

consists in a decrease of the number of protons, — that are the particles observed by the counters — partly by ionisation and radiation but also partly being replaced by neutrons which in their turn will be replaced by protons in a lower level. The examination of this absorption process may be decisive for our knowledge of the nature of the most penetrating rays.

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**Chemistry.** — *Optical Rotation and Rotatory Dispersion in Solution and in the Crystalline State.* By F. M. JAEGER, J. TER BERG and P. TERPSTRA.

(Communicated at the meeting of June 26, 1937).

§ 1. If the molecules of a substance possess a dissymmetrical structure and that substance is dissolved in some solvent, the solution will manifest the phenomenon of rotation of the plane of polarization of an incident beam of linearly polarized light. An explanation of this optical rotation was given by FRESNEL in the well-known way by the supposition of the interference of two circularly polarized vibrations of opposite directions.

The rotation and the rotatory dispersion are dependent on the temperature, because of the motions of the dissolved molecules being a function of the temperature.

In a crystal, the molecules of which oscillate round definite mean positions of equilibrium, there can be *two* causes of a rotation of the plane of polarization of a polarized light-beam traversing the crystal:

1<sup>o</sup>. Either the molecules composing the crystal are themselves symmetrical and, therefore, optically inactive, — but their arrangement in the crystalstructure is a dissymmetrical one (*quartz; sodiumchlorate*). The optical activity of the crystal then is an immediate consequence of that dissymmetrical arrangement and it vanishes as soon as the latter is destroyed, — for instance by dissolving or melting the crystal.

2<sup>o</sup>. Or the molecules themselves possess a dissymmetrical structure and, as a logical consequence of this, their arrangement within the crystalstructure equally must be a dissymmetrical one: for the presence of any symmetry-element of the second order within the structure, necessarily would imply the simultaneous presence of an equal number of other molecules within the latter, which are the "mirror-images" of the original ones and, therefore, the crystal as a whole would appear to be optically inactive.

In this paper the optically activity of a crystal as a consequence of the molecular dissymmetry of its constituting molecules will be distinguished as "molecular" rotation, — in contrast to the "structural" rotation mentioned sub 1<sup>o</sup>. Evidently the "molecular" rotation of a crystallized substance is always accompanied by a "structural" one, the influence of which is, in some way or other, superimposed upon the first one.

§ 2. For the purpose of comparison of the specific rotation  $[\varrho]_\lambda$  of the crystallized solute with the specific rotation  $[\alpha]_\lambda$  of its *solution*, in the first case we can use the formula:

$$[\varrho]_\lambda = \frac{\varrho}{l \cdot d} \quad \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \quad (I)$$

in which  $\varrho$  is the rotation observed,  $d$  the specific gravity of the crystalline substance and  $l$  the thickness, expressed in d.M., of the mass traversed by the beam of light.

Indeed, as for the solution the usual formula:

$$[\alpha]_\lambda = \frac{\alpha}{l} \cdot \frac{100}{p} \quad \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \quad (II)$$

is applied, —  $l$  also here being expressed in d.M., — the data obtained in the two cases now are evidently comparable; for as by  $p$  the number of grammes of the substance present in 100 c.M<sup>3</sup>. of the solution is denoted, in the case of the crystal this number  $p$  is equal to  $100 d$  and the latter formula, therefore, then is transformed into the first one,  $[\alpha]_\lambda$  now becoming  $[\varrho]_\lambda$ .

It must be evident, however, that a direct comparison of  $[\alpha]_\lambda$  and of  $[\varrho]_\lambda$  in the case of the same substance cannot reveal to us the true size of the contribution of the “structural” rotation in the crystal to the whole rotation observed.

For the value of  $[\alpha]_\lambda$  in the solution is a kind of “mean” value, manifested by a random orientation of the dissolved molecules in all possible directions; whilst in the crystal  $[\varrho]_\lambda$  in general also relates, — it is true, — to a set of different orientations of the molecules, but those orientations being restricted to a much smaller number of possible directions. When, therefore, *rubidium-d-tartrate* for instance in solution shows a value  $[\alpha]_D = + 25^\circ, 63$  ( $[M] = + 3779^\circ$ ) and  $[\varrho]_D$  is found to be: —  $380^\circ$ , — it is impossible to draw any conclusion from these numbers about the true value of the “structural” rotation, because those numbers relate, it is true, to the same numbers of contributing molecules, but the latter in quite different orientations.

