

ART. XLIII.—*The Relation between Structural and Magneto-optic Rotation*; by A. W. WRIGHT and D. A. KREIDER.

THE fact that any transparent, simply refracting, optically inactive substance when placed in a powerful magnetic field instantly acquires the property of rotating the plane of polarized light, and that the effect thereon is apparently of the same nature as that characteristic of certain specific atomic groupings in molecules, as, for example, those containing the asymmetric carbon atom, or of a particular molecular aggregation in certain crystalline units, such as sodium chlorate, naturally raises the question of relation between the two causes. Upon this subject literature furnishes no decisive records. Verdet's admirable researches have brought to light many interesting facts in regard to the two rotations, but none upon the subject here proposed.

It is known that when an optically active substance is placed in a magnetic field the two rotations are superposed, so that the resultant optical activity is the algebraic sum of the structural and magnetic rotations. An interesting result is Verdet's observation upon the behavior of iron and some other magnetic substances, to the effect that these, contrary to the general rule, rotate the plane in a direction opposite to that of the electric current or magnetic whirl.

It seemed worth submitting to an experimental investigation whether, if the optically active molecular structure or aggregation were effected in a magnetic field, it would be influenced thereby to an extent sufficient to show in its final optical properties, which would seem probable providing the interatomic or intramolecular forces are electrodynamic.

Experiments on Tartaric Acid.

Tartaric acid, three of the four isomeric forms of which are optically different, seemed applicable in this investigation, and upon it the first experiments were made.

Ordinary dextrotartaric acid, when heated to 175° C. in the presence of water in sealed tubes, is gradually converted into equal amounts of the racemic and the inactive forms.* If the atomic arrangement in this molecule is subject to the influence of magnetic force, it might be expected that by effecting the above change in a magnetic field, the resulting product should differ from that ordinarily obtained. For instance, if the molecules or their factors possess polarity, the magnetic field should exert upon them a directive action, and it

* Jungfleisch, *Jahresb.*, 1872, 515.

might be expected that the resultant polarization would be influential in determining the final form assumed.

In the following experiments two coils, made of german-silver wire carefully insulated by asbestos wrapping, furnished at once the required temperature and magnetic field. The coils were 160^{mm} long, with an opening into which a tube of 16^{mm} diameter would snugly fit. They were composed of four layers of wire each containing forty turns, one end of each layer being brought out so as to permit of connection in series or in opposition, thereby making it possible to eliminate the magnetic effect without altering the temperature. With the current strength employed, which was from two to three amperes, each coil, with layers connected in series, gave a calculated magnetic field of between forty and fifty C. G. S. units.

The determinations were all made in pairs: one in a magnetic, the other in a neutral coil; and the period of heating varied from two to four days for each experiment, this being the limit set by the unavoidable carbonization which, if carried too far, detracts from the delicacy of the polariscope reading; while the incidental evolution of carbonic acid results in such an increase of pressure that, though the tube should withstand it, partial loss of contents by violent effervescence upon opening the tubes is inevitable.*

As a rule the tubes contained 5 grms. of dextrotartaric acid with 3^{cm}³ of water and, in order to reduce the pressure by expelling the air, were sealed while the contents boiled. At the conclusion of the experiment the tubes were emptied into 50^{cm}³ flasks, from which the portions tested were filtered into the polariscope tube.

Preliminary tests seemed to indicate a slight influence pointing toward a tendency of the molecules under these conditions to group in the same way, that is to produce one product more abundantly than the other.

In order to determine certainly whether or not this effect was invariable, a series of some twenty determinations was made under carefully regulated conditions. The quantities of tartaric acid were accurately weighed and the water measured with equal care. To avoid any possible effect due to difference of pressure each pair of tubes was exhausted by a water pump and sealed off at the same instant and at the same length. The temperature of the two coils was accurately equalized, each being then protected from loss by radiation by means of loose coverings of asbestos and finally enclosed in the same

* It may be worth observing that the glass tubes thus employed have so yielded to the pressure at the temperature of these experiments as to make their further use impossible, unless perchance reannealing should restore their strength. The glass, however, did not appear to be chemically acted upon as it is by pure water when heated to that temperature.

wooden box, which was made long enough to permit of their being placed at sufficient distance from each other to avoid any appreciable interference in their magnetic fields. To counteract any possible slight difference in the effect of the two coils, the tubes, after half of the time of heating, were changed from one coil to the other and the magnetic conditions with them. Finally, to avoid any variation in the action due to a difference of density in the two tubes, since the amount of water employed was insufficient for a complete solution of the acid at the ordinary temperature, the tubes were agitated at certain intervals to insure uniform and equal density in each.

