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Chemistry. — "*Investigations on* PASTEUR'S *Principle concerning the Relation between Molecular and Crystallonomical Dissymmetry: VIII. On the spontaneous Fission of racemic Potassium-Cobalti-Oxalate into its optically-active Antipodes.*" By Prof. F. M. JAEGER and WILLIAM THOMAS. B. Sc.

(Communicated in the meeting of Nov 30, 1918).

§ **1.** As a continuation of the fissions, accomplished up to this date, of the racemic complex *trioxalates* of *potassium* and the trivalent metals: *chromium* [1]), *rhodium* [2]), and *iridium* [3]), — it appeared desirable to make an attempt to separate the analogously built *potassium-cobalti-oxalate*: $K_3\{Co(C_2O_4)_3\} + 3\frac{1}{2}H_2O$, into its optically-active components for the purpose of a comparison of their rotatory dispersion and crystal-forms. The series of the complex *oxalates* investigated, would then be really complete. The proposed separation into its antipodes was, however, hindered till now by a number of difficulties of various kinds, partially caused by the salt being not very resistant towards an increase of temperature, and on the other hand by its particular solubility-relations, when combined with active bases; moreover a troublesome circumstance was its sensitiveness to light-radiation, this causing a rapid decomposition of these salts in solution, under formation of a pale pink, hardly soluble precipitate, — a reaction, the study of which is now started in our laboratory.

The racemic salt: $K_3\{Co(C_2O_4)_3\} + 3\frac{1}{2} H_2O$ has been studied by COPAUX [4]). It has, like the corresponding salts of the other metals, triclinic symmetry, but it is *not* isomorphous with them, as follows already from the deviating content of water of crystallisation: while the *iridium-* and *rhodium-*salts contain $4\frac{1}{2}$ molecules of water, the corresponding *chromi-*salt has *three*, the *cobalti-*salt $3\frac{1}{2}$ molecules of it. The salt was prepared in the following way in greater quantities.

A mixture of 25 grammes of *cobalti-carbonate*, 250 ccm of a satu-

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[1]) A. WERNER, Ber. d. d. Chem. Ges. **45**. 3061. (1912).

[2]) A. WERNER, Ber. d. d. Chem. Ges. **47**. 1954 (1914); F. M. JAEGER, Proceed. Ak. v. Wet. Amsterdam, **20**. 263. (1917).

[3]) F. M. JAEGER, Proceed. Kon. Akad. v. Wet. Amsterdam, **20**. 273. (1917); **21**. 203. (1918).

[4]) H. COPAUX, Bull. de la Soc Min. **29**. 75. (1906); Ann. de Chim. et Phys. (8). **6**. 508. (1905).

rated solution of *potassium-oxalate,* and 230 ccm of a saturated solution of *oxalic acid,* was heated on the waterbath under continuous stirring, till all the carbonate had entered into solution. The liquid thus obtained was cooled to 40° C, and then 30 grammes of finely pulverised *lead-peroxide*: PbO_2 were added. After some time 50 ccm of a 50 °/₀ solution of *acetic acid* were slowly added to the rigorously cooled solution under continuous stirring. Then the liquid was filtered and precipitated by 400 ccm of 97 °/₀ alcohol; the green precipitate was sucked off, and several times washed with absolute alcohol. In this way 80 grammes of the dark green *potassium-cobalti-oxalate* were readily collected.

§ **2.** The *silver*-, and the *barium*-salts being both only slightly soluble, we used the *potassium*-salt itself for the preparation of the corresponding *strychnine*-compound, thus avoiding the troublesome use of large volumes of solution; this is of advantage, because also at lower temperatures the solutions are partially decomposed under development of carbondioxide. The *strychnine*-salt [1]) is for the greater part precipitated, if the calculated amount of *strychnine-sulphate* is added to the solution of the *potassium*-salt, and only so much cold water is consequently added as to dissolve the precipitate formed. All these experiments were executed in a dark room, where the solution is left standing in an open vessel for several weeks, at a temperature of about 16° C; the fractions successively deposed from the mother-liquor are collected separately.

The crystals obtained are treated, in the same way as described on former occasions, with an excess of *potassium-iodide,* the *strychnine-iodide* is sucked off, and the filtrate precipitated by means of 97 °/₀ alcohol. The salt obtained is purified by repeated crystallisations from a small quantity of water.

