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Some anomalous optical properties of freshly-prepared mixed crystals of the Seignette salts.

By HAROLD E. BUCKLEY, M.Sc. (Vict.), F.C.S.

Assistant Lecturer in Crystallography.

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THE new crystalline compound triphenyl-bismuthine dichloride, described crystallographically by Mr. G. Greenwood (Min. Mag., 1923, vol. 20, p. 123), possesses the remarkable property of exhibiting crossed axial-plane dispersion of the rhombic 'brookite' type[1] and circular polarization. For purposes of comparison, the author prepared specimens of the mixed Seignette salts, which also exhibit crossed axial-plane dispersion together with circular polarization. The Seignette salts, sodium-potassium tartrate and sodium-ammonium tartrate, crystallize each with four molecules of water in the bisphenoidal class of the rhombic system. They are truly isomorphous and form a continuous

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[1] The term 'crossed axial-plane dispersion' is used in this paper to indicate that the dispersion is of the rhombic 'brookite' type. Where oblique or monoclinic crossed dispersion is implied, the expression 'crossed dispersion' is used.

series of mixtures. The acute bisectrix for sodium-ammonium tartrate is normal to (001) and for sodium-potassium tartrate normal to (100). For all proportions of mixture containing 5% and over of sodium-ammonium tartrate, the acute bisectrix is normal to (001). In a section parallel to (001), prepared from a crystal containing 50% each of sodium-potassium and sodium-ammonium tartrates, it was observed that when the plane of the optic axes for red is parallel to one of the principal planes of the polarizing and analysing nicols, the optic axial plane for light of, say, extreme violet, is not parallel to the other principal plane at right angles to the first, but is inclined to it. The section requires to be rotated through several degrees before the interference-figure in violet light presents a symmetrical form. For light of intermediate colours, the planes of the optic axes do not coincide with those of either red or violet, but are disposed in various positions between the two. In no case is the axial plane for violet at right angles to the axial plane for red when the section is viewed immediately on preparation from freshly-crystallized material. All the crystals clearly exhibited a very marked 'crossed dispersion' of the monoclinic 'borax' type.

Previous workers in this field have made little or no reference to this particular phenomenon. H. Dufet (Bull. Soc. Min. de France, 1878, vol. 1, p. 58), A. Lavenir (ibid., 1894, vol. 17, p. 153), and G. Wyrouboff (ibid., 1879, vol. 2, pp. 91 and 170) throw no light upon it. Wyrouboff (ibid., 1882, vol. 5, p. 272) noticed the optically anomalous behaviour of these mixed tartrates and of an isomorphous mixture of double sulphates and double chromates of sodium and ammonium. He dismissed the mixed tartrates as being too complex for drawing any useful conclusions and studied in detail the latter (double sulphates and double chromates). He thought, however, that the effects in each case were the same. A section (parallel to 010) of his mixed sulphates and chromates viewed between crossed nicols is described by him as follows:—The section was bounded by the forms (100), (001), and (101), and was octagonal in outline. Portions of the crystal-section contiguous to each of these faces, i.e. parallel to (100), (001), or (101), transmitted parallel polarized light of different colours, while, with convergent light, they showed normal interference-figures, which were, however, inclined to each other. The central portion exhibited strong crossed dispersion. Wyrouboff considered these effects to be due to lamellar twinning, but denied that Mallard's condition for such twinning, viz. pseudo-hexagonal symmetry, holds generally, and he showed that the double sulphates and chromates are not pseudo-hexagonal. Wyrouboff may have obtained crystals of mixed tartrates yielding sections precisely similar to those described in this paper, but if so, he seems to have considered them to be like his double sulphates and chromates, and to have confined his further study to the latter compounds.

