

*Citation:*

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From this it appears that this photochemical transformation is quite analogous to that which the acid itself, according to BOËSEKEN, undergoes by *heat*. From what has been stated above, this reaction cannot be put on a level with the photochemical decomposition of the trichloroacetate, without further evidence.

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**Chemistry.** — “*A remarkable case of isopolymorphism with salts of the alkali-metals*”. By Prof. F. M. JAEGER. (Communicated by Prof. P. VAN ROMBURGH.)

(Communicated in the meeting of Sept. 30, 1911).

§ 1. The numerous researches which have been made to explain the morphotropic relation of the alkali-metals, may be said to have led to no other view but the conviction, that the problem of the mutual replacement of these metallic atoms is one of an almost hopeless complexity.

The most accurate researches in this dominion, — those of TUTTON, — lead the author, with complete negation of all other well established facts, to the conclusion that anyhow the metals *K*, *Rb* and *Cs* possess plainly an isomorphotropic relation, which numerically runs parallel with the rise of their atomic weights, and that  $(NH_4)$  and *Tl* are, in many respects, to be placed outside the series; but that with an eventual form relation the  $(NH_4)$ -radical exerts an influence which stands between that of *Rb* and *Cs*. As to the optical properties, no regularities seem to occur. As is well known, TUTTON's beautiful researches only relate to the alkali-sulphates, the alkali-selenates and the monoclinic double sulphates and double selenates of the formula:  $R'_2 Me''(SO_4)_2, 6H_2O$  and  $R'_2 Me''(SeO_4)_2, 6H_2O$ .

Even in these researches it seems here and there, that the conclusions drawn must be considered as being *too* general. For instance, with the selenates, the *Tl*-compound is very analogous to the *Rb*-salt; the difference in molecular volume is here only 0,4%, as against 1,4% between the *Rb*- and  $(NH_4)$ -salt. With the sulphates this difference between the *Rb*- and *Tl*-salt is about 0,8%, between *Tl*- and  $(NH_4)$ -salt only 0,08%, and a similar trifling difference between  $(NH_4)$ - and *Tl*-salt is also observed with ammonium-zinc-sulphate and thallous-zinc-sulphate (0,03%), so that the place of

the  $(NH_4)$  between the *Rb* and the *Cs*, is in these respects less correct than in the proximity of the *Tl*.

That however, as soon as we consider the great number of facts which have been collected by other investigators besides TUTTON, — but little is left of these supposed general rules may be seen from a short recapitulation :

1. The *acid tartrates* of *K*, *Rb*, *Cs*,  $NH_4$  and *Tl* are rhombo-bisphenoidic and form an isomorphous series. In this the *Rb* and the *Tl*-salt are placed the nearest to each other, then follows the  $(NH_4)$ -salt, the *K*-salt and finally the *Cs*-salt.

2. On the other hand, the *Rb*- and *Cs*-salts of the *neutral tartrates* are trigonal ; the *Tl*-salt is monoclinic and trigonal, whereas the  $(NH_4)$ -salt, although also monoclinic with comparable parameters, is certainly *not* isomorphous with the monoclinic form of the *Tl*-salt.

In connection with the following it should be observed that with the *Tl*-salt the angle  $\beta = 86^\circ 43'$ ; with the  $(NH_4)$ -salt,  $\beta = 87^\circ 37'$ .

3. Now, proceeding to the complete series, which are related to inorganic acids, we may mention here, besides the sulphates, selenates and double sulphates investigated by TUTTON, the *K*-,  $(NH_4)$ -, *Rb*-, *Cs*- and *Tl*-alums, derived from *aluminium* (PETTERSSON), those from *vanadium* (PICCINI) and *chromium*, those from *gallium* and *iron* (SORRET), those from *rhodium*, *indium* and *iridium*. There is here nowhere any indication of polymorphism, but with the ordinary alums for instance a quite regular modification of the physical properties has been noticed, which gives no occasion to assign to the  $(NH_4)$ -salt a particular position in the series.

4. Of the *chlorates* the *K*-, *Rb*- and *Cs*-salt are probably isomorphous ; the *Tl*-salt is isodimorphous and has one form which is isomorphous with the *K*-salt ; the  $(NH_4)$ -salt, however, is trigonal-pseudo-cubic, like *K-bromate*. The latter is isodimorphous with *K-chlorate*.

5. In the series of the *perchlorates* which is isomorphous, the *Tl* is also placed nearest to the *Rb*.

6. *K-persulphate*:  $K_2S_2O_8$  is triclinic-pinacoidal : the *Rb*-, *Cs*-,  $(NH_4)$ - and *Tl*-salts are monoclinic and isomorphous. Here we have, therefore, an isodimorphous series.