The first fractions of the *strychnine*-salt in this way gave crystals of the *laevo*gyratory antipode, containing 1 molecule of water of crystallisation. The determination of the water-content cannot be made at 120° C, because of the decomposibility of the substance; it was therefore made by passing a current of dry air at 20° C over the finely powdered substance during a very long time, and a loss of weight corresponding to 0,8 molecules of water was finally observed.

With respect to the light-absorption by the dark green solutions,

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[1]) Originally the separation of the racemic salt was tried by the aid of *cinchonine,* but without success Afterwards we repeated these experiments under somewhat varied conditions, but they gave no positive results either.

it was found that in layers of 20 cm., a solution of 0,41 percentages by weight showed a pronounced absorption-band in the yellow and blue part of the spectrum between the wavelengths of 5510 and 6520 *A.U.* For concentrations of 0,82$^0/_0$ and 1$^0/_0$ no light was transmitted; but the solution just mentioned allowed the light to come through between 4850 and 5515 A.U. With a solution of 0.31$^0/_0$ these limits were: 4770 to 5670 A.U., and 6480 A.U.; with one of 0.27$^0/_0$: 4720 to 5750, and 6450 A.U.; etc. Determinations corresponding to wave-lengths within these limits can only be made with extremely diluted solutions, and the incertitude of the readings caused thereby may explain the deviations of the values obtained in the case of the laevo-, and dextrogyratory components, in so far as these values are observed in the immediate vicinity of the deep minimum in the dispersion-curve. But notwithstanding this incertitude, the characteristic slope of the dispersion-curve is in all cases fixed with full certainty.

For the salt from the first fractions, we found values of the rotation in good agreement with each other, which are suited to elucidate the strange form of the dispersion-curve (fig. 1) immediately:

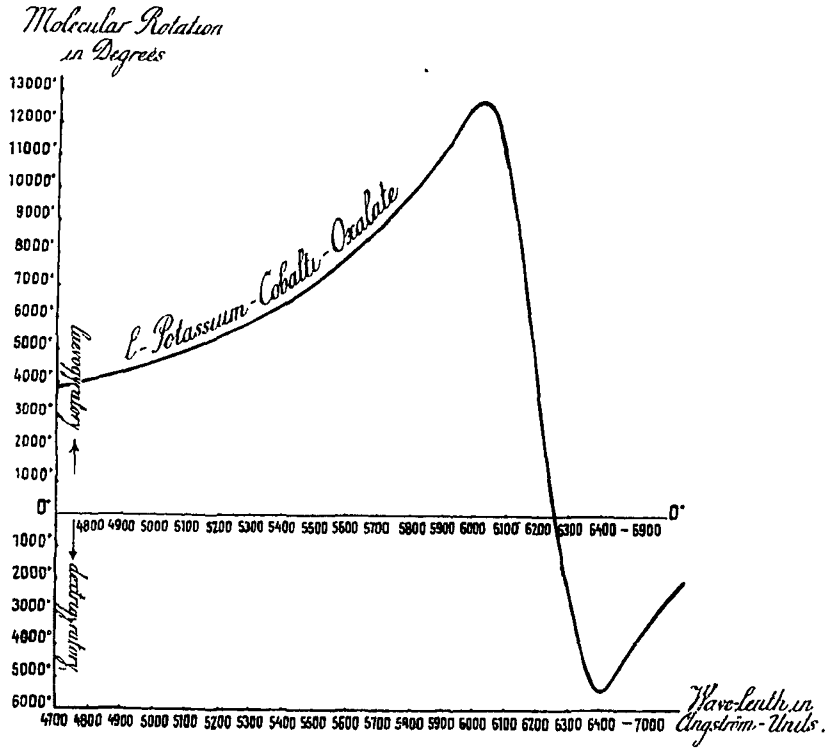


Fig 1. *Molecular Rotatory Dispersion of Laevogyratory Potassium Cobalti-Oxalate* ($+ 1 H_2O$).

MOLECULAR ROTATION OF LAEVOGYRATORY POTASSIUM-COBALTI-OXALATE (+ 1 H_2O).