The crystals of sodium-ammonium tartrate and sodium-potassium tartrate and the mixtures of the two in various proportions prepared by the author differed from the salts studied by Wyrouboff in that they were homogeneous throughout. Sections used for the study of their optical properties were always prepared from large clear specimens and gave well-defined and uniform interference-figures right up to the edge. The original object of the investigation of the Seignette salt mixtures was to ascertain whether the circular polarization known to exist in sections of these salts could be detected when the additional feature of crossed axial-plane dispersion was also present. This question has been dealt with in G. Greenwood's paper cited above. It was also intended to measure the change in the optic axial angle for different colours in this typical series of isomorphous mixtures, but this was rendered unnecessary owing to a paper recently published by L. Bacuvier (Bull. Soc. Franç. Min., 1922, vol. 45, p. 73) in which were given the optic axial angles of a series of mixed Seignette salts of different composition. Bacuvier's paper, however, makes no mention of the peculiar effect, viz. crossed dispersion, observed by the author in his own freshly-prepared crystal-sections; it therefore seemed desirable to study the latter phenomenon in detail. The first sections in which crossed dispersion was observed contained 50 % each of the two pure Seignette salts, and to ascertain whether other proportions of mixture showed the same effect, a large number of mixtures were prepared and examined. In every case, in these apparently rhombic crystals, a section cut parallel to (001) displays in convergent polarized light an interference-figure which has only one axis of symmetry, parallel to the acute bisectrix, and is precisely similar to the interference-figure exhibited by a section of borax cut parallel to (010).

Preparation of the mixed Seignette salts.

The two pure salts, sodium-ammonium tartrate and sodium-potassium tartrate, were prepared by dissolving pure dextro-tartaric acid in hot water, dividing the solution into two parts and neutralizing these with the requisite base. The two portions were then combined, filtered, and allowed to crystallize. This usually took place overnight. A box lined with non-conducting material was used for this purpose and was kept, as far as possible, from rapid heat changes and from disturbance. The other salts used, which were mixtures of the above, were prepared in two different ways: (1) the method described above, modified to suit the particular mixture, and (2) the required proportions of the pure salts were carefully weighed out and dissolved together. In all cases, the best crystals, most suitable for both the study of optical properties and for goniometry, were obtained when the crystals were formed from a warm saturated solution, which took about a day to crystallize.

The cleavage, parallel to (001), and varying from moderately good to highly perfect, enabled sections parallel to this face to be made with comparative ease. Fig. 1 shows typical crystals of sodium-ammonium and sodium-potassium Seignette salts. They are practically identical in appearance and both are very rich in forms, those actually observed by me being *a* (100), *b*(010), *c*(001), *l*(210), *m*(110), *n*(120), *o*(111), *r*(101), *s*(211), *q*(011), and *t*(021), where (111) is the bisphenoid. The more important optical properties are summarized below.

		Sodium-potassium tartrate, $NaKC_4H_4O_6 . 4H_2O$.	Sodium-ammonium tartrate, $Na(NH_4)C_4H_4O_6 . 4H_2O$.
Optic axial plane ...	...	(010) ...	(100)
Acute bisectrix	...	$\perp$ (100) ...	$\perp$ (001)
Optical sign	...	positive ...	negative
Dispersion of optic axes	...	slight, $\rho > v$ ...	very marked, $\rho > v$
Refractive indices for sodium-light	α ...	1·4900 ...	1·4953
	β ...	1·4920 ...	1·4985
	γ ...	1·4951 ...	1·4996
Birefringence, $\gamma - \alpha$	...	0·0054 ...	0·0043

The observations may be divided into the following sections:

(1) Effect of composition of mixture on the total angle of crossed dispersion in freshly-prepared crystal-sections.
(2) Effect of time on the crossed dispersion.
(3) Influence of temperature in hastening the final state.
(4) The action of water-vapour and ammonia.
(5) The conditions for uniaxiality.