7. The *K*- and *Rb-platinum-nitrites* are monoclinic ; *Cs-platinum-nitrite* is also monoclinic, but totally differs from the two others ; finally, the *Tl*-salt is again monoclinic but still again different from all other salts, so that we have here a very interesting case indeed of an isotrimorphous series.

Of the same compounds, but crystallising with  $2 H_2O$ , the *K*-salt

is triclinic, the *Rb*-salt monoclinic, the  $(NH_4)$ -salt rhombic, although so analogous to the *Rb*-salt, that it should be regarded as pseudo-symmetric. Finally in the series of the *alkali-platinum-jodo-nitrites*, the *K*-salt is tetragonal the *Rb*-salt triclinic-pseudorhombododecaedric, the *Cs*-salt monoclinic, with a pseudorhombododecaedric habit.

8. The *K*- and *Rb*-chromates are rhombic-bipyramidal; the *Cs*-salt is dimorphous, namely rhombic and ditrigonal-scalenoedric; and finally the  $(NH_4)$ -salt is monoclinic-prismatic, but certainly dimorphous, — as it can form with  $(NH_4)_2SO_4$  mixed crystals of great concentration.

The *K*- and *Cs-dichromates* are isomorphous: the  $(NH_4)$ -salt is monoclinic and totally different from the two other salts; the *Rb*-salt is dimorphous, namely monoclinic and triclinic, whereas the monoclinic form is probably isomorphous with the  $(NH_4)$ -salt.

Still more complicated is the matter with the *trichromates*. The *K*-salt is monoclinic-prismatic; the *Rb*-salt is hexagonal and rhombic; the *Cs*-salt is trigonal and quite different from the hexagonal *Rb*-salt; finally the  $(NH_4)$ -salt is rhombic but quite different from the second form of the *Rb*-salt. We must therefore assume here an isotri- or isotetra-morphous replacement of the alkali-metals.

9. But by far the most complicated of all is the behaviour of the alkali-metals in their nitrates!

The *K*-salt is dimorphous: rhombic-pseudo-hexagonal and trigonal; the *Rb*-salt is rhombic but *not* isomorphous with the *K*-salt; at  $161^\circ$  it becomes cubic and at  $219^\circ$  trigonal, while all the conversions are reversible; the *Cs*-salt is rhombic and cubic; the *N*-salt is trimorphous, namely rhombic, cubic and hexagonal. Finally, the  $(NH_4)$ -salt is tetramorphous: rhombic, monoclinic, tetragonal and cubic, whereas according to WALLÉRANT the tetragonal form again returns at  $-16^\circ C$ . Here we have a rich field for the study of the binary systems concerned, which is still very incomplete.

§ 2. The above summary, which could be easily extended by quoting other examples, for instance, from the nitrides, polyhalogenides, hexafluosilicates, tetrachloro- and tetrabromoaurates may prove our contention, that the mutual morphotropic relations of the alkali-metals form an *exceedingly complicated* problem, and that it is unwarrantable to lay down rules, which are not supported by a sufficient number of facts.

A peculiar contribution to the above question is given here. During an investigation concerning trichloroacetic acid, I obtained the acid potassium-salt of this acid; it forms extraordinarily beautiful crystals, which on investigation showed a few peculiarities of

importance. I then prepared also all the other salts of the series, whose general formula is represented by  $R'CO_2 \cdot CCl_3 + HCO_2 \cdot CCl_3$ . The results of the investigation are given below. A detailed description of these compounds, also that of the acid *thallium-tribromoacetate* (investigated by way of comparison) will be given first.

§ 3. I. POTASSIUM-SALT:  $KCO_2 \cdot CCl_3 \cdot HCO_2 \cdot CCl_3$ .

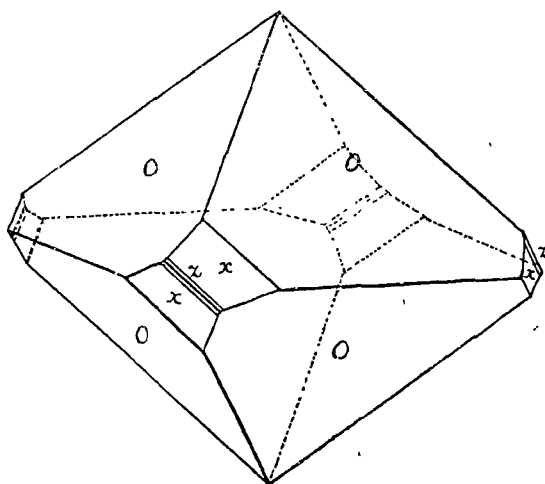
The analysis gave 10,60 %  $K$ ; calculated 10,68 %.

Sp. Gr.: at 18° C., 2,005; molecular volume: 182,04.