With these precautions to have the conditions of each tube identical save in the magnetism, the series of determinations referred to failed to indicate any influence of the magnetic field, the rotation having been diminished by the same amount in each case.

Experiments upon Racemic acid.

Experiments were also made, under the same conditions, upon racemic acid; it being thought that this, being an equimolecular union of both forms, would be more likely to show an effect when placed in a magnetic field more favorable to the existence of one form than the other. Finally a small percentage of the dextro acid was added in the hope that a little excess of dextro would help the turning, but in neither case was any effect noted.

Experiments on Sodium Chlorate.

Identical considerations led to a like investigation of the crystallization of sodium chlorate in a magnetic field.

Landolt and others have found that ordinarily sodium chlorate will, if undisturbed during spontaneous evaporation, deposit equal quantities of dextro- and laevo-rotatory crystals. The experiments here recorded also confirm this observation in general. Presumably Landolt has not meant that the quantities of dextro and laevo crystals are exactly equal, but that they are practically so, and the number of determinations recorded in this paper, which are only a small part of the number actually made, will show that while there is a tendency to form in equal amounts, there is almost invariably a slight excess of one or the other which often may be considerable, yet to all appearance wholly accidental.

That there is nothing inherent in the individual molecules of this substance which possesses rotary power or which determines the optical activity of the crystalline aggregate, is

pretty well established. Its solution possesses no activity,* and Landolt† has further proved that even the supersaturated solution fails to exhibit the slightest optical activity. Moreover, the form which the crystals assume can be influenced and determined by external causes. Thus it has been pointed out by Gernez‡ and by Landolt,§ in a slightly different way, that if into a supersaturated solution of sodium chlorate some fragments of dextro or laevo crystals are placed, only crystals of a like nature result. These experiments we have repeated but not with the extreme results noted above. While invariably there is a very marked preponderance of the same kind of crystals as those introduced, we have never failed of finding a very considerable quantity of the opposite kind. In order to put on record something more definite in regard to the relative quantities of the two forms deposited under these circumstances, we give in Table I the results of three experiments chosen at random from a considerable number. The rotation was determined by suspending 0.2 gm. of the finely powdered product in a liquid of the same refractive index, according to the method given at the end of this paper.

TABLE I.

Crystals deposited from a saturated solution of NaClO_3 , to which had been added :

	Resultant rotation in divisions of scale.	
1. A sprinkling of powdered <i>dextro</i> crystals -----	+ 4.36 (i. e., 74%)	} Large crop; all small crystals, but distinctly crystalline.
2. A sprinkling of powdered <i>laevo</i> crystals -----	- 4.2 (i. e., 73%)	
3. One large and five small <i>dextro</i> crystals -----	+ 1.86	The six original crystals, which had doubled in size, were removed before testing the rotation.

Rotation of an equal wt. of pure dextro or laevo forms, ± 8.96 division.

It has even been claimed|| that the influence of a small percentage of some other optically active body in solution with the sodium chlorate influences the formation of the crystals, a conclusion which, however, our results as recorded in Table IV, with comment, do not sustain.

* Marbach. Pogg. Ann., xci, 487.

† Ber., xxix, 2, 2410.

‡ Compt. Rend., lxvi, 855.

§ Loc. cit.

|| Pope and Kipping, Chem. News, lxxv, 45.

One convincing proof of the optical indifference of the ultimate molecule of sodium chlorate is found in the fact observed in one of our experiments, that from a filtered solution of pure dextro-rotatory crystals, upon spontaneous evaporation, a very decided *excess* of laevo crystals was obtained.