(1) *The effect of composition of mixture on the total angle of crossed dispersion in freshly-prepared crystal-sections.*

The following observations made upon a comprehensive series of freshly-prepared mixtures of the Seignette salts show that, for mixtures falling between the limits of 0 to 80 % sodium-potassium tartrate, there is a regular change in the dispersion of the axial planes for different colours. This reaches a maximum value in the region of the 45 % mixture (fig. 2). The angles given in Table I are those between the optic axial

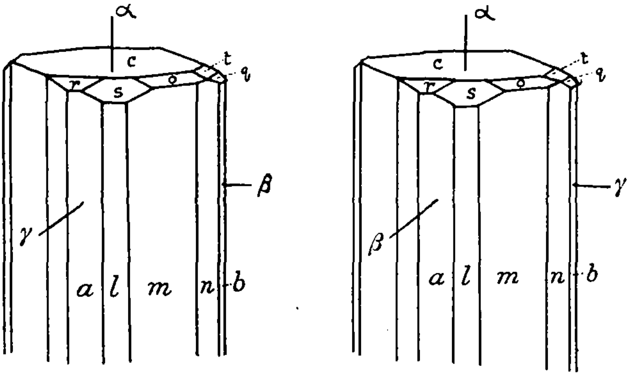

Fig. 1 a. Fig. 1 b.

Crystals of the Seignette salts showing the optical orientation. a, Sodium-potassium tartrate ; b, Sodium-ammonium tartrate.

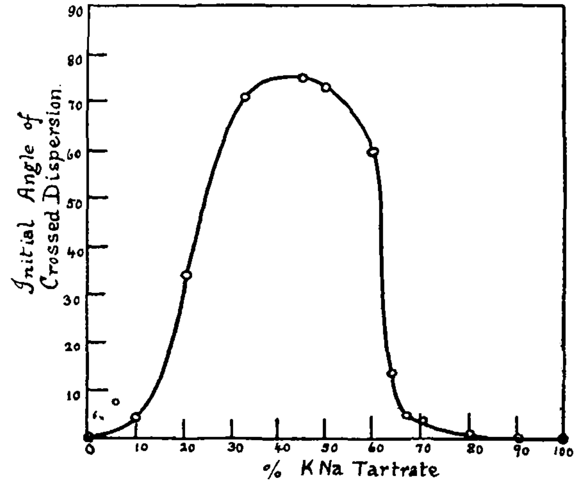

Fig. 2. Variation of initial angle of crossed dispersion with change in composition.

planes for extreme red and extreme violet. In freshly-prepared crystals the optic axial planes for different colours do not coincide with either (100) or (010).

TABLE I.

Percentage of sodium-potassium tartrate.	Angle of crossed dispersion.	Percentage of sodium-potassium tartrate.	Angle of crossed dispersion.
100	0°	60	60°
95	0	50	73
90	0	45	75
80	0	33	70½
70	5	20	34
67	5	10	4
64	14	0	0

(2) *The effect of time on the crossed dispersion.*

It was noticed that the angles between the optic axial planes for different colours were not permanent, but changed with lapse of time. This unexpected result was more closely investigated in the following experiments: Sections of various mixtures were cemented and preserved in Canada balsam. This is necessary because the mixtures, as well as the pure constituent Seignette salts, are efflorescent, and change on the surface to a hard white crust (further change being then inhibited). A section of the 45% sodium-potassium tartrate thus preserved was observed at intervals for a period extending over several months. Table II gives the changes, which occurred at successive intervals of time, in the angles between the optic axial planes for red to yellow, yellow to green, and green to violet light, respectively.

TABLE II.

	Angle of crossed dispersion.			
Time (days).	Red to yellow.	Yellow to green.	Green to violet.	Total.
0	3°	6°	66°	75°
14	1	3	72	75
37	½	1	74	75½
49	½	1	79	80½
70	0	1	82½	83½
88	0	½	85	85½
127	0	½	85½	86

A section cut from a freshly-prepared crystal containing 20% of the sodium-potassium tartrate was observed in the same manner. The results are shown in Table III A. The 'total angle' column gives the angle between the optic axial planes for extreme red and extreme violet light. Table III B summarizes the observations on a 10% sodium-potassium tartrate mixture under similar conditions.

TABLE III A.

Time (days).	Total angle of crossed dispersion.
0	34°
6	28½
10	24
14	12½
22	10
43	5
50	3½
60	0

TABLE III B.