Large clear, very lustrous crystals, which are generally flattened along two parallel planes. Small isometrically developed, colourless octahedra also occur. The crystals are represented in fig. 1.

*Tetragonal-trapezohedric.*

$a : c = 1 : 0,7808$ .



Potassium-salt.

Fig. 1.

*Forms observed:*  $o = \{111\}$ , large, with a high lustre and well developed;  $x = \{311\}$ , with four planes above and four below in the alternate spacial-octants, but often wanting, and in all cases small and rather dull;  $z = \{511\}$ , very small and narrow, dull and mostly quite absent.

<i>Angular values:</i>	<i>Measured:</i>	<i>Calculated:</i>
$o : o = (111) : (\bar{1}\bar{1}1) =^*$	63°13'	—
$o : o = (111) : (11\bar{1}) =$	84 20	84°20'
$o : x = (111) : (311) =$	30 1	29 57
$o : x = (\bar{1}\bar{1}1) : (311) =$	55 54	56 0
$x : x = (311) : (1\bar{3}\bar{1}) =$	68 12	68 0 1/2
$x : o = (311) : (11\bar{1}) =$	68 48	68 44 2/3

<i>Angular values:</i>	<i>Measured:</i>	<i>Calculated:</i>
$o : x = (\overline{111}) : (\overline{311}) =$	29 55	29 57
$o : x = (111) : (\overline{311}) =$	86 49	86 50 $\frac{1}{2}$
$o : x = (\overline{111}) : (\overline{311}) =$	68 49	68 44 $\frac{2}{3}$
$x : z = (\overline{311}) : (\overline{511}) =$	10 26	10 26 $\frac{1}{2}$
$z : o = (\overline{511}) : (111) =$	76 29	76 24

A distinct cleavage was not found; the symmetry must be deduced from the development of the forms, while etching experiments carried out for the purpose of further confirmation did not give positive results.

The crystals are optically monaxial and do not exhibit circular polarisation. Refraction and double refraction are both strong; the latter is positive.

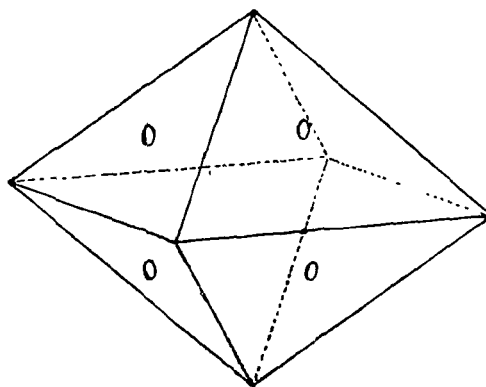
Topical parameters:  $\chi : \psi : \omega = 6,1545 : 6,1545 : 4,8061$ .

## II. AMMONIUM-SALT: $(NH_4) CO_2 CCl_3 \cdot HCO_2 CCl_3$ .

The analysis gave: 4,92%  $NH_3$ ; calculated: 4,94%.

Sp. Gr. at 19° 1,775; molecular-volume = 193,80.

Large octahedra, besides some smaller ones which are generally flattened along two parallel planes; the habit is that of the potassium-salt. The crystals are shown in Fig. 2.



Ammonium-Salt.  
Fig. 2.

*Tetragonal-trapezohedric,*

$$a : c = 1 : 0,7678.$$

*Forms observed:* Only  $o = \{111\}$ , large and very lustrous; in the smaller crystals the planes were mostly dull and inflected, but in the larger ones they gave very sharp reflexes.

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<i>Angular Values :</i>	<i>Measured :</i>	<i>Calculated :</i>
$o : o = (111) : (\bar{1}\bar{1}\bar{1}) =^*$	$62^\circ 41'$	—
$o : o = (111) : (\bar{1}\bar{1}\bar{1}) =$	$94^\circ 41\frac{1}{2}'$	$94^\circ 42\frac{2}{3}'$
$o : o = (111) : (\bar{1}\bar{1}\bar{1}) =$	$85^\circ 18\frac{1}{2}'$	$85^\circ 17\frac{1}{3}'$

A distinct cleavage was not found.

The compound is isomorphous with the potassium-salt.

The crystals are optically monaxial; the character of the double refraction is positive. They exhibit no circular polarisation.

Topic parameters :  $\chi : \psi : \omega = 6,3197 : 6,3197 : 4,8522$ .