Wave-length in Angström-Units:	Molecular Rotation in Degrees:
4730	— 3913°
4780	4031
4870	4196
4945	4399
5020	4619
5105	4916
5180	5123
5260	5487
5340	5900
5420	6387
5515	7086
5610	7805
5700	8682
5800	9708
5910	11327
6020	12508
6140	— 8506
6260	+ 263
6380	5391
6520	4126
6660	1799
6800	+ 160

This curve therefore appears to possess the peculiarity, that the rotation at first rapidly increases for greater wave-lengths, but decreases then very steeply in the vicinity of the absorption-band, to assume the opposite algebraic sign at circa 6260 A.U. The right-handed rotation now reached, shows a minimum at about 6400 A.U., and decreases at first rapidly, afterwards more slowly, so that the curve approaches more and more the axis of the *zero*-value. The dispersion has therefore, properly speaking, only a really "normal" character between 6240 A.U., and 6400 A.U. The maximum of the laevogyratory rotation is situated at about 6000 A.U.

On comparing the magnitude of the rotations for corresponding wave-lengths, in the cases of the complex *oxalates* of *chromium, cobaltum, rhodium,* and *iridium,* — the influence of the specific nature of the central metallic atom on the whole character, as well as on the absolute values of the rotation, is immediately evident. The figures 2 and 3 will show this clearly; in fig. 2 the curves of the *cobalti-, rhodium-* and *iridium*-salts are drawn, in fig. 3 those of the *chromium-*, and *cobalti*-salts. While the complex *rhodium-*, and *iridium-oxalates* show an analogous dispersion, the *cobalti*-salt seems to have a

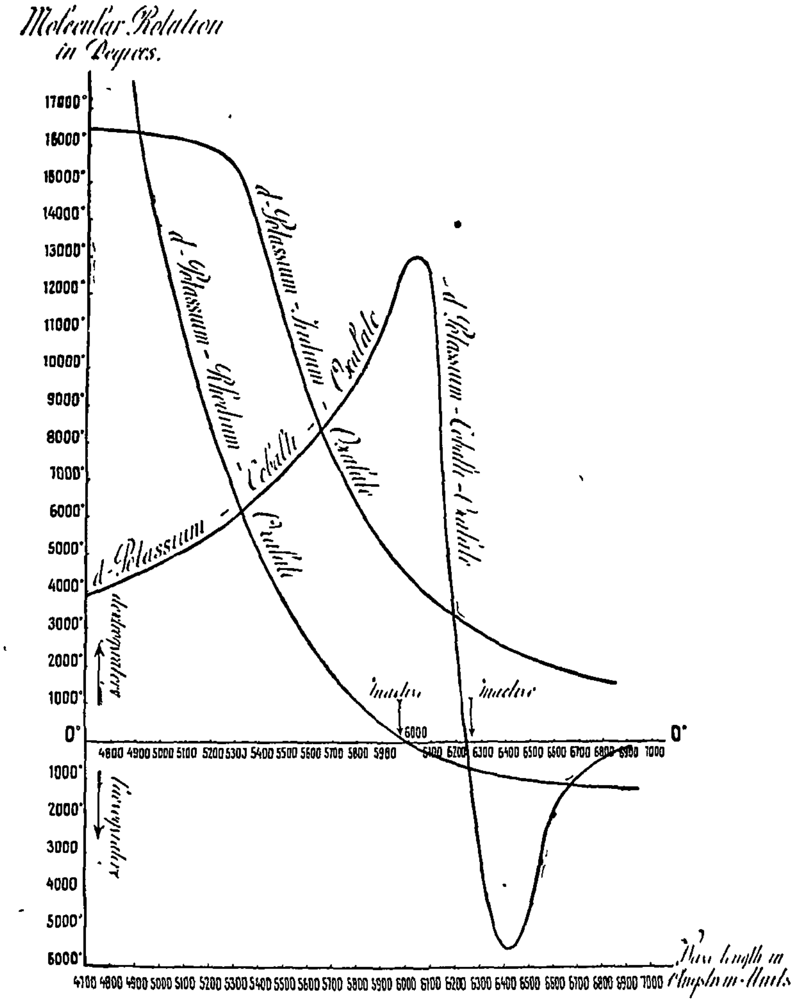
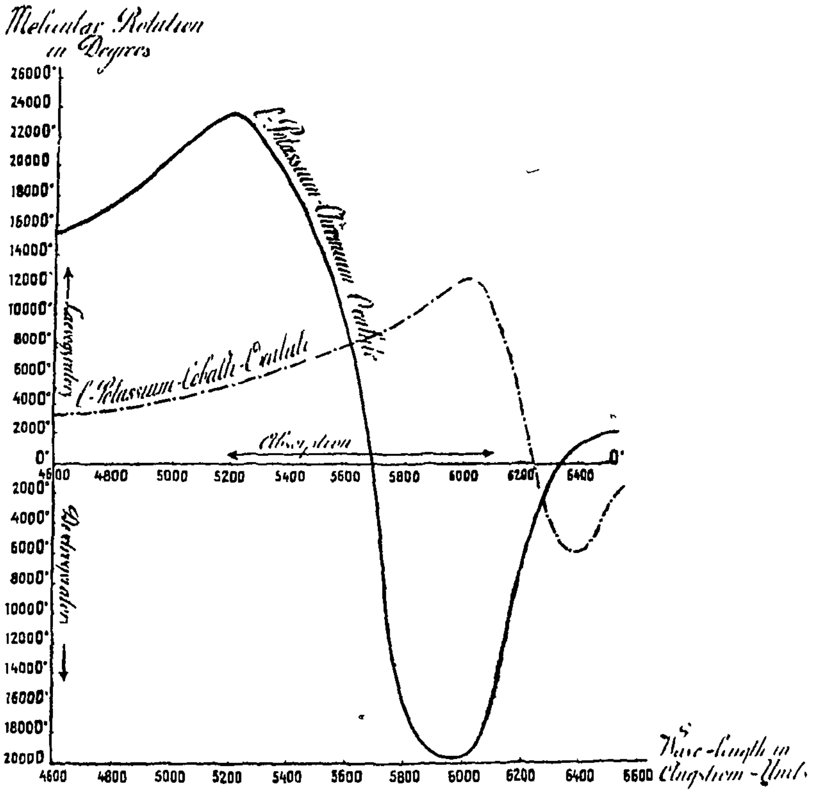