Time (days).	Total angle of crossed dispersion.
0	4°
6	1½
21	0

In addition to the 45, 20, and 10 % sodium-potassium tartrate mixtures, given in some detail above, sections of the 70 and 67 % sodium-potassium tartrate mixtures were also examined. Both these mixtures gave interference-figures with an initial angle of crossed dispersion of about 5° (fig. 2). The optic axial planes for extreme red and extreme violet light, however, closed up and coincided with each other in about a week.

From the data given above, it is apparent that this anomalous crossed dispersion, which exists in most freshly-prepared crystals, gradually disappears. The optic axes for different colours tend to close on one another and settle down in one of the two planes (100) and (010), or for some mixtures in both (crossed axial-plane dispersion). In the case of the 45 % sodium-potassium tartrate mixture the effect has not quite disappeared after four months, but there is no doubt as to its tendency to do so. In all other cases a much shorter period of time is sufficient. It is possible that there is some connexion between the extra length of time needed for the 45 % sodium-potassium tartrate mixture to settle down as compared with sections of other composition, and the more complicated nature of the mixture itself, viz. 11 parts of sodium-ammonium tartrate to 9 parts of sodium-potassium tartrate. The curves shown in fig. 3 illustrate the way in which the angle of crossed dispersion decreases with time, and roughly in logarithmic fashion.

(3) *Influence of temperature in hastening the final state.*

Sections embedded in Canada balsam were heated in a hot-air bath at temperatures of 32° C. and 40° C. for several days. The variation in temperature was not more than ± 1° throughout the whole time of heating. The effect of heat was to hasten considerably the settling down of the optic axial planes to the final state, in which the dispersion of the optic axes has rhombic symmetry. This is shown in Tables IV A and IV B, V A and V B, and VI. Curves constructed from these data are given in fig. 4. It will also be seen that a uniform movement of all the optic axes into one orientation or another at right angles to it does not take place, but that it is possible for two axial planes, inclined at some angle to each other, to recede a little before finally closing up. The total angle of crossed dispersion, however, always shows a uniform increase or decrease to 90° or 0°. In such sections as show uniaxiality for some colour in the visible spectrum, the invariable rule is that the optic axes, in the final state, for colours towards the red end of the spectrum align themselves parallel to (100), and for colours towards the violet end of the spectrum parallel to (010).

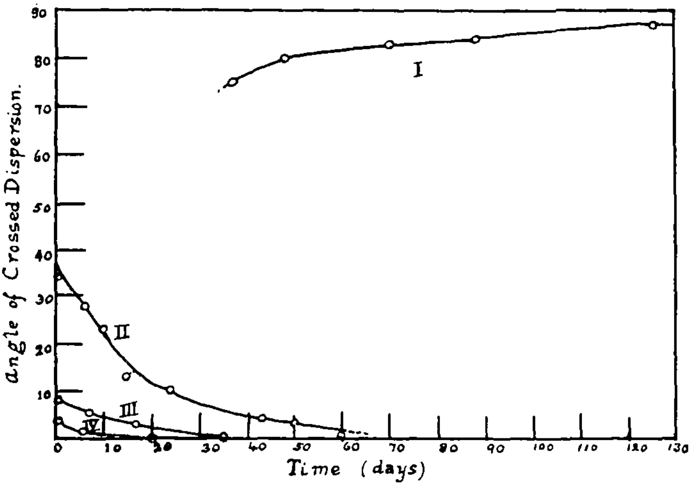

FIG. 3. Effect of time on crossed dispersion, temperature remaining constant. Curve I for 45 % sodium-potassium tartate mixture; II for 20 %; III for 20 % (in contact with water-vapour and ammonia); IV for 10 % mixture.

TABLE IV A. 60 % *sodium-potassium tartrate heated to* 40° C.

	Angle of crossed dispersion.				
Time.	Red_3 to red_2.	Red_2 to red_1.	Red_1 to green.	Green to violet.	Total.
0	8°	16°	$26\frac{1}{2}$°	$9\frac{1}{2}$°	60°
$1\frac{1}{2}$ hours	$6\frac{1}{2}$	13	30	10	60
5 ,,	?	5	47	17	?
24 ,,	0	2	78	8	88
30 ,,	0	1	$79\frac{1}{2}$	8	$88\frac{1}{2}$
48 ,,	0	0	90	0	90

Table IV b. 60 % *sodium-potassium tartrate at* 40° C.