III. RUBIDIUM-SALT:  $RbCO_2.CCl_3.HCO_2.CCl_3$ .

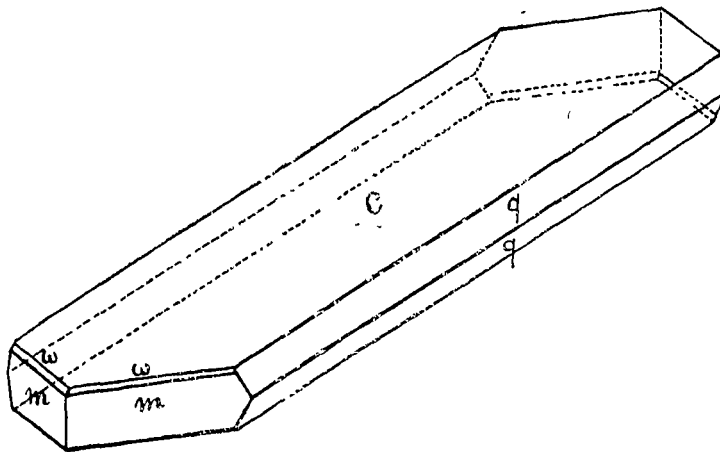
The analysis gave : 20,68 % *Rb*; calculated : 20,65 %.

Sp. gr. at  $18^\circ C.$ , 2,150; molecular volume = 191,21.

The first crystallisation-experiments showed at once, that we were dealing here with crystals of a quite different habit. Further investigation proved indeed that the *Rb*-salt has a form quite different from that of the two former ones.

Colourless, very thin, elongated-hexangular little plates which often form on the surface of the liquid, or deposit on the walls of the vessel.

The crystals are shown in Fig. 3.



Rubidium-Salt.  
Fig. 3.

*Monoclinic-prismatic.*

$$a : b : c = 1,4649 : 1 : 3,1596$$

$$\beta = 86^\circ 35\frac{1}{4}'.$$

*Forms observed* :  $c = \{001\}$ , large, lustrous and strongly predomi-

nant:  $q = \{011\}$ , well developed and yielding sharp reflexes;  $m = \{110\}$  also always present and better reflecting:  $w = \{112\}$ , narrow, somewhat dull and sometimes wanting altogether.

In the orthodiagonal zone the forms:  $\{1.0.18\}$ ,  $\{105\}$  and  $\{102\}$  were sometimes met with, in a very rudimentary form. The crystals are elongated along the clino-axis.

Angular values:		Measured: Calculated:	
$c:q = (001):(011) = ^\circ$	$72^\circ 24\frac{1}{2}'$	—	
$c:m = (001):(110) = ^\circ$	$88^\circ 4\frac{1}{2}'$	—	
$m:m = (110):(1\bar{1}0) = ^\circ$	$111^\circ 16'$	—	
$m:q = (110):(011) =$	$37^\circ 2'$	$37^\circ 9'$	
$q:q = (011):(01\bar{1}) =$	$35^\circ 12'$	$35^\circ 11'$	
$c:w = (001):(112) =$	$60^\circ 48'$	$60^\circ 52'$	
$w:m = (112):(110) =$	$27^\circ 14'$	$27^\circ 12\frac{1}{2}'$	

Probably, a not very distinct cleavage is present along  $\{001\}$ . The substance is optically biaxial; the exact situation of the axial plane could not, however, be traced microscopically.

Topical parameters:  $\chi : \psi : \omega = 5,0670 : 3,4590 : 10,9290$ .

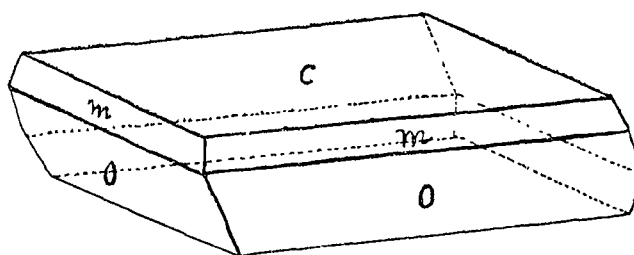
#### IV. CAESIUM-SALT: $CsCO_3.CCl_3.HCO_3.CCl_3$ .

The analysis 28,90%  $Cs$ ; calculated 28.98%.

Sp. gr. at  $20^\circ C$ . 2,143; molecular volume 214,18%.

The salt is very soluble in water. At first, small square plates are deposited; later, on slow evaporation, splendid thick very lustrous plate-like crystals, which sometimes have a surface of several cm.<sup>2</sup>

It is characteristic, that they may be cleaved as completely as mica, parallel  $\{001\}$ . The crystals are represented in fig. 4.



Caesium-salt.  
Fig. 4.

*Monoclinic-prismatic*, pronounced *pseudotetragonal*.

$$a : b : c = 1,0434 : 1 : 0,9706$$

$$\beta = 88^\circ 42'.$$

*Forms observed*:  $c = \{001\}$ , strongly developed and reflecting;



$o = \{\bar{1}11\}$ , very broad and very lustrous;  $m = \{110\}$ , brightly reflecting, but much narrower than  $o$ ;  $\omega = \{111\}$  very narrow and mostly wanting. The crystals are thin or flattened upon  $\{001\}$ , and sometimes elongated along a side  $c : o$ .