In the light of these facts as to the optically indifferent nature of the molecule of sodium chlorate and the ease with which its optically active molecular aggregation in the crystalline unit is influenced, it certainly is not unreasonable to suppose that, since this particular molecular aggregation results in the rotation of the plane of polarization in a certain direction, if by means of the magnetic field we introduce forces tending to produce rotation, it should result in a directive action upon the molecules in this field, thus producing a preponderance of those crystals whose optical activity corresponds to the field in which they were formed.

In the theoretical consideration of the possible influence of magnetism upon the formation of optically active structure, it should be recalled that a very characteristic difference exists between natural and magneto-optic rotation, namely, that if a ray of polarized light is caused to retrace its path through an optically active natural substance, the plane is rotated in the opposite direction so that the resultant rotation is zero, while in the magneto-optic phenomenon the rotation is independent of the direction in which the ray travels, the rotation being increased as many times as the ray has passed through the medium. Moreover, structural rotation is active and specifically equal in every direction, while the magnetic rotation varies from a maximum in the direction of the lines of magnetic force, to zero at right angles thereto; in other words, varies as the cosine of the angle which the ray makes with the lines of force. However, the magnetic whirl by itself appears to be incapable of rotating the plane of polarization, at least to any perceptible extent. The molecules of the medium placed in the magnetic field seem to be essential to the phenomenon, from which fact it is evident that the action in the ether which takes place about the lines of magnetic force, causes a change in the orbit or nature of the vibration of the molecule, which consideration would still leave probable, during the period of formation at least, some influence of the magnetic field upon the molecular aggregation in the crystalline unit of a substance such as sodium chlorate, in which there is nothing inherent in the molecule which determines the optical nature of its aggregation.

Nor can this fact, that the natural and magneto-optic rotations are superposable without permanently affecting the structure, be considered conclusive against the supposition, the

experimental investigation of which forms the subject of this paper; unless indeed it should be possible by superposition of the magneto-optic rotation to *completely reverse* the structural rotation, i. e., so that the resultant rotation should be of opposite sense to the original structural rotation, under which circumstances it might be possible that the molecules would rearrange themselves by swinging over into the enantiomorphic forms possessing that rotation, just as by external force the molecules in a crystal of calcite may be made to slide or swing from one position of equilibrium to another, or from one form to its twin, under the influence of pressure; the phenomenon being unaccompanied by any serious disturbance such as the disintegration of the crystal.

However, since the magneto-optic rotation is small, even in the most powerful electro-magnetic fields, the facts observed would appear to be accounted for, and the reversal of the structure would not be expected though an influence might be looked for during the period of formation of the body.

To determine the truth or error of this supposition, as to the possible control of the final product, by securing conditions favorable to one and antagonistic to the other of the enantiomorphic forms, a large number of crops of sodium chlorate crystals were allowed to grow by spontaneous evaporation in magnetic fields with the results recorded in the following tables.*

TABLE II.
Crystals grown *over* N-pole of a vertical bar magnet.

	Crystals.		Excess by		Dextro % by wt.	Remarks.
	No.	Wt.	No.	Wt.		
1. { Dextro --	5	----	--	one crystal	about	All large crystals.
{ Laevo --	9	----	4	not weighed	60	
2. { Dextro --	--	1.232	--	0.675	{ 68.8	{ Dextro crystals larger than the laevo.
{ Laevo --	--	0.557	--	----		
3. { Dextro --	77	0.857	35	0.317	60.9	
{ Laevo --	42	0.540	--	----		
4. { Dextro --	31	0.418	--	0.083	55.5	
{ Laevo --	31	0.335	--	----		

Table II shows the results of four crops obtained over the north pole of a bar magnet. Here the excess of dextro crystals in each case is conspicuous, and taken by themselves these results are misleading. Viewed in the light of the succeeding tables it appears probable that the uniformity here noted is purely accidental.

* A thin ring of vaseline along the sides of the vessel was found very effectual in preventing the creeping of the solution during crystallization.

TABLE III.
(a) Crystals grown *over* S-pole of the vertical bar magnet.