(This section was cut one day after the crystals had been prepared.)

Time.	Angle of crossed dispersion.					
	Red$_3$ to red$_2$.	Red$_2$ to red$_1$.	Red$_1$ to yellow.	Yellow to green.	Green to violet.	Total.
0	—	24°	25°	11°	8½°	69°
5 hours	2°	8	31½	25	11½	80
24 ,,	1	1	6½	62½	14	85
30 ,,	1	1	5½	64½	15½	87½
48 ,,	0	0	0	80	8½	88½
56 ,,	0	0	0	83½	5	88½
72 ,,	0	0	0	90	0	90

Table V a. 33⅓ % *sodium-potassium tartrate at* 40° C.

Time.	Angle of crossed dispersion.		
	Red$_3$ to green.	Green to violet.	Total.
0	16°	53½°	69½°
6 hours	7½	63½	71
24 ,,	3	81	84
48 ,,	0	90	90

Table V b. 33⅓ % *sodium-potassium tartrate at* 32° C.

Time.	Angle of crossed dispersion.		
	Red$_3$ to green.	Green to violet.	Total.
0	18°	54°	72°
48 hours	4	76	80
72 ,,	2	82½	84½
96 ,,	1	84	85
120 ,,	1	86½	87½
144 ,,	0	90	90

Table VI. 20 % *sodium-potassium tartrate at* 32° C.

(Measurements begun after the total angle of crossed dispersion had sunk from 34° to 10½°.)

Time.	Total angle of crossed dispersion.
0	10½°
1 hour	5½
2½ ,,	5
24 ,,	4
48 ,,	3
72 ,,	1½
96 ,,	0

Note.—In the above tables, green and violet are mercury green and mercury violet; yellow is sodium yellow; and red$_1$, red$_2$, and red$_3$, are three red screens of increasing wave-length, red$_1$ about 6200 Å. and red$_3$ from 7000 to 7500 Å.

(4) *The action of water-vapour and ammonia on the observed crossed dispersion.*

All the crystals from which sections were to be cut for the foregoing research were carefully stocked in air-tight glass specimen tubes. After a section of the 20 % sodium-potassium tartrate mixture had been left cemented in Canada balsam for experiments described in section (2) until its angle of crossed dispersion had fallen in value to 11°, a new section was prepared from the same set of crystals and its angle of crossed dispersion was found to be 10½°. This is sufficiently near to the value obtained from the cemented section to indicate that the alteration in the interference-figures in these crystal mixtures was not due to the escape of dissolved ammonia or water-vapour, but was probably occasioned by some 'straightening-out' process inside the crystal. To test this latter point further, another section of the same composition (20 %) was prepared. By this time, its total angle of crossed dispersion had diminished to 7½°. The section was kept in a tube over some of the mother-liquor from which it had been originally drawn, together with a little free ammonia. The conditions were such as to inhibit any tendency to escape on the part of ammonia or water-vapour, if any,

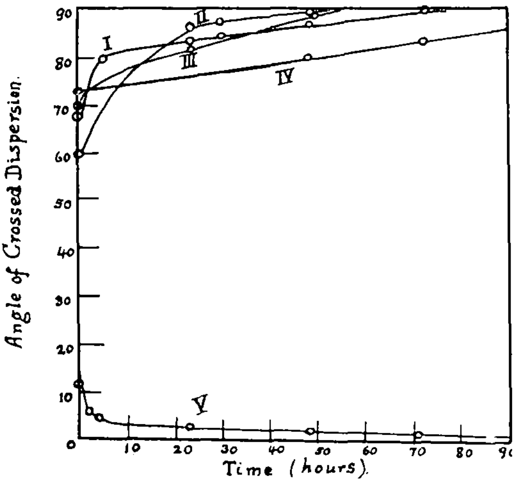

FIG. 4. Effect of temperature on crossed dispersion. Curves I and II for 60 % sodium-potassium tartrate mixture at 40° C.; III for 33⅓ % at 40° C.; IV for 33⅓ % at 32° C.; V for the 20 % mixture at 32° C.