<i>Angular values:</i>	<i>Measured:</i>	<i>Calculated:</i>
$c : o = (001) : (\bar{1}11) = *$	$53^\circ 56'$	—
$c : m = (001) : (110) = *$	$89 \quad 6$	—
$o : o = (\bar{1}11) : (\bar{1}\bar{1}1) = *$	$71 \quad 24$	—
$o : m = (11\bar{1}) : (\bar{1}10) =$	$87 \quad 29$	$87^\circ 30\frac{1}{4}'$
$m : m = (111) : (\bar{1}\bar{1}1) =$	$92 \quad 28$	$92 \quad 24\frac{2}{3}$

An exceedingly perfect cleavage is present along  $\{001\}$ . On  $\{001\}$  diagonal extinction; in convergent polarised light a beautiful biaxial interference- image is observed. The pseudotetragonal character of the compound is also shown in the fact, that the first bisectrix stands nearly perpendicular on  $\{001\}$ , and that the axial angle is exceedingly *small*. The dispersion is extraordinarily strong, has a weakly-inclined character, while  $\rho < v$ ; the axial plane is  $\{010\}$ . The double refraction is negative.

After some time some of the clear crystals become locally opaque, like porcelain.

Although monoclinic, the whole character of the *Cs*-compound is so different from that of the *Rb*-compound, that an isomorphism of the two salts cannot be assumed.

Topic parameters:  $\chi : \psi : \omega = 6,2170 : 5,9585 : 5,7835$ .

From the last motherliquor of the caesium-salt, are sometimes obtained large, rudimentary crystals, which are flattened prisms and generally exhibit no well developed terminal planes; on analysis they appear to contain a trifle more than the quantity of caesium<sup>1)</sup> required, but to show accurately  $Cs : Cl = 1 : 6$ .

They are also monoclinic-prismatic; the parameters are:

$$a : b : c = 0,9968 : 1 : 0,2538$$

$$\beta = 80^\circ 18\frac{2}{3}'$$

The forms observed are:  $m = \{210\}$ , broad and lustrous;  $p = \{110\}$ , narrower, but brightly reflecting;  $a = \{100\}$  and  $b = \{010\}$ , about equally broadly developed as  $p$ ;  $c = \{001\}$  small and very lustrous;  $o = \{211\}$  very lustrous and sometimes fairly well developed.

<sup>1)</sup> The crystals contain *Cs* only; this was proved spectroscopically

Angular values:	Measured:	Calculated:
$a : m = (100) : (210) =^*$	$26^\circ 10'$	—
$b : o = (010) : (211) =^*$	$67 \quad 18$	—
$o : m = (211) : (\bar{2}10) =^*$	$107 \quad 2\bar{3}$	—
$m : p = (210) : (110) =$	$18 \quad 20$	$18^\circ 20'$
$p : b = (110) : (010) =$	$45 \quad 30$	$45 \quad 30$
$o : m = (211) : (\bar{2}10) =$	$72 \quad 37$	$72 \quad 37$
$o : o = (211) : (\bar{2}\bar{1}1) =$	$45 \quad 24$	$45 \quad 24$
$a : c = (100) : (001) =$	$80 \quad 28$	$80 \quad 18^\circ \frac{2}{3}$
$o : m = (211) : (210) =$	$50 \quad 21$	$50 \quad 16$

No distinct cleavage was found. The habit is thick-prismatic with elongation along the vertical axis.

On  $\{100\}$  normal extinction, on  $\{110\}$  obtuse extinction, symmetrically orientated in regard to the  $c$ -axis. The etching figures on  $m$  and  $a$  prove the said symmetry. On  $\{100\}$  one branch of the dark hyperbola is visible; the optic axial-plane is  $\{010\}$ .

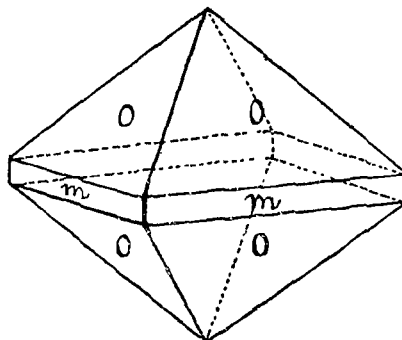
On account of its two monoclinic forms, the caesium salt must, therefore, be considered as dimorphous.

V. Thallous-salt:  $Tl CO_2 CCl_3 \cdot HCO_2 CCl_3$ .

The analysis gave:  $38,3\%$   $Tl$ ; calculated  $38,46\%$ .

Sp. gr. at  $18^\circ$   $2,822$ ; molecular volume  $= 187,74$ .

