg-yellow	
Hg-green	
Deep-green	
Hg-violet	

TABLE III *a.* $\{80(\text{NH}_4)\text{Na}, 20(\text{NH}_4)\text{K}\}\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$.

Crossed dispersion of freshly prepared crystals.			2E of freshly prepared crystals.
Deep-red to red	Deep-red ... 94°
Red to orange	Red 87
Orange to Hg-yellow	Orange 80
Hg-yellow to Hg-green	Hg-yellow 68
Hg-green to deep-green	Hg-green 57
Deep-green to Hg-violet	Deep-green 34
			Hg-violet $18\frac{1}{2}$

The sections attained equilibrium after heating for 4 days at 37°C ., when the following results were obtained:

	2E in final state.			Optic axial plane.
Deep-red	} (100)
Red	
Orange	
Hg-yellow	
Hg-green	
Deep-green	
Hg-violet	

TABLE III *b.* $\{50(\text{NH}_4)\text{Na}, 50(\text{NH}_4)\text{K}\}\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$. (See fig. 2.)

Crossed dispersion of freshly prepared crystals.			2E of freshly prepared crystals.
Deep-red to red	Deep-red 78°
Red to orange	Red 69
Orange to Hg-yellow	Orange 62
Hg-yellow to Hg-green	Hg-yellow 56
Hg-green to deep-green	Hg-green 49
Deep-green to Hg-violet	Deep-green 34
			Hg-violet 46

After heating to 32° C. for 3 days the crystals were in an intermediate stage of the settling-down process and gave the following results :

Crossed dispersion of crystals
in intermediate stage.

Deep-red to red	0°	} Total, 77° (as at first).
Red to orange	0	
Orange to Hg-yellow	0	
Hg-yellow to Hg-green... ..	0	
Hg-green to deep-green	2	
Deep-green to Hg-violet	75	

After a total heating of 6 days at 32° C., the final state of the crystals was reached and is shown by the following figures :

2E in final state.				Optic axial plane.			
Deep-red	89°	} (100)	} (010)				
Red	79						
Orange	73						
Hg-yellow	69						
Hg-green... ..	62						
Deep-green	52						
Hg-violet... ..	13						

TABLE III c. $\{20(\text{NH}_4)\text{Na}, 80(\text{NH}_4)\text{K}\}\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$.

Crossed dispersion of freshly prepared crystals.		2E of freshly prepared crystals.	
Deep-red to Hg-yellow	9°	Deep-red ...	67°
Hg-yellow to Hg-green	3½	Hg-yellow ...	61
Hg-green to Hg-violet	38½	Hg-green ...	56
} Total, 51°		Hg-violet ...	51½

The following figures from the interference-figures in the final state of the crystals were obtained after heating for 4 days to 37° C. :

2E in final state.				Optic axial plane.			
Deep-red	62°	} (100)	} (010)				
Hg-yellow	53						
Hg-green	45						
Hg-violet	44						

TABLE IV a. $\{83\frac{1}{3}(\text{NH}_4)_2, 66\frac{2}{3}(\text{NH}_4)\text{Na}\}\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$.

2E of freshly prepared crystals.				2E after heating to 37° C. for 4 days.			
Deep-red	98°	...	95°				
Hg-yellow	90	...	88				
Hg-green	84	...	82				
Hg-violet	50	...	48½				

Optic axial plane throughout is (100).

TABLE IV b. $\{50(\text{NH}_4)_2, 50(\text{NH}_4)\text{Na}\}\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$.

	2E of freshly prepared crystals.				2E after heating to 35° C. for 4 days.			
Deep-red	90°	94°
Hg-yellow	87½	91
Hg-green	83	85
Hg-violet	48	51½

Optic axial plane throughout is (100).

TABLE IV c. $\{66\frac{2}{3}(\text{NH}_4)_2, 33\frac{1}{3}(\text{NH}_4)\text{Na}\}\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$.

	2E of freshly prepared crystals.				
Deep-red	} beyond field of view
Hg-yellow	
Hg-green	
Hg-violet	116° (edge of field)	

Accurate measurements of changes in crystals of this composition could not be obtained on account of the wideness of the optic axial angles. The optic axial plane, as before, is (100).

TABLE V a. $\{33\frac{1}{3}\text{Na}_2, 66\frac{2}{3}(\text{NH}_4)\text{Na}\}\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$.

	2E of freshly prepared crystals.				2E after heating to 37° C. for 4 days.			
Deep-red	100°	101°
Hg-yellow	92	90
Hg-green	85	83½
Hg-violet	50	51

Optic axial plane throughout is (100).