dissolved in the crystal; and had either or both of these substances been responsible for the crossed dispersion, the decrease in value of the latter with time would have been suspended. Table VII indicates that the crystal-section behaved just as though neither water-vapour nor free ammonia had been present (fig. 3, curve III). Another section of the same composition was kept until its crossed dispersion had completely disappeared. It was then placed, like the last-mentioned, in contact with water-vapour and ammonia. Observations made upon it at intervals extending to 21 days showed that there was no alteration whatever in the final state of the interference-figure.

It would appear, therefore, that escape of dissolved ammonia and water-vapour is not responsible for the 'straightening-out' process which takes place inside these mixed crystals on standing or on heating.

TABLE VII.

Time.	Total angle of crossed dispersion.
0	7½°
7 days	5½
17 ,,	4
35 ,,	0

(5) *The conditions for uniaxiality.*

The colour for which any particular section is finally uniaxial depends upon the composition of the mixture. Table VIII shows approximately the way in which the uniaxiality colour travels across the spectrum from the red to the violet end as the percentage of sodium-potassium tartrate in the mixture decreases. It is probable that in the case of the mixtures containing from 95 to 67 % of sodium-potassium tartrate on the one hand, and 10 % and less on the other hand, there will be no real uniaxial point, as the values of the optic axial angles with change in wave-length converge to a limit which is greater than zero.

TABLE VIII.

Percentage of sodium-potassium tartrate.	Approximate uniaxial point.
95, 90, 80	infra-red (if any)
70, 67	,, ,,
64	very deep red.
60	5461 Å. to 5893 Å. (closer to former).
50	a wave-length rather less than 5461 Å.
45	blue-green region.
33	blue-violet region.
20	ultra-violet.
10	ultra-violet (if any).

From data included below, moreover, it would appear that a section cannot be uniaxial so long as there is *any* crossed dispersion. The values of the optic axial angles are, except in the case of the 50 % mixture, only approximate to about 1°, but are sufficiently close to verify the statement emphasized above. Figs. 5 and 6 are stereographic projections of the optic axes in air for light of different colours and show the crossed dispersion, the optic axial plane for extreme red being the base line. The optic axes lie on curves which do not at any point touch the centre of the projection (corresponding to the acute bisectrix of the interference-figure). In fig. 6 are given curves for the 60 % sodium-potassium tartrate mixture. Projections of the optic axes for different colours at two different times have been superimposed and indicate that

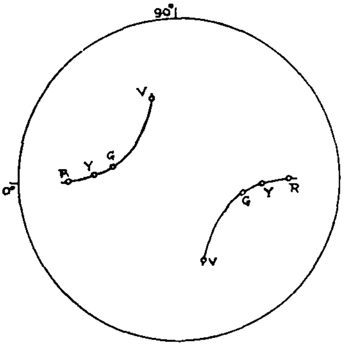

FIG. 5.

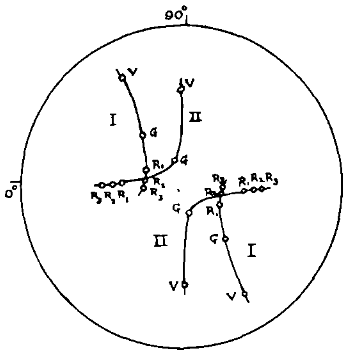

FIG. 6.

FIG. 5. 50 % sodium-potassium tartrate mixture (see Table IX). Stereographic projection parallel to (001) of the optic axes for four different colours, of a freshly-prepared crystal, showing absence of uniaxiality.

FIG. 6. 60 % sodium-potassium tartrate mixture (see Tables X A and X B). Stereographic projection parallel to (001) of the optic axes for red of three kinds, green, and violet; I, when freshly prepared; II, after 30 hours heating at 40° C.

in addition to a change in the angle of crossed dispersion with time there is also a change of optic axial angle, slight for red and violet, but relatively great for all colours near that which ultimately becomes the colour of uniaxiality.