Small and also larger, colourless very lustrous crystals of the form of the  $K$ -, and  $(NH_4)$ -salt. They give sharp reflexes and may be measured very accurately.



Thallo-Salt.  
Fig. 5.

*Tetragonal-trapezohedric.*

$a : c = 1 : 0,7672$ .

*Forms observed:*  $o = \{111\}$  large, predominant and yielding almost perfectly sharp images;  $m = \{110\}$ , narrow, but always present and brightly reflecting.

<i>Angular values :</i>	<i>Measured :</i>	<i>Calculated :</i>
$o : m = (111) \ (110) =^*$	$42^\circ 40'$	—
$o : o = (111) \ (\bar{1}\bar{1}\bar{1}) =$	$62 \ 40$	$62^\circ 39\frac{1}{3}'$
$m : m = (110) \ (\bar{1}\bar{1}0) =$	$90 \ 0$	$90 \ 0$
$o : o = (111) \ (\bar{1}\bar{1}\bar{1}) =$	$85 \ 20$	$85 \ 20$
$o : o = (111) \ (\bar{1}\bar{1}\bar{1}) =$	$117 \ 20$	$117 \ 20\frac{2}{3}$
$o : o = (111) \ (\bar{1}\bar{1}\bar{1}) =$	$94 \ 40$	$94 \ 40$

No distinct cleavage was found. The compound is certainly isomorphous with the  $K$ -, and the  $(NH_4)$ -salt; the parameters are *nearly identical* with those of the ammonium-salt. The crystals are optically monaxial without circular polarisation.

In contrast, however, with the  $K$ -, and  $(NH_4)$ -salts, they possess a negative double refraction.

The clear crystals, if kept for a long time, sometimes become, locally, opaque and white like porcelain. While retaining their outward shape, they gradually become so altogether.

Topic parameters :  $\chi : \psi : \omega = 6,2547 : 6,2547 : 4,7987$ .

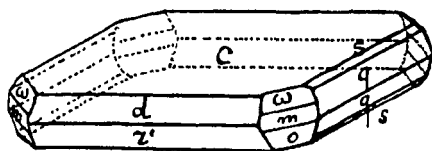
§ 4. VI. In order to confirm experimentally the presumption of a possible existence of eventual monoclinic, less stable modifications of the thallium-salt, the THALLOUS-TRIBROMOACETATE was prepared and investigated.

And indeed, the *monoclinic* form proved to be here the more stable one, and the analogy with the form of the *rubidium*-salt of the previous series is at once a striking one.

ACID THALLIUM-TRIBROMOACETATE :  $TlCO_2CBr_3$ .  $HCO_2CBr_3$ . The analysis gave : 25,6 %  $Tl$ ; calculated 25,59 %.

Sp. gr. at  $18^\circ$ , 3,923; molecular volume = 203,16.

Small, colourless or very pale, very lustrous crystals, which mostly have the form of thick crystal-plates of quadratric shape. They are shown in Fig. 6.



Acid Thallous-Tribromoacetate.  
Fig. 6.

*Monoclinic-prismatic.*

$$a : b : c = 1,5515 : 1 : 3,3007.$$

$$\beta = 87^\circ 48'.$$

*Forms observed:*  $c = \{001\}$ , large, very lustrous and predominant;  $\{101\}$  and  $r = \{101\}$  about equally strongly developed, and giving sharp reflexes;  $q = \{011\}$  reflecting very perfectly, broad and never wanting;  $s = \{013\}$ , very narrow and mostly absent;  $\omega = \{112\}$  yielding good reflexes;  $o = \{112\}$  even reflects better still.

<i>Angular values:</i>	<i>Measured:</i>	<i>Calculated:</i>
$c : q = (001) : (011) =$	$\approx 73^\circ 8'$	—
$c : d = (001) : (101) =$	$\approx 66^\circ 38\frac{1}{2}'$	—
$d : r = (101) : (10\bar{1}) =$	$\approx 50^\circ 19\frac{1}{2}'$	—
$c : s' = (001) : (013) =$	$47^\circ 44'$	$47^\circ 42\frac{2}{3}'$
$s : q = (013) : (011) =$	$25^\circ 24'$	$25^\circ 25\frac{1}{3}'$
$r : c = (10\bar{1}) : (001) =$	$63^\circ 2'$	$63^\circ 2'$
$c : o = (00\bar{1}) : (112) =$	$63^\circ 59'$	$63^\circ 57'$
$o : m = (11\bar{2}) : (110) =$	$27^\circ 21'$	$27^\circ 14\frac{1}{2}'$
$m : \omega = (110) : (112) =$	$26^\circ 48'$	$26^\circ 45\frac{1}{4}'$
$\omega : c = (112) : (001) =$	$62^\circ 4'$	$62^\circ 3\frac{1}{4}'$

Indistinctly cleavable along  $\{101\}$ .