Fig. 2.



Molecular Rotation-Dispersion of Laevogyrate Potassium-Chromium Oxalate (+3H₂O) and Potassium-Cobalti-Oxalate (+1H₂O)

Fig.3.

deviating position amongst them. [1]) However, this salt shows a complete analogy in this respect with the corresponding *chromium*-salt, as may be easily seen from the measurements made in this laboratory by Mr. P. J. **Becker** with the *potassium-chromi-oxalate:* $K_3\{Cr(C_2O_4)_3\} + 3H_2O$, which was separated into its antipodes after **Werner**'s method[2]). On comparing the rotation of this salt with that of the *cobalti*-salt at corresponding wave-lengths, it may be seen that the rotations of the *chromium*-salt are, up to 5640 A.U., and above

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[1]) According to an investigation of G. **Bruhat** (Bull. de la Soc. Chim. (4), **17**, 226 (1915)), there is also a maximum in the dispersion-curve of the complex *iridium*-oxalate at short wave-lengths (about 4930 A.U.). It therefore seems probable, that the character of the anomalous dispersion curves is really very analogous in all these cases, however with a considerable difference in the positions of the maxima.

[2]) A. **Werner**, Ber. d. d. Chem. Ges. **45**. 3061 (1912). It is difficult to obtain good crystals of this compound which, moreover, rapidly autoracemises in solution; therefore crystallographic measurements could till now not be made in any way.

6280 A.U., considerably *greater* than those of the *cobalti*-salt; while between 5640 and 6280 A.U. the reverse occurs, and the two salts even show an opposite rotation as a consequence of the shift of their maximum and minimum; this shift is, in its turn, intimately connected with the very different situation of the absorption-bands: for the *chromium*-salt has a very broad band in the orange, yellow, partially in the green and the violet. It must, moreover, be remarked, that our former experience has made it clear, that the *triethylenediamine-chromi*-salts show in general only about half the rotations of the *triethylenediamine-cobalti*-salts for corresponding wave-lengths. From this it is evident how great and unexpected an influence the presence of *basic* groups, or that of *acid* radicles, has, on the magnitude of the rotation when they are dissymmetrically arranged round the central metal-atoms of such complex salts.