LONGCHAMBON<sup>1)</sup> tried to compare the “dispersion” of the dissolved and the crystallized substance, by determining for the two phases considered the values  $\frac{[\alpha]_\lambda}{[\varrho]_\lambda}$  at each wave-length.

He found, that the “dispersion” thus determined, in several cases of *colourless* salts were practically the same, so that:  $[\alpha]_{\lambda_1} : [\alpha]_{\lambda_2} : [\alpha]_{\lambda_3}$ ; etc. =  $[\varrho]_{\lambda_1} : [\varrho]_{\lambda_2} : [\varrho]_{\lambda_3}$ ; etc.

From this he drew the conclusion, that the molecular and the structural

<sup>1)</sup> L. LONGCHAMBON, Bull. Soc. franç. de minéral, 45, 244, (1922).

rotations of the crystalline substance must have *the same* rotatory dispersion.

§ 3. In our opinion the latter conclusion, seems, however, in general hardly to be backed by the experimental data, — as the following results may demonstrate.

In his investigation of the optically-active *potassium-rhodiumoxalate* LONGCHAMBON<sup>1)</sup> erroneously emphasizes, that in this case *no* structural rotation will be present, because of the fact that the complex ions of these salts have the same symmetry  $D_3$  as the crystals. Even in this case, however, some facts seem to point in the direction of a divergency from the author's empirical "rule"; and it seemed of interest, to check the latter by some other data concerning such coloured salts endowed with an appreciable rotatory power and manifesting a pronounced circular dichroism within the visible part of the spectrum, as well in solution as in the crystalline state.

As objects we choose the complex salts of *cobaltum* and *chromium* with the optically-active *trans-Cyclohexane-1-2-diamines* recently investigated in this laboratory<sup>2)</sup>, which in solution show a strong rotatory dispersion and COTTON-effect; whilst because of their typical hexagonal-pyramidal symmetry and their characteristic hemimorphic crystal-habitus, the preparation of accurately orientated plan-parallel plates of varied thicknesses easily could be performed.

For the measurement of the rotation of the crystalplates at different wave-lengths, use was made of a polarizing microscope provided with an ocular according to WRIGHT and an ordinary removable NICOL's prism as analyser. As a "half-shadow"-equipment, the apparatus of MACÉ DE LEPINAY was used, whilst a WÜLFING monochromator (FUESS) with an electric arc-lamp was applied for the observations to be made at different definite wave-lengths. The thickness  $l$  of each plate was microscopically measured in the usual way; it could be determined with an accuracy of 0,01 of a millimeter. The rotations, in general, could be measured with an accuracy of about  $0^\circ,1$ ; in the case of strong absorption the thinner plates were used without any considerable diminution of the accuracy in the rotation-measurements.

The results thus obtained in the case of levogyrotory

$\{\text{Co}(d - \text{Chxn})_3\} \text{Cl}_3 + 4 \text{H}_2\text{O}$  and of levogyrotory

$\{\text{Cr}(d - \text{Chxn})_3\} \text{Cl}_3 + 3 \text{H}_2\text{O}$  are collected in the Tables I and II.

§ 4. These rotations  $[\rho]$  and the specific rotations  $[\alpha]$  of the compounds studied here<sup>2)</sup> are graphically represented in the Figures 1 and 2, in which the curves I relate to the values of  $[\alpha]$ , the curves II to

1) L. LONGCHAMBON, *Compt. rend. Paris*, **178**, 1828, (1924).

2) F. M. JAEGER and L. BIJKERK, *these Proceed.*, **40**, 112, 258, 316, (1937).