		Crystals.		Excess by		% of Dextro by wt.	Remarks.
		No.	Wt.	No.	Wt.		
1.	{ Dextro..	--	1.258	--	----	42.4	Laevo rather larger. Uncertain, 0.333 grm. ∴ Excess if <i>all</i> this counts as laevo = 0.117 grm.
	{ Laevo ..	--	1.709	--	0.451		
2.	{ Dextro..	30	2.040	--	1.320	73.9	All good size. Dex- tro rather larger.
	{ Laevo ..	64	0.720	34	----		
3.	{ Dextro..	75 ₁	0.510	--	----	43.0	
	{ Laevo ..	77	0.677	2	0.167		
4.	{ Dextro..	58	0.350	10	0.107	59.0	
	{ Laevo ..	48	0.243	--	----		
5.	{ Dextro..	23	1.610	2	0.129	52.1	5 of laevo crystals large, remainder very small.
	{ Laevo ..	21	1.481	--	----		
6.	Resultant rotation	-----	=	- 0.5		47.2	Crystals distinct but small. Determined by method given at end of this paper.
7.	"	"	-----	- 0.1		49.4	
8.	"	"	-----	- 0.03		49.8	
9.	"	"	-----	- 1.96		39.1	

(b) Crystals grown *under* the N-pole.

10.	{ Dextro..	34	0.450	--	----	46.1	All clear and beauti- fully crystallized.
	{ Laevo ..	42	0.525	8	0.075		
11.	{ Dextro..	18	0.880	--	----	35.0	Irregular in size. Un- certain 0.045 grm.
	{ Laevo ..	33	1.633	15	0.753		
12.	Resultant rotation	-----	=	- 3.5		30.5	Crystals distinct but small. Determined by method given at end of the paper.
13.	"	"	-----	- 1.9		39.4	
14.	"	"	-----	- 2.8		34.4	
15.	"	"	-----	- 0.04		49.8	

Here again, especially in (b), a curious preponderance, this time of laevo crystals, is noted: but providing the effect to be sought for is that due to the *direction* of the magnetic whirl the results in (a) and (b) are inconsistent, since in both cases the direction of the lines of force and hence of the magnetic whirl is the same. However, from what has been said in regard to the difference of the structural and magnetic rotations, it is evident that the sense of the resultant activity could not be predicted.

In order to test the effect of a more powerful magnetic field a Jamin magnet was supported vertically, so that a thin glass, flat-bottomed beaker having a diameter marked upon it, could be symmetrically placed over the poles and the crystals formed on each side of the dividing line be separately tested. But the result of a large number of crops so far as the optical activity is concerned was disappointing. While an increased effect might have been expected or at least a verification of the experiments with the bar magnet, the results are

practically identical with those obtained without the use of any magnet.

However, there seemed to be a tendency to group over the poles. Though nothing very definite could be said about the observed arrangement of these clusters, it may be positively asserted that the distribution of the crystals under these circumstances was different from that ordinarily obtained, that is without the use of a magnet.

In order to get a still more intense field the Jamin magnet was supported horizontally with its poles in a vertical line and the crystallization was effected in a small vessel made of tin-foil of just the proper size to fit between the poles, so as to be in the strongest part of the field. Measurements proved the field at this point to be about 800 C. G. S. units. Some difficulty was experienced in getting the crystals to grow in this vessel, but by cutting a plate of thin glass to fit the bottom this difficulty was overcome, doubtless because the glass afforded more nuclei about which the crystals form. A number of crops thus collected failed to reveal any effect of this magnetic field upon the optical property of the crystals.

Crystallization of Sodium Chlorate in Electrostatic Field.

Incidentally the effect of an electrostatic field was also investigated. For this purpose a Leyden jar was charged from an electric machine. The poles from the two surfaces, after being capped by fairly thick glass tubes in order to prevent discharge, were brought as close together as was permitted by the solution contained in a shallow, thin-glass, flat-bottom beaker placed between them. Several preliminary experiments were made, but no particular effect was noted upon the formation or arrangement of the crystals in this field, nor upon the resultant optical activity of the crop of crystals.

Experiments on Ferrous Sulphate.

The tendency of the crystals of sodium chlorate to group over the poles of the magnet, led also to some experiments upon the crystallization of an iron salt in a magnetic field. It was thought that because of its magnetic property the iron would show a more decided effect. A number of experiments fully confirmed this expectation. In each case the grouping over the poles was very conspicuous and unmistakable. There was, however, nothing definite in the arrangement of these crystals or of their axes beyond the marked tendency to form in the strongest part of the magnetic field.

