THE APPLICATION OF POLARIMETRY TO THE ESTIMATION OF TARTARIC ACID IN COMMERCIAL PRODUCTS.[1]

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In comparing the optical rotation of the sugars with that of active substances generally, we meet with one great point of difference. While concentration and the presence of foreign substances play only a subordinate part in the rotation of the former, so that their influence may usually be ignored, in the case of other active substances the effects of these disturbing factors may be extremely complex. The object of the present research has been to investigate the influence of various commonly occurring substances on the rotation of tartaric acid, and, by taking these effects into account, to devise methods for the polarimetric estimation of tartaric acid in its chief commercial compounds.

Tartaric acid, in aqueous solution, rotates the plane of polarization to the right. Strong acids slightly decrease this rotation. The rotation of the salts is, in general, a little greater than that of the free acid, and, in case of dilute solutions, is independent of the nature of the base.

The facts, so far, are in accordance with the hypothesis of electrolytic dissociation. There are, however, a number of substances which exert a much greater effect on the rotation, and whose action is best explained on the assumption of the formation of complex molecules. As early as 1837 Biot observed that borax increased the rotation of tartaric acid, and subsequently Gernez[2] and others pointed out that the acids of arsenic, antimony, molybdenum and tungsten, also the salts of beryllium and uranium, exercised a similar influence.

The present writers, besides confirming the observations of the earlier experimenters, have studied the influence of a number of other elements on the rotation of tartaric acid. The following is a summary of the conclusions arrived at, the results given being the effects noted, except where otherwise stated, in the presence of ex-

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[1] A preliminary note on this subject was published in the Appendix to Bulletin No. 65 (p. 157) of the Bureau of Chemistry, U. S. Department of Agriculture. In the present paper fuller details are given, and some slight changes have been made in the methods of analysis.

[2] *Compt. rend.*, **105**, 803 (1887).

cess of ammonia. Where the effects are described as small, the slight changes observed in the rotation were often within the limits of experimental error.

The Alkali Metals.—Lithium, sodium, potassium and caesium were found to have a small effect only on the rotation.

Copper and Silver.—These metals, the former in the presence of potassium cyanide, had practically no effect on the rotation.

The Alkaline Earth Metals.—Although the tartrates in this group are nearly insoluble, small quantities of the salts of calcium, strontium and barium may be added to an ammoniacal solution of tartaric acid and the solution polarized before the tartrates have time to crystallize out. It was found that, while calcium exercised an insignificant effect only, strontium and barium lowered the rotation.

Magnesium, Zinc and Cadmium.—The first two had a small effect only; cadmium increased the rotation.

Boron and Aluminum.—Boracic acid (in alkaline solution) lowered the rotation; compounds of aluminum had the opposite effect.

Tin and Lead.—Both stannous and stannic salts increased the rotation; lead diminished it.

Arsenic, Antimony and Bismuth.—These all lowered the rotation in the presence of an excess of ammonia. It has long been known that a solution of tartar emetic has a much higher rotation than a solution containing the equivalent quantity of tartaric acid. The authors found that when ammonia is added in excess to an aqueous solution of tartar emetic part only of the antimony is precipitated. The filtrate then has a *lower* rotation than an equivalent solution of ammonium tartrate. Similarly, if an ammoniacal solution of cream of tartar is shaken up with excess of antimony oxide, a certain quantity of antimony passes into solution. The solution so obtained has a lower rotation than the original cream of tartar solution, its rotation corresponding, in fact, to that of the filtrate referred to above—provided, of course, the solutions of cream of tartar and tartar emetic are made of equivalent strength.

Manganese.—Manganese sulphate, added to an ammoniacal solution of tartaric acid and made up to volume with freshly boiled water, gives a colorless solution, and the rotation of the tartaric acid is practically unaffected. But if this mixture is exposed to the air it very quickly turns to a deep, reddish brown, and a considerable decrease in the rotation takes place.

Iron, Nickel and Cobalt.—Iron and nickel compounds increase the rotation, while salts of cobalt have a lowering effect. Owing to the fact that these metals give deeply colored solutions with ammoniacal tartaric acid, only very small quantities of the salts can be added to the solutions for polarization.