TABLE I.							
Rotatory Dispersion of Crystalline $L\text{-}\{Co(d\text{-}Chxn)_3\}Cl_3 + 4H_2O$ .							
Wave-length in A.U.:	Plate 1. $l = 0.42$ m.M.		Plate 2. $l = 0.12$ m.M.		Plate 3. $l = 0.08$ m.M.		Mean Specific Rotation [ $\rho$ ] · 10 <sup>-1</sup>
	Observed rotation	Rotation pro m.M.:	Observed rotation	Rotation pro m.M.:	Observed rotation	Rotation pro m.M.:	
6650	+ 4.4 <sup>o</sup>	+10.5 <sup>o</sup>	—	—	—	—	+ 77 <sup>o</sup>
6500	4.8	11.4	—	—	—	—	84
6300	5.8	13.8	—	—	—	—	101
6200	—	—	+1.8 <sup>o</sup>	+15.0 <sup>o</sup>	—	—	111
6100	7.2	17.1	—	—	—	—	126
5900	9.9	23.6	—	—	—	—	174
5700	13.3	31.6	3.9	32.4	—	—	237
5600	—	—	4.8	40.0	+3.0 <sup>o</sup>	+37.6 <sup>o</sup>	287
5500	20.2	48.2	5.7	47.5	3.8	47.5	351
5400	23.3	55.5	6.8	56.7	4.5	56.3	425
5360	—	—	7.2	60.0	5.0	62.5	453
5300	—	—	7.8	65.0	5.1	63.7	476
5260	—	—	7.2	60.0	4.9	61.3	449
5220	—	—	7.0	58.3	4.5	56.3	424
5200	—	—	—	—	4.3	53.8	396
5170	—	—	—	—	4.0	50.0	368
5130	—	—	—	—	3.5	43.7	322
5110	—	—	—	—	2.5	31.2	230

Specific Gravity  $d$  of the Crystals: 1.356.

TABLE II.					
Rotatory Dispersion of Crystalline $L\text{-}\{Cr(d\text{-}Chxn)_3\}Cl_3 + 3H_2O$ .					
Wave-length in A.U.:	Plate 1. $l = 0.16$ m.M.		Plate 2. $l = 0.10$ m.M.		Mean Specific Rotation [ $\rho$ ] · 10 <sup>-1</sup> :
	Observed rotation	Rotation pro m.M.	Observed rotation	Rotation pro m.M.	
6650	+1.0 <sup>o</sup>	+ 6.2 <sup>o</sup>	—	—	+ 46 <sup>o</sup>
6600	1.1	6.8	—	—	51
6400	1.3	8.1	—	—	61
6200	1.7	10.1	—	—	76
6000	1.8	11.3	—	—	85
5900	2.0	12.5	—	—	94
5800	2.2	13.8	—	—	103
5600	3.0	18.9	—	—	142
5500	4.0	25.0	—	—	188
5400	4.8	30.0	—	—	225
5300	6.0	37.5	+3.7 <sup>o</sup>	+37.0 <sup>o</sup>	280
5200	6.8	42.5	4.2	42.0	317
5170	7.2	45.0	4.4	44.0	334
5130	—	—	4.6	46.0	346
5100	—	—	5.0	50.0	376
5000	—	—	4.8	48.0	361
4930	—	—	4.2	42.0	316

Specific Gravity  $d$  of the Crystals: 1.328.

$[\rho] \cdot 10^{-1}$ . In first instance it at once gets clear, that the crystals are for all wave-lengths in the visible spectrum, — even in the red part, — *dextro*-gyratory, although *in solution* the two salts are *levo*-rotating.