On  $\{001\}$  the extinction is parallel and perpendicular to the direction of the  $b$ -axis, an axial image was not observed.

Topic parameters:  $\chi : \psi : \omega = 5,2928 : 3,4115 : 11,2601$ .

§ 5. From all these experiments may, therefore, be deduced the remarkable fact, that the acid alkali-salts of trichloroacetic acid form an isopolymorphous, and in all probability an isotetramorphous, series with three monoclinic and one tetragonal-trapezohedric modification.

It seems very peculiar that the two first terms of the series are tetragonal and isomorphous; that the  $Rb$ -salt exhibits the second, the  $Cs$ -salt the third and fourth possible form; and that, — with a further increase of the atomic weight, — the original optic monaxial form of the  $Tl$ -salt returns, but this time with an opposite optical character!

The  $Tl$ -salt is the nearest situated to the  $(NH_4)$ -salt and is also very adjacent to the  $K$ -salt. The two forms of the  $Rb$ - and  $Cs$ -salt exhibit — notwithstanding their great differences — an undeniable analogy, while, from the analysis of the *thallous-tribromo*-derivative, it appears that the eventual, more labile form of the thallous-salt, occurring in mixed crystals, will probably be the nearest situated to

that of the *Rb*-salt; the analogy with the second form of the *Cs*-salt is, however not so conspicuous.

By these relations it has been clearly demonstrated how complicated the family-relation of the crystal-building alkali-molecules is, and how much the expected isomorphism may be confused by the occurrence of polymorphism.

§ 6. Efforts to find definite transition-points with the acid of the crystallisation-microscope, were without result. On heating, an apparent melting-phenomenon occurs in the crystals, to be attributed to the fact that the split-off trichloroacetic-acid-molecule, causes the occurrence of a liquid phase in the pores of the crystals, which then become porcelain-like and opaque, while they are crossed with innumerable cracks. On account of the decomposition of the substance, it is not possible to prove the occurrence of another modification by a thermic method.

#### § 7. *Mixing-experiments.*

Although a more complete investigation of the mixing-phenomena of these salts must be postponed till later, still a few experiments have been made, for a first orientation, which already have brought to light some very peculiar phenomena.

##### 1. *Thallium-, and Ammonium-salts.*

From mixtures of the *thallous*- and the *ammonium*-salt crystallise small, well formed quadratic octahedra, afterwards larger ones of the type of the  $(NH_4)$ -salt. The first crop of crystals are optically *positive*. In the last fractions there were found small crystal-clear, tetragonal double-pyramids, which were faintly negative; the axial image was normal. In the very last fractions there were found similar crystals, which however, possessed a strongly negative double refraction. Their angular values agree with those of the *Tl*- and the  $(NH_4)$ -salt. There can be no doubt as to the complete isomorphism of the two compounds; probably, their mixing-series is an uninterrupted one.

##### 2. *Potassium-, and Rubidium-salts.*

From mixtures of the *potassium*-, and the *rubidium*-salt are first deposited crystals, which are quite analogous to those of the pure *Rb*-salt. Later, small little plates appear with hexagonal limitations. Measurements showed that they were well built, possess monoclinic symmetry, and that their angles differ but little from those of the *Rb*-salt.

$$(001) : (011) = 72^\circ 35' \text{ (measured)} \quad (110) : \bar{1}\bar{1}0 = 111^\circ 10' \text{ (measured)}$$

The first angle is  $11'$  larger, the latter  $6'$  smaller than that of the *Rb*-salt. From the last fractions however, — which, of course, are very rich in potassium-salt, — both monoclinic crystals and tetragonal double pyramids are deposited. They are monaxial and faintly positive.

### 3. *Potassium*-, and *Caesium*-salts.

Up to the present the most peculiar phenomenon, however, was found with mixtures of the *potassium*-, and the *caesium*-salt. The latter is exceedingly soluble; from the mixed solution are deposited first mixed crystals, richer in potassium. Although possessing a somewhat different habit (Figs. 7 and 8), these crystals, which,

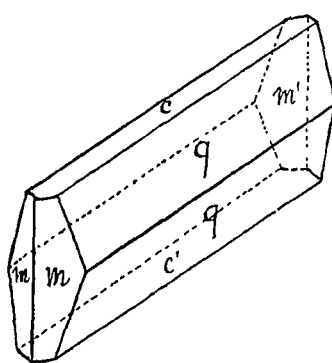


Fig. 7.