Non-Metallic Radicals.—The majority of the common acids have little or no effect on the rotation of tartaric acid. Observations were made on the following: Chlorides, bromides, iodides, cyanides, chlorates, carbonates, nitrates, phosphates, sulphates, acetates, oxalates, and citrates.

As in the case of antimony and certain other elements, the magnitude of the effect produced by molybdic acid was found to depend very largely on whether the solution was acid, neutral, or alkaline.

Considering the common occurrence of iron and aluminum in commercial products, it is unnecessary to emphasize the importance of a knowledge of the effects of these metals in estimating tartaric acid by the polariscope. From the fact that the alkaline tartrates dissolve the hydroxides of iron and aluminum, even in the presence of ammonia, it might be anticipated that these metals would influence the optical activity of tartaric acid by the formation of complex molecules. It was found indeed that even the comparatively small quantities of iron and aluminum, such as occur as impurities in the superphosphates employed in baking-powders, exerted sufficient influence to invalidate determinations based on direct measurements of the rotation of the tartaric acid in the mixture (Appendix 27 and 40).

The chief commercial products containing tartaric acid as an essential ingredient are: cream of tartar, cream of tartar "compounds", tartar baking-powders and certain pharmaceutical salts and mixtures. The latter include not only the official preparations of the different pharmacopoeias, but also the proprietary effervescing remedies, etc. These different materials may be conveniently classed into three main groups, corresponding to the methods of analysis described below.

Group I.—Tartaric acid and mixtures containing tartaric acid and calcium tartrate, but no other optically active material, or any substance, such as iron or aluminum, capable of modifying the rotation of tartaric acid in ammoniacal solution. To this class belong Rochelle salt, potassium tartrate, cream of tartar, and many of the effervescing preparations of the pharmacopoeias.

Group II.—Mixtures containing both tartaric acid and sugar. Some of the officinal effervescing compounds and most of the similar patent preparations fall into this division.

Group III.—Mixtures containing tartaric acid with one or more modifying agents, or traces of optically active substances. This group comprises materials of which alum is an ingredient, mixtures containing traces of iron or aluminum, and those of which starch is a constituent. Consequently all tartar baking-powders and mixtures of cream of tartar with cream of tartar substitutes are included in this group. For apart from the fact that the latter are liable to contain iron and alumina, the authors found that the starch mixed with baking-powders[1] and superphosphates almost invariably contained traces of active substances soluble in cold water (Appendix 87-101).

METHODS OF ANALYSIS.

In the following section, working details of the several methods are given, corresponding to the classification indicated above. In the Appendix (109-112) examples of the different methods will be found.

Group I.—The method employed in the analysis of materials of this group is based on the fact that in the presence of excess of ammonia the rotation of the solution is proportional to the concentration of the tartaric acid, and is independent of the other bases and acids present.

(1) *The Tartrates Present are Completely Soluble in Dilute Ammonia.*—A weighed quantity of the substance containing not more than 2 grams tartaric acid is placed in a 50 cc. measuring flask, moistened with 3 or 4 cc. of water, and concentrated ammonia (sp. gr. 0.924) added in quantity sufficient to neutralize all acid that may be present and leave about 2 cc. in excess. The

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[1] There are, however, a few tartar baking-powders on the market which are entirely free from starch. These may be classed in Group I.

actual amount of the excess is not of importance, but a greater quantity than 2 cc. of free ammonia should be avoided. The solution is then made up to 50 cc. with water, filtered, if necessary, through a dry filter, and the rotation read in a 200 mm. tube.

The amount of tartaric acid ($C_4H_6O_6$) in grams (y) in the material taken is given by the formula

$$y = 0.00519x,$$

where x is the rotation in minutes.