§ **3**. As was already mentioned before, the racemic *cobalti*-salt has already been investigated by COPAUX, who described it as a *triclinic* substance, but *not* isomorphous with the corresponding *rhodium*-salt. As will be soon demonstrated, COPAUX most probably obtained his crystals from solutions evaporated in the darkness and at low temperatures; for even in diffuse day-light the solution is decomposed with development of carbondioxide and precipitation of *cobalto-oxalate*, — a decomposition which is quite analogous to the photochemical decomposition of the corresponding *ferric*-salt. It must be remarked that in this photochemical reaction, *blue* light decomposes the solutions much more rapidly, than *red* or *green* light, — in full agreement with DRAPER's law. But it is a remarkable fact that *yellow* and *orange* light, which is absorbed also to a considerable amount, has scarcely any stronger influence than the only slightly active green or red rays.

In our experiments the saturated solutions were evaporated in a dark space, the temperature of which differed only slightly from 0° C. In this case we really obtained *triclinic-pinacoidal* crystals of a dark green, almost black colour, and showing in most cases curved faces and rudimentary forms; accurate measurements were therefore very difficult. The angular values obtained really differ not inconsiderably from those published by COPAUX, at least within some zones; but the identity of his crystals and ours need not be doubted in any way, as may appear from the following values:

Angular values:	*Observed:*		*Calculated:*
	JAEGER:	COPAUX:	
$m:\mu = (110):(1\bar{1}0) =$	60° 37′	60° 36′	—
$c:m = (001):(110) =$	79 22	79 26	—

$q:m = (011):(110) =$	65 10	65 28	—
$a:b = (100):(0\bar{1}0) =$	89 2	88 42	88° 40′
$c:q = (001):(011) =$	33 10	32 28	—
$b:c = (010):(001) =$	88 37	88 39	88 32

etc.

The specific gravity of these crystals, which commonly only showed the combination-forms: $m = \{110\}$, $\mu = \{1\bar{1}0\}$, $c = \{001\}$, $q = \{011\}$, $\omega = \{\bar{1}12\}$, and $a = \{100\}$ and $b = \{010\}$ very narrow, — was at 15° C. determined at: $d_{4^\circ} = 1,877$; the molecular volume is therefore: 268,14.

An analogy of form with the corresponding *rhodium*-, and *iridium*-salts is not present; neither is this the case with the monoclinic *chromium*-salt, which possesses $3\,H_2O$. [1]).

These facts prove in every case undeniably, that at temperatures in the neighbourhood of 0° C., the saturated solutions deposit crystals of the *racemic* compound. But the stranger therefore appeared to us originally the behaviour of solutions evaporating at room-temperature. For from an also inactive solution, which during the summermonths was slowly evaporated in a dark room at temperatures only slightly differing from 18° C., dark green, almost black needles were obtained, which even on superficial examination appeared to differ appreciably from the triclinic racemate. Crystal-measurements taught us, that they had *trigonal* symmetry, and that their form was identical with that of the laevogyratory antipode. A crop of small crystals of this crystallisation-product, dissolved in water, did however not show any appreciable rotation. Suspicion immediately arose, that the racemic salt might have been split under these circumstances into its antipodes spontaneously, and that no trace of rotation could be detected according to our way of investigation, only because the solution deposes the crystals of the two antipodes besides each other in about equal number, so that a crop of several crystals, which by the lack of hemihedral faces cannot be discerned from each other, contains in general almost an equal number of dextro- and laevogyratory individuals, when collected from the solution at random. It is evident that such a mixture will not exhibit any appreciable optical activity. If this suspicion were true, the optical activity must appear immediately, if only a single crystal at the same time were dissolved. Indeed, experience proved,

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[1]) The parametres of the *cobalti*-salt are: $a:b:c = 0,5963:1:0,6590$; $\alpha = 91°42'$; $\beta = 101°23'$; $\gamma = 88°22'$. The *chromium* salt is monoclinic, with: $a:b:c = 1,0060:1:1,3989$; $\beta = 86°0'$. For the *rhodium*- and *iridium*-salts, cf. these Proceedings, **20**, p. 270, (1917); and **21**, 214, (1918).

that the first crystal thus investigated, showed the full activity of the *dextro*gyratory component, which then had not yet been obtained in the pure state by our fission-experiments; the following numbers can convincingly demonstrate the fact mentioned:

Molecular Rotation of the Dextrogyratory Potassium-Cobalti-Oxalate (+ 1 H_2O).