TABLE V b. $\{50\text{Na}_2, 50\text{Na}(\text{NH}_4)\}\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$.

	2E of freshly prepared crystals.				2E after heating to 35° C. for 4 days.			
Deep-red	105°	105°
Hg-yellow	92	91
Hg-green	84	85
Hg-violet	50	51

Optic axial plane throughout is (100).

TABLE V c. $\{66\frac{2}{3}\text{Na}_2, 33\frac{1}{3}\text{Na}(\text{NH}_4)\}\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$.

	2E of freshly prepared crystals.				2E after heating to 37° C. for 4 days.			
Deep-red	91°	95°
Hg-yellow	89	92
Hg-green	82½	85
Hg-violet	49½	52

Optic axial plane throughout is (100).

TABLE VI a. $\{33\frac{1}{2}\text{K}_2.66\frac{2}{3}\text{KNa}\}\text{C}_4\text{H}_4\text{O}_6.4\text{H}_2\text{O}$.

2E of freshly prepared
crystals.

Deep-red	out of field	} Optic axial plane (010); acute bisectrix \perp (100); optical sign positive.
Hg-yellow	115° ±	
Hg-green	108	
Hg-violet	86½	

TABLE VI b. $\{50\text{K}_2,50\text{KNa}\}\text{C}_4\text{H}_4\text{O}_6.4\text{H}_2\text{O}$.

2E of freshly prepared
crystals.

Deep-red	...	} out of field	} Optic axial plane (010); acute bisectrix \perp (100); optical sign positive.
Hg-yellow	...		
Hg-green	...		
Hg-violet	...		

TABLE VI c. $\{50\text{Na}_2,50\text{NaK}\}\text{C}_4\text{H}_4\text{O}_6.4\text{H}_2\text{O}$.

2E of freshly prepared
crystals.

Deep-red	...	} out of field	} optic axial plane (010); acute bisectrix \perp (100); optical sign positive.
Hg-yellow	...		
Hg-green	...		
Hg-violet	...		

TABLE VII a. Pressure experiment.

Crossed disper- sion in freshly prepared crystals.	Temperature, and duration of pressure.	Pressure on section.	Crossed disper- sion in section heated but not compressed.	Crossed disper- sion in section both heated and compressed.
35½°	20°C. for 24 hours	10 lb.	25°	29°
35½°	37°C. for 48 hours	15 lb.	11°	17°

TABLE VII b. Pressure experiment.

In this experiment the temperature was 42° C. and the pressure of 15 lb. was applied for 24 hours. The following figures show the effect obtained :

Crossed disper- sion in freshly prepared crystals.	Crossed disper- sion in section heated but not compressed.	Crossed disper- sion in portion of section shielded from pressure (A, fig. 5).	Crossed disper- sion in portion of section partly shielded from pressure (B, fig. 5).	Crossed disper- sion in section heated and compressed.
35½°	5°	5°	7½°	12°

TABLE VIII a. Homogeneity experiment.

a. In terminal sections :

	Crossed dispersion of freshly prepared crystals.		2E of freshly prepared crystals.
Deep-red to red ...	$\frac{1}{2}^\circ$	} Total, $32\frac{1}{2}^\circ$	Deep-red ... 94°
Red to orange ...	$\frac{1}{2}$		Red ... 87
Orange to Hg-yellow ...	0		Orange... ... 80
Hg-yellow to Hg-green	$\frac{1}{2}$		Hg-yellow ... 68
Hg-green to deep-green	$1\frac{1}{2}$		Hg-green ... 57
Deep-green to Hg-violet	$32\frac{1}{2}$		Deep-green ... 34
			Hg-violet ... $18\frac{1}{2}$

β. In sections cut at a distance from terminal (001) faces of 1 cm. :

	Crossed dispersion in freshly prepared crystals.		2E of freshly prepared crystals.
Deep-red to red ...	0°	} Total, 10°	Deep-red ... 96°
Red to orange ...	0		Red ... 89
Orange to Hg-yellow ...	1		Orange ... 81
Hg-yellow to Hg-green...	0		Hg-yellow ... 79
Hg-green to deep-green	1		Hg-green ... 71
Deep-green to Hg-violet	8		Deep-green ... 62
			Hg-violet ... 32

TABLE VIII b. Homogeneity experiment.

2E in final state of both sets of sections α and β.

Deep-red ...	104 $\frac{1}{2}$	} Optic axial plane (100)
Red ...	91	
Orange ...	84	
Hg-yellow ...	80	
Hg-green ...	74	
Deep-green ...	64 $\frac{1}{2}$	
Hg-violet ...	35	