Specific Rotations  $[\alpha]$  and  
 $[\rho] \cdot 10^{-1}$  in Degrees

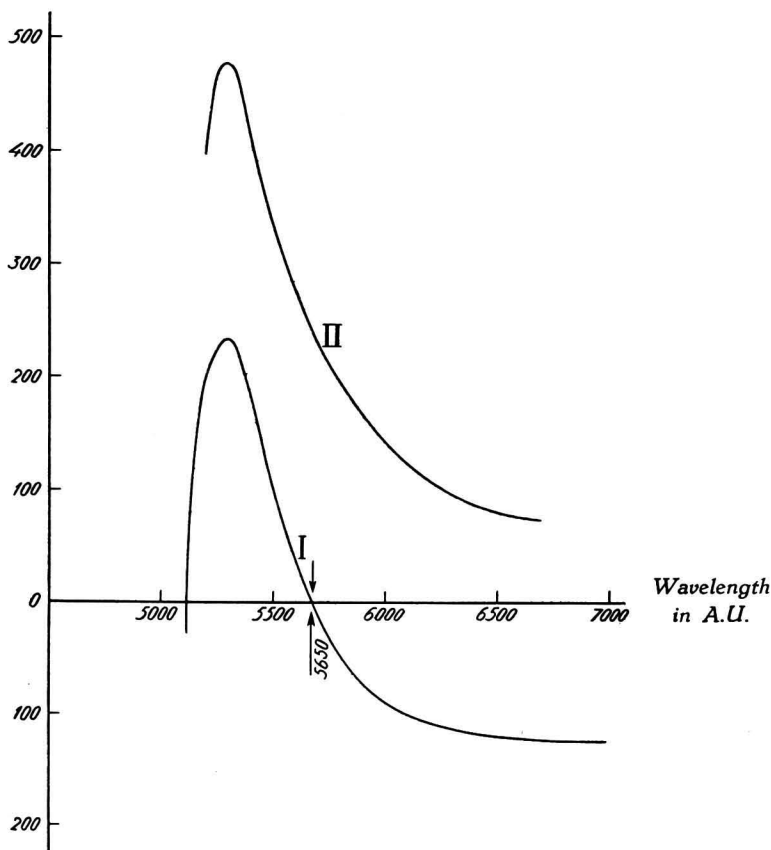


Fig. 1. Rotatory Dispersion of the Solutions (I) and of the Crystals (II) of  
 $L-\{Co(d-Chxn)_3\}Cl_3 + 4H_2O$ .

Secondly, the wave-lengths of *maximum* rotation in both the solutions and in the crystalline state prove to *coincide*, — the situation of the absorption-bands evidently being practically identical in the two phases; also the *algebraic sign* of the COTTON-effect is doubtlessly the same, although obviously its absolute value is different.

As to LONGCHAMBON'S "rule", however, it must be remarked that it evidently does *not* hold in these cases. For if  $\frac{[\alpha]_{\lambda_1}}{[\rho]_{\lambda_1}}$  shall be constant, both dispersion-curves surely must pass the X-axis at the *same* wavelength  $\lambda$ ; i.e. the two curves necessarily there must intersect in the same point of

zero-rotation. Now in our cases, this certainly is *not* true <sup>1)</sup> and, therefore, the relation emphasized by the French author can, in general, *not* be valid:

Specific Rotations  $[\alpha]$  and  
 $[\rho] \cdot 10^{-1}$  in Degrees

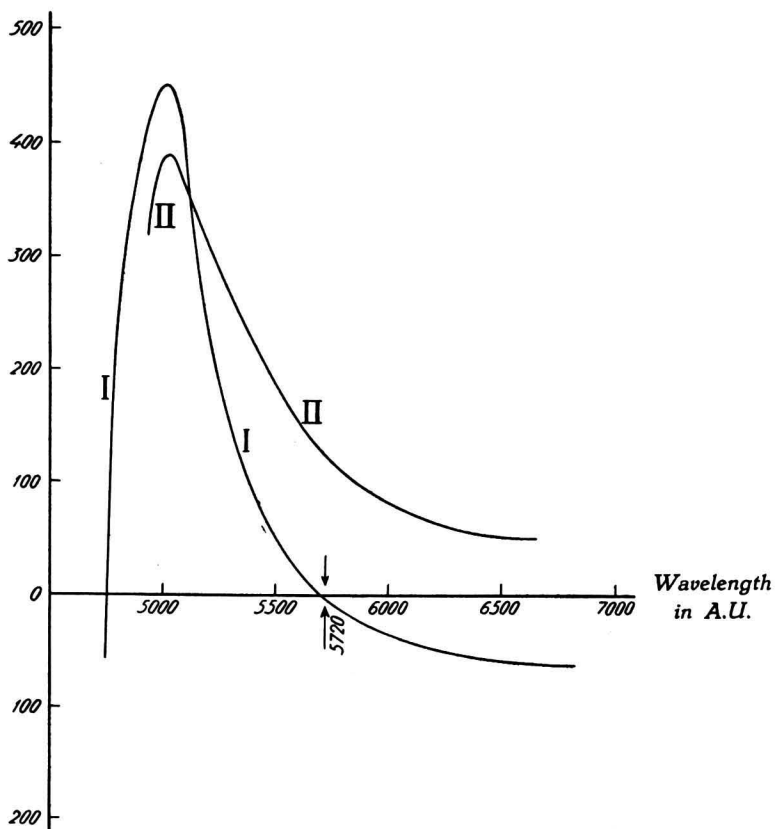


Fig. 2. Rotatory Dispersion of the Solutions (I) and of the Crystals (II) of  
 $L\text{-}\{Cr(d\text{-}Chxn)_3\}Cl_3 + 3H_2O$ .

the dispersion of the solution and the crystal, as defined by him, can, therefore, *not* be the same for the two phases considered.

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<sup>1)</sup> Also in LONGCHAMBON's results with  $K_3\{Rh(C_2O_4)_3\}$  this condition evidently is *not* fulfilled.