Method of determining the resultant optical activity of a crop of crystals.

There is one point in the determination of the *resultant* optical activity of crops of crystals which does not appear to have been fully appreciated heretofore, which we would specially emphasize. It has been observed* that not all crystals which show a dextro or laevo rotation are necessarily pure forms. At times the twinning is almost if not entirely imperceptible, so that a crystal which may appear homogeneous and as a whole rotates the plane of polarization to the right or to the left, is found not to have the proper specific rotation, showing that in fact it is a combination of both forms with a preponderance of one or the other. It is evident, therefore, that in the determination of the excess of one or the other of the enantiomorphic forms in a crop of crystals, whether the basis of comparison be the number of crystals or their weight, an error might result.

Among the many crops of crystals prepared during this investigation, a number of crystals of this kind appeared, some of which were more or less conspicuous for irregularities in structure and yet to all appearances were decidedly more like a single crystal than an aggregate, but the magnitude of their rotation was not commensurate with their thickness.

Moreover, very often the crystals are small and intergrown to such an extent as to make an accurate investigation of their rotation very tedious and difficult, if not impossible.

It is evident then, from both of these considerations, that greater accuracy and economy of time would result from a direct determination of the resultant rotation of the whole crop. This may be accomplished by the elegant method developed by Landolt,† founded upon Christiansen's experiments,‡ according to which the finely powdered crystals are suspended in a liquid of the same refractive index which has no solvent effect upon them. This method, with some slight modifications which we found desirable, was as follows.

The crystals were finely powdered in an agate mortar, and in order to secure greater uniformity in size and thoroughness of mixture, passed through a very fine sieve. Having the crystals hot at the start greatly facilitates the attrition as well as the sifting. A mixture of absolute alcohol and carbon disulphide in the proportion of one part of the former to two of the latter furnishes a liquid of the same refractive index in which the crystals are entirely insoluble. Commercial "abso-

* Marbach, Pogg. Ann., xci, 486; Landolt, Ber., xxix, 2, 2412.

† Ber., xxix, 2, 2404.

‡ Wied. Ann., xxiii, 298.

lute" alcohol will answer the purpose so far as the transparency of the mixture is concerned, and any slight solvent effect can be eliminated by preparing the mixture in a test tube containing some powdered sodium chlorate, which is further required as an indicator since the carbon bisulphide must be added finally drop by drop till the maximum transparency is secured, then filtering into the polarimeter tube containing the powder to be tested.

The greater specific gravity of the sodium chlorate necessitates continual rotation of the polarimeter tube in order to keep the powder in suspension. This was effected in a very simple way by slipping corks of proper size for the polarimeter over both ends of the tube and turning a slight groove in each, in which ran an endless string from two wheels on an axis directly above. By wrapping the tube with a small piece of sheet lead, sufficient weight was given it to cause a regular and smooth rotation when the wheels from which it hung were rotated by a small electric motor worked with one Grove cell. This simple device makes it possible, with a very little rigging, to rotate a tube in any polarimeter which may be at hand.

Landolt has pointed out that the rotation should be maintained at between 50 and 80 revolutions per minute, in order to have uniform suspension without the centrifugal action.

In all of the experiments in which we employed this method, 0.200 grm. of the sodium chlorate was taken after the whole crop of crystals had been reduced to a uniform powder and thoroughly mixed.

Effect of the presence of optically active substances in the solvent medium.

During the course of this investigation the peculiar results obtained made it seem worth while to repeat the experiments of Pope and Kipping* previously referred to, since the suspicion had arisen that their conclusions may have been based upon insufficient data, just as it might have been inferred from the results recorded in Table II of this paper, had not further experiment failed to verify it, that the magnetic field determined the form of the crystals.