(2) *The Mixture Contains Insoluble Calcium Tartrate.*—In this case proceed as follows: Treat 2 grams of the sample (or an amount containing not more than 2 grams of tartaric acid) in a small beaker with 30 cc. water and 20 drops concentrated hydrochloric acid. Heat gently till both the potassium and calcium tartrates have passed into solution, and then, while still hot, add 4 cc. concentrated ammonia (or enough to produce an ammoniacal smelling liquid) and about 0.2 gram sodium phosphate dissolved in a little water. Transfer to a 50 cc. measuring flask, cool, make up to the mark with water, filter through a dry filter, and polarize the filtrate in a 200 mm. tube. The tartaric acid is calculated by the formula given under (1).

The precipitation of the calcium by sodium phosphate is not absolutely necessary, but, when this is not done, in cases where the proportion of calcium tartrate in the sample is high, there is a great tendency for the calcium tartrate to crystallize out from the ammoniacal solution before the reading is made.

The tartaric acid present as bitartrate of potash may be determined by proceeding as in (1), the calcium tartrate being practically insoluble in cold ammonia solution.

The tartaric acid in the calcium tartrate may be obtained with sufficient accuracy for most purposes from the difference between the results in (1) and (2). If more exact results are required, the residue insoluble in ammonia in (1) may be dissolved in a little hydrochloric acid, and treated as above with sodium phosphate and ammonia.

It may be noted that the method given below under Group III, is applicable to this group also, but in most cases the course described above will be found more simple.

Group II.—The method of analysis for substances of this group is essentially the same as the one just described, but takes into account the presence of sugar in the mixtures. In ammoniacal solutions containing both tartaric acid and sugar, the rotation of each is unaffected by the presence of the other (Appendix 45-46), and consequently the rotation of the tartaric acid may be obtained by subtracting from the total rotation the part due to the sugar. The cane-sugar may be determined by Clerget's method, but in carrying out the process the additional precautions described below must be observed.

Although magnesium sulphate, even in comparatively large proportions, has but little effect on the rotation of solutions of sugar and of tartaric acid alone, it is a curious fact that the rotation of these two substances when present together is considerably decreased by the addition of magnesium sulphate (Appendix 22 and 67). In "effervescing magnesium sulphate", and in other mixtures where magnesia is present, it is therefore necessary to precipitate the magnesium by means of sodium phosphate and ammonia before making the polarimetric readings.

In carrying out the inversion of cane-sugar, moreover, it must be remembered that in order to effect complete inversion in ten minutes, without further decomposing the products of hydrolysis, a fairly definite concentration of free hydrochloric acid is required, and that when salts of weak acids (such as citric and tartaric) are present, it is only the hydrochloric acid added over and above the amount necessary to completely set free all these weak acids that is to be considered capable of effecting the inversion in the prescribed time. The difficulty of finding the point where hydrochloric acid is free in the solution was overcome by the use of methyl violet as indicator. This indicator was found to be quite unaffected by citric and tartaric acids, yet sufficiently sensitive to hydrochloric acid for the purpose in hand.

It is also to be noted that in some commercial samples the sugar is already partly in the inverted condition. In such cases the reducing sugar must be determined by Fehling's process, and due allowance made for it.

(1) *Magnesium Absent.*—An amount of the sample containing not more than 8 grams of tartaric acid or 5 grams of sugar is dissolved in cold water and made up to 100 cc. (Solution *A*).

Twenty-five cc. of this solution are pipetted into a 50 cc. measuring flask with a few drops of methyl orange solution and, if alkaline, approximately neutralized with concentrated hydrochloric acid. One cc. concentrated ammonia (sp. gr. 0.924) is then put in, the flask filled to the mark, and the solution polarized in a 200 mm. tube (reading a).

To another 25 cc. of Solution *A* a little methyl violet solution is added, and concentrated hydrochloric acid run in from a burette till the indicator turns pale green, the amount of acid required being noted.

A third 25 cc. portion of Solution *A* is placed in a 50 cc. measuring flask (without methyl violet, the color of which would interfere with the polarimetric readings) and a quantity of hydrochloric acid run in equal to the amount required in the last experiment, *plus* 2.5 cc. The flask and contents are next heated to 70° C. for ten minutes, as in the ordinary Clerget process, and immediately cooled to ordinary temperature. A little methyl orange is then added and enough ammonia to turn the indicator yellow and leave about 1 cc. in excess. Finally, after making up the volume to 50 cc., and cooling to the temperature of the room, the solution is polarized in a 200 mm. tube (reading b).