Table IX gives the axial angles for a freshly-prepared 50 % mixture. The upper row of figures gives the optic axial angles for the colours indicated in the vertical columns, the lower row showing the angle of crossed dispersion between the colour at the head of the column and the next. Tables X (A and B) give the changes of axial angle in a 60 % mixture. The data for mercury green and sodium yellow are specially noteworthy. In the former case, there is a closing up of the optic axes when the section is heated at 40° C. equal in amount to $44° - 16° = 28°$. For sodium-light the closing up amounts to $31° - 25\frac{1}{2}° = 5\frac{1}{2}°$. Now when the section assumes uniaxiality, it does so for light between these two colours, but closer to the mercury green. Its optic axial angle, when freshly prepared, for this colour can be roughly estimated from the data in Table X A to be about 40°. As in the final state, its optic axes have closed up to coincidence, the total amount of closing is 40°. This is the maximum change observed in the optic axial angle for any colour in the 60 % mixture.

TABLE IX. 50 % *sodium-potassium tartrate mixture.*

Colour	Red.		Yellow.		Green.		Violet.
2E	69° 10′		56° 2′		45° 4′		54° 40′
Angle of crossed dispersion ...		4°		8°		61°	

TABLE X A. 60 % *sodium-potassium tartrate mixture.*

	Optic axial angles.		
Colour.	Freshly prepared.	After 30 hours.	Final state.
Hg violet	$74\frac{1}{2}°$	59°	61°
Hg green	44	19	16
Na yellow	31	$25\frac{1}{2}$	$25\frac{1}{2}$
Red$_1$	28	42	42
Red$_2$	28	50	50
Red$_3$	28	52	52

TABLE X B. *Same mixture.*

	Angle of crossed dispersion.			
	Red$_3$ to red$_2$.	Red$_2$ to red$_1$.	Red$_1$ to green.	Green to violet.
Freshly prepared	8°	16°	$26\frac{1}{2}°$	$9\frac{1}{2}°$
Heated for 30 hours at 40° C.	1	1	70	$15\frac{1}{2}$
Final state	0	0	90	0

It would appear from the foregoing experimental evidence that a definite structural change takes place within the crystal, possibly an inter-molecular or 'inter-lattice' change, but there is no evidence of this in the outward symmetry of the crystal. A large number of crystals were measured both before and after the changes indicated in this paper had taken place and no change of angle was detected. All the specimens measured, including the two pure constituent Seignette salts and a wide range of mixtures, were found to possess the symmetry of the digonal holoaxial or bisphenoidal class of the rhombic system.

Summary.

I. It is shown that freshly-prepared rhombic crystals of the mixed Seignette salts exhibit abnormal interference-figures. The type of dispersion observed in freshly-prepared crystals is that belonging properly to the monoclinic system, viz. crossed dispersion, of the 'borax' type. The extent of crossed dispersion varies with the composition of the mixed crystals and rises to a maximum of 75° for the 45 % sodium-potassium tartrate mixture.

II. The effect observed in freshly-prepared crystals does not persist, but gradually disappears, the process occupying from one week to three or four months.

III. Increase of temperature hastens the process of change. The most pronounced cases of crossed dispersion disappeared on uniform heating to 30° or 40° C. in less than a week.

IV. The effect is shown to be independent of the concentration around the crystal of either ammonia or water-vapour.

V. An interesting feature of the change to be observed on leaving these crystals to stand is that there is a change in optic axial angle for all colours in addition to a closing in to coincidence of optic axial planes. The maximum change of optic axial angle for any section observed was that of 40° for yellow-green light with the 60 % sodium-potassium tartrate mixture. The observations indicate that there is *no uniaxiality* for any colour so long as crossed dispersion persists.

The author takes this opportunity of expressing his gratitude to Sir Henry Miers for his valuable help and advice, without which the foregoing work could not have been carried out.

NOTE (January 22).—A paper by F. Wallerant (Bull. Soc. Franç. Min., for Jan.–May, 1923) dealing with similar phenomena in mixtures of racemates has reached me while the above pages are passing through the press.