

ethyl alcohol containing a very little water. 691 parts of the salt are soluble in 1000 parts of water at 80° C. and 147 parts are soluble in 1000 parts of water at 27° C. On being heated in the air-bath at 100°–110° C. it becomes somewhat lighter in color and loses in weight corresponding to five molecules of water of crystallization.

0.1792 gram of the substance yielded 0.0167 gram of water and 0.0499 gram of barium sulphate.

	Calculated for (NO ₂ .C ₁₂ H ₇ O.CH ₃ .SO ₃) ₂ Ba+5H ₂ O.	Found.
Barium	16.25	16.35
Water	9.54	9.33

This study is being continued and extended to the reaction between parabromnitrobenzene and the cresols.

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OPTICAL ROTATIONS OF CERTAIN TARTRATES IN GLYCEROL.

By J. H. LONG.

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NEARLY all active substances exhibit different rotations in different solvents. In some cases the causes of these variations, are known while in other and numerous instances no satisfactory explanation of the variable activity has yet been given. The several important factors in this variation in specific rotation have been grouped by Landolt as follows :

- a. Electrolytic dissociation in aqueous solution.
- b. Formation or breaking down of molecular aggregations.
- c. Presence of complex so-called crystal molecules in solution.
- d. Formation of hydrates or corresponding bodies with solvent.
- e. Hydrolysis.

It was pointed out by Landolt, and confirmed by Oudemans, that in dilute solutions the molecular rotations of salts of active acids are independent of the base combined with the acid, and that in salts of active bases the molecular rotations are independent of the inactive acid. This is well illustrated by the following table in which $[M]_D$ refers to the molecular rotation.

	[<i>M</i>] _D .
(NH ₄) ₂ C ₄ H ₄ O ₆	63.0
Na ₂ C ₄ H ₄ O ₆	59.9
K ₂ C ₄ H ₄ O ₆	64.4
NaNH ₄ C ₄ H ₄ O ₆	61.7
KNH ₄ C ₄ H ₄ O ₆	63.8
KNaC ₄ H ₄ O ₆	62.4
MgC ₄ H ₄ O ₆	61.7

For a number of solutions containing thallium tartrate and thallium double tartrates, I found molecular rotations much smaller than these for the higher concentrations but approaching them on increasing dilution.¹

Hädrich, in 1893,² gave the most plausible explanation of this behavior when he showed by conductivity experiments that the variations in molecular rotation keep pace with variations in the degree of ionization. He pointed out that for many cases of dissolved active salts the molecular rotation in dilute solution is independent of the inactive ion.

From this standpoint it is of interest to note the behavior of bodies in glycerol in which solvent the degree of ionization must be relatively small. The compounds which I have examined to test this were the following: potassium sodium tartrate, potassium antimonyl tartrate, potassium boryltartrate, ammonium tartrate, ammonium hydrogen tartrate, and ammonium antimonyl tartrate. These salts were all prepared in condition of high purity and were dissolved in a special glycerol kindly prepared for me by Dr. A. G. Manns, chief chemist of Armour & Co., to whom my thanks are due. This glycerol was not only practically anhydrous but was remarkably free from traces of other bodies.

It is difficult to secure clear crystals of the ammonium antimonyl tartrate, as on concentration of the solution a gummy mass is usually obtained. But after many trials one solution deposited an abundant crop of crystals, which by determination of the antimony and the water were found to have the composition (NH₄)(SbO)C₄H₄O₆ + ½H₂O. Another product secured had approximately the composition (NH₄)(SbO)C₄H₄O₆ + 2½H₂O.

The tartrates of ammonium and the potassium boryltartrate were made in the laboratory by well-known methods. The following table contains the results of polarizations made partly with

¹ *Am. J. Sci. and Arts*, **38**, 264.

² *Ztschr. phys. Chem.*, **12**, 476.

the large Landolt-Lippich instrument in a 400 mm. tube, and partly in a Laurent instrument from Schmidt and Haensch with a 200 mm. tube.

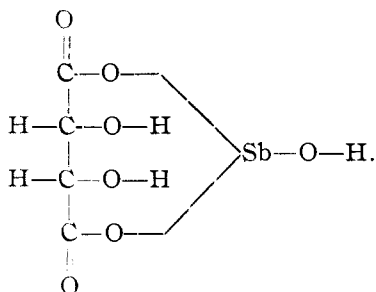
Salt.	$[\alpha]_D^{20}$ for water.	$[\alpha]_D^{20}$ for glycerol.
$\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O} \dots\dots\dots$	$22.1^\circ \quad c = 5 \text{ to } 30$	$28.85^\circ \quad c = 5$ $28.35^\circ \quad c = 10$ $27.87^\circ \quad c = 15$ $27.40^\circ \quad c = 20$ $26.96^\circ \quad c = 25$
$\text{KSbOC}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O} \dots\dots\dots$	$140.69^\circ \quad c = 2$ $141.27^\circ \quad c = 5$ $141.40^\circ \quad c = 6$	$139.25^\circ \quad c = 2$ $141.17^\circ \quad c = 3$ $143.75^\circ \quad c = 4$
$\text{KBOC}_4\text{H}_4\text{O}_6 \dots\dots\dots$	$58.10^\circ \quad c = 5$	$30.9^\circ \quad c = 5$
$(\text{NH}_4)_2\text{C}_4\text{H}_4\text{O}_6 \dots\dots\dots$	$34.50^\circ \quad c = 5$	$43.50^\circ \quad c = 4$
$(\text{NH}_4)\text{HC}_4\text{H}_4\text{O}_6 \dots\dots\dots$	$26.0^\circ \quad c = 1.5$	$27.7^\circ \quad c = 0.75$
$(\text{NH}_4)\text{SbOC}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O} \dots\dots$	$150.0^\circ \quad c = 5$	$146.10^\circ \quad c = 3$ $146.25^\circ \quad c = 4$
$\text{NH}_4\text{SbOC}_4\text{H}_4\text{O}_6 \cdot 2\frac{1}{2}\text{H}_2\text{O} \dots\dots$	$115.7^\circ \quad c = 5$	$109.37^\circ \quad c = 4$