The weight of sugar (z) in the amount of the sample taken is given by the formula

$$z = \frac{2(a - b)\,1.254}{142 - 0.5t},$$

where t is the temperature and a and b are the readings expressed in minutes.

The rotation of z grams uninverted sugar is $79.7z$, and the rotation (x) of the tartaric acid is consequently

$$x = 2a - 79.7z,$$

from which the tartaric acid (y) is found by the formula

$$y = 4 \times 0.00519x \text{ (see 1)}.$$

(2) *Magnesium Present.*—A solution of the substance is prepared as in (1) above (Solution *A*). Ten cc. of this solution are placed in a beaker and about 25 cc. of water and 4 cc. of concentrated ammonia added. If a precipitate forms, enough ammonium chloride is added to keep it in solution. The magnesium is then precipitated by sodium phosphate. Since it is desirable to keep

the bulk of the solution as small as possible, and to avoid unnecessary excess of salts in solution, the required quantity of phosphate (about 8 grams $Na_2HPO_4 10H_2O$ to every 5 grams $MgSO_4 7H_2O$) should be dissolved in a small volume of hot water (10 cc. to 8 grams phosphate) and the solution added gradually while hot. After the precipitate has completely formed it is filtered off on the filter-pump and washed with small quantities of water, care being taken not to bring the total volume to more than 100 cc. Even a fairly bulky precipitate can be sufficiently washed in this way.

The filtrate is now made up to 100 cc. (Solution *B*), and part of this solution read at once in the polarimeter (reading *c*.)

Twenty-five cc. of Solution *B* are now titrated with hydrochloric acid and methyl violet, and another 25 cc. inverted as described under (1), made up to 50 cc. and polarized (reading *d*).

The weight of sugar (z) in the substance taken is

$$z = \frac{10\,(c - 2d)\ 1.254}{142 - 0.5\,t}.$$

The rotation of the tartaric acid is, therefore,

$$x = 10c - 79.7z$$

and the weight of tartaric acid,

$$y = 4 \times 0.00519x.$$

The directions given for this method are, of course, subject to slight modification depending on the relative amount of magnesium present; in some cases, for instance, more ammonia than 6 cc. might be necessary. It may be stated, however, that the amount of free ammonia in the uninverted solution is not of much consequence, but in the inverted solution the excess should not exceed 1 cc. (Appendix 51-66).

On account of the bulk of the magnesium precipitate, and because large quantities of neutral salts affect the rotation, it is necessary to work with weaker solutions when magnesium is present. For this reason only 10 cc. of Solution *A* are taken in (2).

In the Appendix test analyses are given of some effervescing mixtures, as illustrating the methods used in Group II. It may, however, be pointed out here that the results of the analyses of commercial *granulated* effervescing preparations do not agree with results calculated from the formulas in the pharmacopoeias. This is owing to the fact that a considerable amount of decomposition takes place in the process of manufacture. Hence tartaric acid, and all other constituents with the exception of carbon dioxide, come out higher in the analysis than in the result calculated from the formula. This consideration does not apply to the test analyses given, as in these the whole of the mixture made up was taken for analysis, and no attempt was made to imitate exactly the "granulated" commercial article.

Group III.—Direct readings of rotation in ammoniacal solution are inadmissible in analyses of the substances of this group on account of the influence of iron and aluminum on the rotation of tartaric acid, and owing to the small, but unknown, rotation of the trace of inverted starch (Appendix 27, 40, 87-101).

Accurate determinations may, however, be made in the presence of excess of ammonium molybdate in neutral solution. The latter salt not only annuls the effect of iron and aluminum, but also has the property of greatly increasing the rotation of tartaric acid, so that by its use the small rotation of the inverted starch is rendered insignificant. It is to be noted, however, that this increased rotation is very sensitive to the presence of acid and alkali, and is, moreover, modified by the presence of phosphates. It therefore becomes necessary to first remove the phosphoric acid, and then to bring the solution to a definite state of neutrality. These results are attained by the following procedure, the details of which must be strictly adhered to.