Wave-length in Angström-Units:	Molecular Rotation in Degrees:
4730	+ 3876°
4780	4009
4870	4167
4945	4428
5020	4689
5105	4923
5180	5106
5260	5553
5340	6013
5420	6416
5510	7023
5610	7916
5700	8703
5800	9764
5910	11365
6020	12812
6140	+ 8269
6260	— 103
6380	5468
6520	4317
6660	1678
6800	526
6940	— 198

The minimum in the dispersion-curve is here somewhat steeper than our former measurements with the laevogyratory component indicate, — a deviation probably caused by the uncertainty of the readings in the interval of the absorption-band. But the correspondence of the curves cannot be doubted any longer. Continued study of the single crystals deposited from the solution, taught, that besides the lefthanded crystals, also those of the laevogyratory component occur. It is commonly quite impossible to recognise the two kinds of crystals from each other by their outward appearance, and thus to select them, because the facets of the right- or lefthanded trapezohedra or trigonal bipyramids are commonly lacking, so that the aspect of the crystals is in both cases quite the same.

It cannot be doubted therefore any longer, that we have found here a *first instance of a fission into optically active antipodes* of such complex metallic compounds, *by spontaneous crystallisation*; for the case of *potassium-rhodium-oxalate* formerly indicated by WERNER as an instance of this kind, can no longer be considered as such, as was some time ago proved by us.[1])

For the purpose of justifying this view, it was necessary to determine the *temperature of transition* of the racemic compound into its antipodes as accurately as possible. This was done in two ways: by means of the dilatometrical method, and by the study of the

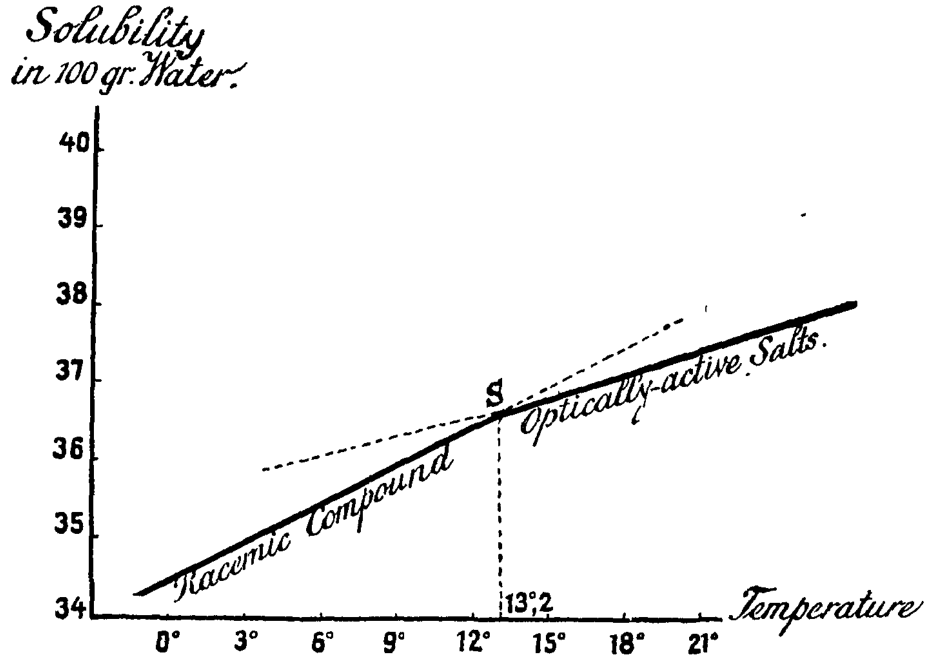

Fig. 4.