Accordingly a five per cent solution of dextrose was prepared as they have stated and subsequently saturated with sodium chlorate. Three portions of this solution were filtered and allowed at the same time to crystallize by spontaneous evaporation in a place free from vibrations or any apparent cause of disturbance. Curiously each of the three crops was found to have an excess of dextro crystals. Pope and Kipping

* Chem. News, lxxv, 45.

have announced that under these circumstances an invariable excess of laevo crystals should form. Three more crops were grown under the same conditions and curiously again these three all had an excess of laevo crystals. Other crops were then grown and the percentage of dextrose in solution increased, but it was found to have no effect, the crystals coming down one time with an excess of dextro and the next time with an excess of laevo, as is shown by Table IV, results which in no way differ from those obtained where the crystals are formed in the ordinary way.

TABLE IV.

				% of Dextro.	Remarks.	
1.	Resultant rotation	-----	= + 2.84	65.8	First set. Good crop of sharp and clear but small crystals.	
2.	"	"	-----	+ 2.46		
3.	"	"	-----	+ 0.94		
4.	"	"	-----	- 0.37	From mother liquor of 1-3.	
5.	"	"	-----	- 0.7		
6.	"	"	-----	- 1.24		
		Crystals by	Excess by			
		No.	Wt.	No.	Wt.	
7.	{ Dextro--	9 ?	0.670	--	----	Clusters and fragments made number uncertain.
	{ Laevo --	16 ?	0.825	7 ?	0.255	
8.	{ Dextro--	3	1.060	--	0.455	4 large crystals, of which 3 were dextro and 1 laevo; remainder small and all laevo.
	{ Laevo --	13 ?	0.505	10	----	
9.	Resultant rotation	-----	= - 0.55	46.9	From mother liquor of 7-8.	
10.	{ Dextro--	32	1.640	18	0.875	Mother liquor of No. 9 with addition of some of original solution. Large, fine crystals.
	{ Laevo --	14	0.765	--	----	
11.	{ Dextro--	104	1.172	15	0.147	Uncertain, 0.031 gm.
	{ Laevo --	89	1.025	--	----	
					53.3	

Pope and Kipping do not state the number of results upon which they have based their conclusions, but our experience indicates that, whatever be the undetermined cause* of this varying excess of dextro or laevo crystals, whenever several crops are allowed to grow under the same circumstances, each being portions of the same solutions, taken at the same time, the causes acting on each are likely to be the same, and to give rise to an excess of the same kind of crystals in each case. Therefore to determine whether or not any special influence is exerted by extraneous forces a sufficient variety should be given to the experimental conditions to assure the unmistakable revelation of this influence.

* Is it the influence of the first crystal formed?

TABLE V.

Sodium chlorate from saturated solution by spontaneous evaporation.

		Crystals by		Excess by		γ of Dextro.	Remarks.
		No.	Wt.	No.	Wt.		
1.	{ Dextro ..	41	0.870	7	0.37		
	{ Laevo ..	34	0.500	--	--	63.5	
2.	{ Dextro ..	18	0.546	--	--		
	{ Laevo ..	24	0.630	6	0.084	46.4	All clear and large.
3.	{ Dextro ..	30	1.306	--	0.130		Uncertain = 0.130
	{ Laevo ..	30	1.176	--	--	52.6	gram.
4.	{ Dextro ..	4	0.285	--	0.183		
	{ Laevo ..	7	0.102	3	--	73.6	
5.	{ Dextro ..	10	0.612	--	--		Uncertain 0.025
	{ Laevo ..	18	1.127	8	0.515	35.2	gram.
6.	Resultant rotation				= -4.0	27.7	} After evaporating to dryness (spontaneous).
7.	" ..				+0.6	53.3	
8.	" ..				-0.6	46.7	
9.	" ..				-1.4	42.2	

Conclusion.

The results obtained from these experiments show no marked and indisputable evidence of the influence of the magnetic field upon optically active structure. However, a review of the results seems to indicate a disturbance of the equilibrium by the magnetic field which results in a rather greater variation from the neutral crop of sodium chlorate crystals than is ordinarily obtained, but without revealing any definite influence in regard to the *direction* of the resultant rotation.

It might appear that a force however feeble should be sufficient to exert a directive action upon the substance during the period of formation, which, if true, gives the results previously discussed the greater weight, since even the strongest magnetic fields employed have failed to control the *direction* of the resultant activity.

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