Solutions Required.—The following solutions must be prepared, but need not be made up very accurately.

Molybdate solution, 44 grams ammonium molybdate in 250 cc.
Citric acid solution, 50 grams citric acid in 500 cc.
Magnesium sulphate solution, 60 grams $MgSO_4.7H_2O$ in 500 cc.
Ammonia solution, 165 cc. ammonia (sp. gr. 0.924) in 500 cc.
Hydrochloric acid, 60 cc. concentrated acid in 500 cc.

An amount of the sample containing not more than 0.2 gram tartaric acid, not more than 0.3 gram alum and not more than 0.3 gram calcium acid phosphate is weighed into a dry flask. To this, 10 cc. citric acid and 10 cc. molybdate solution are added, and allowed to react with the substance for ten or fifteen minutes, shaking the liquid occasionally. Next, 5 cc. magnesium sulphate solution are added and 10 cc. ammonia solution are stirred in. These solutions are all measured exactly, so that the total volume will be 35 cc. If the original substance is a liquid, room may be made for it by taking a smaller volume of stronger ammonia. After a few minutes (not more than an hour), the solution is filtered through a dry filter, a slight turbidity of the filtrate being disregarded. To 20 cc. of the filtrate, measured into a 50 cc. flask, are then added a few drops of methyl orange, and hydrochloric acid from a burette till the pink color appears (two or three drops too much or too little are of no consequence). Finally 10 cc. more molybdate solution are added to the pink solution, which now becomes colorless or pale yellow, and water to make up the volume to 50 cc. This solution, after filtering if necessary, is polarized in a 200 mm. tube.

The amount of tartaric acid in grams (y) in the weight of sample taken is given by the following formula, in which x is the rotation in minutes (Appendix 105-108).

$$y = 0.00121x.$$

A word of explanation may be given here with regard to the function of the citric acid in the above method. It was found that although under ordinary circumstances tartaric acid entirely prevents the precipitation of aluminum hydroxide by ammonia, this is not the case when molybdate is present, and, consequently, when the ammonia was added to the solution to precipitate the magnesium ammonium phosphate, the aluminum was simultaneously thrown down. This not only produced a liquid which was extremely difficult to filter, but the precipitate appeared to carry down a considerable quantity of the tartaric acid. The addition of citric acid prevents the precipitation of the aluminum without interfering with the formation of the magnesium phosphate; indeed, this precipitate may be ignited and used for the quantitative determination of the phosphoric acid in the sample.

It may also be mentioned in this connection that the removal of the phosphoric acid by means of molybdate in acid solution is not practicable, for when sufficient acid is added to effect this result, the molybdic acid rapidly oxidizes the tartaric acid and is itself converted into one of the blue reduction products.

The above methods cover most of the cases that occur in practice. Samples containing tartar emetic cannot, however, be analyzed by these methods (without modification), and great caution should be exercised in extending any of the methods described to cases involving the presence of foreign substances not taken into account in this paper.

APPENDIX.

In this section some of the experimental data are recorded. The readings were made mostly with a Schmidt & Haensch half-shadow instrument, graduated in degrees and minutes. A 200 mm. tube was used for the readings. The light was supplied by a flame in which sodium chlorate was heated on platinum. It was found that the readings for tartaric acid were practically independent of the temperature, and, except where otherwise indicated, the observations were made at room temperature. The rotations recorded in the following tables are expressed in minutes. In this section TH_2 stands for tartaric acid; KHT, potassium bitartrate; CaT, calcium tartrate tetra-hydrate; NH_3, ammonia of sp. gr. 0.924 (11 normal); HCl, concentrated hydrochloric acid, 9.2 normal; alum, crystallized ammonia alum.

The potassium bitartrate and calcium tartrate used in these experiments were specially prepared for this work, and found by analysis to be almost absolutely pure.

THE EFFECT OF VARIOUS SUBSTANCES ON THE ROTATION OF TARTARIC ACID IN AMMONIACAL SOLUTION.