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[1]) F. M. JAEGER, Proceed. Kon. Akad. v. Wet. Amsterdam, **20**, 264, 265. (1917).

solubilities of the salts at different temperatures. For we have already formerly drawn attention[1]) to the fact, that below and above the transition-temperature, the metastable forms must have, as in all such cases, the greater solubility; and this was exactly one of the arguments used by us to reject WERNER's conclusions about the occurrence of a spontaneous fission in the case of the *potassium-rhodium-oxalate.*

Indeed, our experiments fully confirmed this view: we were able to demonstrate, that below 14° C. the solubility of the inactive form is really *smaller* than that of the optically-active antipodes, whereas above 14° C. the reverse was the case. Thus 100 grammes of water at 0° C. e.g. appeared to dissolve 34,50 grammes of the racemic salt, at 14° C. 36,81 grammes; etc. On the other hand, 100 grammes of water at 20° C. dissolved 37.40 grammes of the laevogyratory salt, at 22° C. 37,6 grammes; etc. The fig. 4 shows, that the transitionpoint to be determined, without appreciable error, may be fixed as 13,2° C.; this temperature, at which the reaction:

$$2\,rac.\,[K_3\{Co(C_2O_4)_3\} + 3\tfrac{1}{2}H_2O] \overset{13°,2}{\rightleftarrows} [d\text{--}K_3\{Co(C_2O_4)_3\} +$$

$$+ 1H_2O] + [l\text{--}K_3\{Co(C_2O_4)_3\} + 1\,H_2O] + 5H_2O,$$

takes place, is therefore a *minimum*-temperature for the existence of the optically-active salts.

The dilatometrical experiments were rather difficult, because of the tendency of the compound to decompose, when its solution is kept at somewhat higher temperatures for a long time, and because of the inevitable retardation-phenomena. Notwithstanding this, we were able to prove a sharp discontinuity of the volume-temperature-curve, at a temperature between 12° and 16° C. That such retardation-phenomena really occur, cannot be doubted; even in solution, the active salt is transformed just below the transition-temperature into the racemic one, with considerable slowness. Thus we found, that at 12° C, the dilute solution of the laevogyratory antipode lost in one day about half, in two days two thirds, in three days almost five sixths, and in four days about nine tenths of its original optical activity, while at the said temperature the optical antipodes beyond all doubt are already metastable with respect to the racemic salt.

Crystallisation-experiments made in a thermostate at 22° C gave results in full agreement with our conclusions: the solutions deposited

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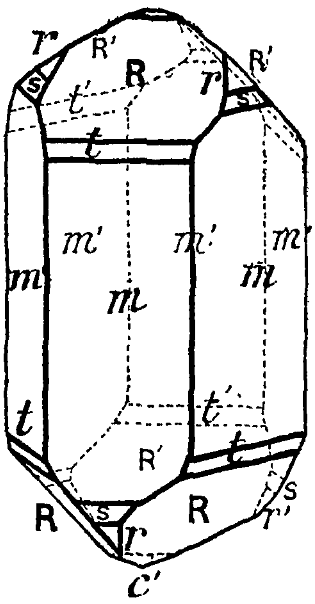
[1]) A. WERNER, Ber. d. d. Chem. Ges. **47**. 1954 (1914).

always the trigonal needles of the active components besides each other, but at 0° C we got only the triclinic crystals of the racemate. Therefore complete proof has been given now, that a fission of the *potassium-cobalti-oxalate* by spontaneous crystallisation into its optically active components really occurs at temperatures above 13°,2 C.

§ 4. Crystallographical research taught us, that both the optically active components occur in commonly not distinguishable crystals of *trigonal-trapezohedrical* symmetry, which are completely *isomorphous* with those of the optically-active *rhodium*-, and *iridium*-salts. They have the appearance (fig. 5 and 6) of a prismatic forms of more or less extension; the *dextro*gyratory component hitherto always presented the rhombohedron-like shape of fig. 6.

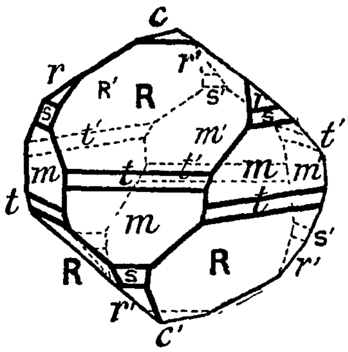
Trigonal-trapezohedrical.

$a : c = 1 : 0{,}8968$ (Bravais); $\alpha = 100°27'$ (Miller).



Laevogyratory Potassium-Cobalti-Oxalate ($+ 1\,H_2O$)
Fig 5.