It will be observed in this table that the values of the specific rotations obtained in glycerol solution for potassium sodium tartrate, ammonium tartrate and ammonium hydrogen tartrate are greater than the rotations found in aqueous solution. In the first two cases the differences are extremely marked and the active ion is probably no longer the simple group, $\text{C}_4\text{H}_4\text{O}_6$. It is interesting to note in the case of Rochelle salt that the specific rotation is greatest in the glycerol solution of lowest concentration, or greatest degree of separation into single molecules.

The behavior of the two antimonyl tartrates is the most characteristic and important. We have here very high specific rotations in water, and but slightly different in glycerol. For the first of these substances Hädrich¹ has shown that there is almost no dissociation, and it is evident that the same ion is active in both aqueous and glycerol solutions. The molecular rotations of the two bodies in water are almost identical, but for the ammonium salt the molecular rotation in glycerol is a little lower. This concordant behavior naturally suggests the existence of a peculiar acid as active in these salts, and this may be, as Clarke's investigations² of some years ago seemed to prove, a body of the formula

¹ *Loc. cit.*

² *Am. Chem. J.*, **2**, 319.



The heavy ion of this acid has about seven times the effect on the polarized ray that is exerted by the lighter ion of the ordinary tartaric acid in both media.

But the case is different with the potassium boryltartrate, the composition of which has usually been assumed as similar to that of the antimony compound. We have here a much lower rotation in glycerol than in water, indicating the presence of different active ions in the two media. By hydrolysis in aqueous solution, as found by Hädrich,¹ the rotation decreases very rapidly and finally approaches that of the simpler ion, $\text{C}_4\text{H}_4\text{O}_6$. It is likely therefore that this body is not perfectly analogous to tartar emetic, as in their electrical and optical behavior the arsenyl tartrates are likewise not.

It is well-known that glycerol is a remarkably good solvent for boric acid, and the low rotation of the borotartrate in that medium may possibly be accounted for by assuming that in the solution the whole or a part of the boric acid radical is withdrawn to form a glycerol compound. This kind of hydrolysis would leave then a simple tartrate. The molecular rotation calculated from the glycerol solution is almost normal which lends color to the assumption, while that from the water solution is nearly twice as great.

The main points shown then with reference to the glycerol solutions are these: The simple metallic tartrates examined dissolve in glycerol and show a larger specific rotation than in water. The antimony tartrates, which are but slightly dissociated, show nearly the same rotation in water and glycerol, and their behavior in general suggests a composition different from that usually assumed. Potassium boryltartrate shows in glycerol a much lower

¹ *Loc. cit.*

rotation than in water, the calculated specific rotation suggesting the presence of the simple tartrate in the glycerol solution.

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NOTE ON THE DETERMINATION OF SILICON IN STEEL.

BY GEORGE AUCHY.

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ALTHOUGH it has been mentioned by Dudley that silicon results in steel by Drown's method are apt to be low, on account of the iron sulphate enclosing and protecting the silicic acid from the dehydrating action of the sulphuric acid, it is probable that this fact is one not generally appreciated by chemists.

When the method is used for pig iron, as was originally intended by its author, there is no error from this cause less;¹ but in steel the loss amounts to from 0.01 per cent. to 0.035 per cent. silicon in medium silicon (0.15 to 0.20 per cent.) steels, which is too much to be ignored. Dr. Dudley thinks that it may be prevented by taking great pains to insure sufficient contact by stirring. Four experiments made by the writer, in which five minutes' stirring in each case was done after the appearance of sulphuric fumes, showed this to be true, only 0.006 per cent. silicon in each case being lost. But in a busy laboratory with many silicon determinations being made, or with much other work demanding the attention of the operator, this stirring adds considerably to the labor of the method, and the time it requires can hardly be allowed. Says Dr. Dudley: "If by some modification the iron salts could be kept in solution until the silica is rendered quite insoluble, it would apparently be a decided step forward with this method."

Several years ago the writer found that if aqua regia be used in the method instead of nitric acid alone, and the proportion of strong sulphuric acid be about 3.2 cc. per gram of drillings,² the iron salt in that case did not separate out until just a little before

¹ There is loss, it is true, of about 0.10 to 0.15 per cent. silicon in high silicon pig, but it is due to the same cause (whatever this cause may be) that in silicate analysis brings the result too low. It is a well-known fact that from 1.5 to 3 per cent. of the total silica of silicates remains in the filtrate from the first silica separation, no matter what method of dehydration be employed, or how many evaporations be made before filtration (Cameron: *Chem. News*, 69, 171). We should therefore expect the same proportion of loss in pig iron and steel analysis, or about 0.006 per cent. silicon in a 0.20 per cent. silicon steel, and about 0.10 per cent. in a 3 per cent. silicon pig iron.

² The liquid boiled down rapidly in a capacious covered casserole (evaporating dishes do not serve) on a very hot plate.