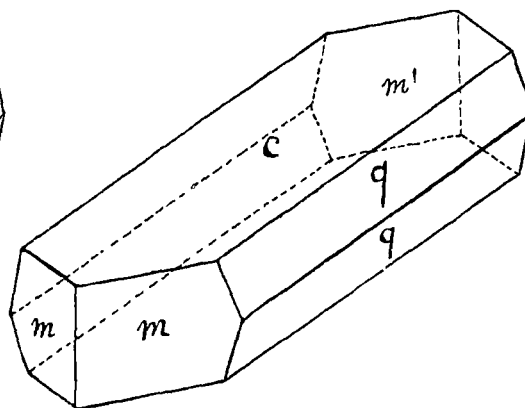


Fig. 8.

Mixed crystals of *Potassium*- and *Caesium*-salt. They exhibit the form of the *Rubidium*-salt.

though small, were irreproachably built, appeared to exhibit the monoclinic form of the *Rb*-salt! The remarks made in the description of the *thallous-tribromoacetate* also apply here: the monoclinic form, which was the more stable one in the *Rb*-salt, appears to also occur by preference in the mixed crystals as an exceedingly stable structure. If we adhere to the principal difference between *Rb*- and *Cs*-forms, there must, probably, be three hiatus in this mixing series.

That indeed the form of the monoclinic *Rb*-salt and *not* that of the monoclinic *Cs*-salt was present is proved by the following measurements:

$$\begin{aligned} c : q = (001) : (011) &= 72^\circ 32' & m : m &= (110) : (\bar{1}\bar{1}0) = 111^\circ 40' \\ & & m : q &= (110) : (011) = 37^\circ 13' \\ c : m &= (001) : (110) = 88^\circ 21' & q : q &= (011) : (0\bar{1}\bar{1}) = 34^\circ 52' \\ & & m : q &= (\bar{1}\bar{1}0) : (011) = 38^\circ 21' \end{aligned}$$

The angles in the different mixed crystals of this series diverge about  $+4'$  and  $-5'$  from the above values.

Up to the present, no tetragonal mixed crystals have been observed; also no monoclinic ones in the second form of the *Cs*-salt.

4. *Potassium-, and Ammonium-salts.*

From mixed solutions of *K*- and  $(\text{NH}_4)$ -trichloroacetate, on slow evaporation, mixed crystals are deposited which exhibit solely the tetragonal-bipyramidal form, and often possess a pronounced layer-structure. They are optically positive, — even the crystals deposited later; the interference image is often a little distorted, which points to a not quite homogeneous structure.

5. *Rubidium-, and Thallium-salt.*

From mixed solutions were obtained the mixed crystals of the form of the *Rb*-salt and chiefly in the habit of Fig. 7. The angle  $(110) : (\bar{1}\bar{1}0) = 72^\circ 42\frac{1}{2}'$ ;  $(011) : (0\bar{1}\bar{1}) = 111^\circ 41'$ . Up to the present no individuals of the *Tl*-type have been noticed.

6. *Caesium-, and Thallium-salts.*

Even with a very small *Tl*-salt content, mixed crystals of the form of the *Rb*-salt are deposited from the solutions of the two trichloroacetates. At a very large concentration of the *Cs*-salt, however, there were also found — besides the said monoclinic forms, — monoclinic, rectangular thick plates, which were cleavable towards  $\{001\}$  and exhibited in convergent light a beautiful axial-image, with a very small axial-angle, a strong dispersion:  $\rho > v$ , and with the first bisectrix nearly  $\perp$  upon  $\{001\}$ . The character of the first diagonal was negative. The following measurements were taken:  $(001) : (\bar{1}11) = 53^\circ 51'$ ;  $(\bar{1}11) : (\bar{1}10) = 37^\circ 1'$ ;  $(\bar{1}10) : (00\bar{1}) = 89^\circ 9'$ . The mixed crystals, therefore, possess the first form of the pure caesium-salt; those with the second form have never been found as yet.

7. *Caesium-, and Rubidium-salts.*

As in the case of the caesium-thallium-salt-mixtures, mixed crystals of the *Rb*-type appear first; these possess chiefly the habit shown in Fig. 8.

The following measurements were taken:  $(110) : (\bar{1}\bar{1}0) = 72^\circ 24\frac{1}{2}'$ ;  $(011) : (0\bar{1}\bar{1}) = 111^\circ 20\frac{1}{2}'$ ;  $(001) : (111) = 61^\circ 4'$ ;  $(111) : (110) = 27^\circ 21'$ ;  $(001) : (110) = 88^\circ 25'$ .

At a very great concentration of the caesium salt, however, one finds very thin, square, little plates, which appeared to be mixed crystals of the first caesium-type, which are deposited alongside with the other mixed crystals. They are biaxial, with a very small axial angle and negative character of the bisectrix. The dispersion is weak:  $\rho < v$  and with rhombic symmetry. Mixed crystals of the second *Cs*-type have neither here been met with as yet.

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