Forms observed: $R = \{10\bar{1}1\}$ [100], large and very brilliant; $c = \{0001\}$ [111], always present, but subordinate; $m = \{10\bar{1}0\}$ $[2\bar{1}\bar{1}]$, commonly predominant with the lefthanded crystals, and in the case of the dextrogyratory individuals small, but well developed and yielding sharp images; $r = \{01\bar{1}1\}$ [221], and $s = \{02\bar{2}1\}$ $[1\bar{1}\bar{1}]$, always present, small, but very lustrous; $t = \{20\bar{2}1\}$ $[5\bar{1}\bar{1}]$, rather large and yielding good reflections. Hemihedral combination-forms were hardly ever observed; only once a crystal of the *laevo*gyratory antipode presented the *right*handed trigonal bipyramid $x = \{22\bar{4}1\}$ $[71\bar{5}]$ as an extremely narrow truncation of the edge $R : m$. From this it may be concluded, that in this case too, the substance manifests only a very weak tendency to present hemihedral forms, unregarded the enormous optical activity, which these salts exhibit in aqueous solution; and, moreover, that also in the case of the complex *oxalates*, the same morphological relation between the *cobalti*- and the *rhodium*-salts appears to exist, as between the corresponding *cobalti*- and *rhodium-triethylenediamine nitrates* [1], in so far, as the *oppositely* rotating *cobalti*- and *rhodium*-salts, which are separated from the less soluble compounds with optically-active bases (*strychnine*) or acids (*tartaric acid*), yet exhibit hemihedral forms of *the same* algebraic sign:



Dextrogyratory Potassium-Cobalti-Oxalate (+ $1H_2O$).
Fig 6.

Substance:	Rotation of the salt separated from the less soluble compound:	Algebraic sign of the hemihedral forms present:
Triethylenediamine-Cobalti-Nitrate.	*(Chloro-tartrate)*: **d.**	+ sphenoid.
Triethylenediamine-Rhodium-Nitrate.	*(Chloro-tartrate)*: **l.**	+ sphenoid.
———	———	———
Potassium-Cobalti-Oxalate.	*(Strychnine salt)*: **l.**	+ bipyramid.
Potassium-Rhodium-Oxalate.	*(Strychnine-salt)*: **d.**	+ bipyramid.
Potassium-Iridium-Oxalate.	*(Strychnine-salt)*: **d.**	+ bipyramid.

At the same time it is evident that the *cobalti*- and *rhodium*-salts

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[1] F. M. JAEGER, Proceed. Kon. Akad. v. Wet. Amsterdam, **20**. 258, 261 (1917).

set free from the less soluble compounds with optically active bases or acids, in the case of *triethylenediamine*-derivatives exhibit just the *opposite* rotatory power, as is observed in the case of the complex *trioxalates*; a fact, which sustains the view, according to which it is the basic or acid nature of the radicles placed round the central metallic atom, rather than the special nature of the latter, which in the first instance determines the direction of the rotation.

Angular Values:	*Observed*:		*Calculated*:	
$c:R = (0001):(10\bar{1}1) =$	* 46°	5′	—	
$m:t = (10\bar{1}0):(02\bar{2}1) =$	25	43	25°	46½
$m:m = (10\bar{1}0):(01\bar{1}0) =$	60	0	60	0
$R:R = (10\bar{1}1):(\bar{1}101) =$	77	11	77	12
$c:r = (0001):(01\bar{1}1) =$	46	8	46	5
$r:s = (01\bar{1}1):(02\bar{2}1) =$	18	0	18	8½
$s:m = (02\bar{2}1):(01\bar{1}0) =$	25	55	25	46½
$s:R = (02\bar{2}1):(10\bar{1}1) =$	51	13	51	5
$R:t = (01\bar{1}1):(02\bar{2}1) =$	17	58	18	8½
$R:m = (10\bar{1}1):(10\bar{1}0) =$	43	55	43	55
$x:R = (22\bar{4}1):(01\bar{1}1) =$	78	13	78	9

No distinct cleavage was observed.

The specific gravity of these crystals was at 15° C. determined at: $d_{4^0} = 1{,}8893$; the molecular volume is therefore: 242,57, and the topical parameters become: $\chi : \omega = 7{,}4676 : 6{,}6971$; or $\chi' = 6{,}3789$. The values of χ of the *Co-*, *Rho-*, and *Ir*-compounds appear to decrease therefore continuously with increasing atomic weight of the metallic atom, while ω reaches a minimum in the case of the *Rho*-salt.

Groningen, November 1918.

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