					Rotation.
(1)	4 g. TH_2	4 cc. NH_3		in 100 cc.	193.5
(2)	4 g. TH_2	8 cc. NH_3		in 100 cc.	194
(3)	4 g. TH_2	40 cc. NH_3		in 100 cc.	193
(4)	4 g. TH_2	8 cc. NH_3	4 g. ammonium chloride	in 100 cc.	196
(5)	4 g. TH_2	8 cc. NH_3	4 g. ammonium nitrate .	in 100 cc.	194
(6)	4 g. TH_2	8 cc. NH_3	4 g. ammonium sulphate	in 100 cc.	196
(7)	4 g. TH_2	8 cc. NH_3	4 g. ammonium oxalate	in 100 cc.	192
(8)	4 g. TH_2	8 cc. NH_3	4 g. lithium chloride ..	in 100 cc.	187
(9)	4 g. TH_2	8 cc. NH_3	4 g. sodium chloride ..	in 100 cc.	194
(10)	4 g. TH_2	8 cc. NH_3	4 g. sodium phosphate .	in 100 cc.	188
(11)	4 g. TH_2	8 cc. NH_3	4 g. sodium acetate	in 100 cc.	186
(12)	4 g. TH_2	8 cc. NH_3	4 g. potassium chloride	in 100 cc.	197
(13)	4 g. TH_2	8 cc. NH_3	4 g. potassium bromide	in 100 cc.	194
(14)	4 g. TH_2	8 cc. NH_3	4 g. potassium iodide...	in 100 cc.	194

					Rotation.
(15)	4 g. TH_2	8 cc. NH_3	4 g. potassium cyanide	in 100 cc.	194
(16)	4 g. TH_2	8 cc. NH_3	4 g. potassium chlorate	in 100 cc.	192
(17)	4 g. TH_2	8 cc. NH_3	4 g. potassium nitrate	in 100 cc.	196
(18)	4 g. TH_2	8 cc. NH_3	4 g. potassium sulphate	in 100 cc.	197
(19)	4 g. TH_2	8 cc. NH_3	1 g. caesium sulphate	in 100 cc.	197
(20)	4 g. TH_2	8 cc. NH_3	4 g. copper sulphate + potassium cyanide	in 100 cc.	196
(21)	4 g. TH_2	8 cc. NH_3	4 g. silver nitrate	in 100 cc.	197
(22)	4 g. TH_2	8 cc. NH_3	4 g. magnesium sulphate	in 100 cc.	194
(23)	4 g. TH_2	8 cc. NH_3	4 g. zinc sulphate	in 100 cc.	194
(24)	4 g. TH_2	8 cc. NH_3	4 g. zinc acetate	in 100 cc.	190
(25)	4 g. TH_2	8 cc. NH_3	4 g. cadmium sulphate	in 100 cc.	220
(26)	4 g. TH_2	8 cc. NH_3	4 g. boracic acid	in 100 cc.	150
(27)	4 g. TH_2	8 cc. NH_3	2 g. alum	in 100 cc.	246
(28)	4 g. TH_2	8 cc. NH_3	4 g. stannic chloride	in 100 cc.	305
(29)	4 g. TH_2	8 cc. NH_3	4 g. stannous chloride (precipitate filtered off)	in 100 cc.	233
(30)	4 g. TH_2	16 cc. NH_3	2 g. lead acetate	in 100 cc.	83
(31)	4 g. TH_2	8 cc. NH_3	4 g. sodium arsenite	in 100 cc.	179
(32)	4 g. TH_2	8 cc. NH_3	4 g. sodium arsenate	in 100 cc.	185
(33)	4 g. TH_2	14 cc. NH_3	4 g. bismuth subnitrate + 6 cc. hydrochloric acid	in 100 cc.	25
(34)	4 g. TH_2	28 cc. NH_3	4 g. bismuth subnitrate + 6 cc. hydrochloric acid	in 100 cc.	114
(35)	4 g. TH_2	8 cc. NH_3	excess of antimony oxide	in 100 cc.	177
(36)	8.86 g. tartar emetic, ammonia in excess (filtrate)			in 100 cc.	178
(37)	4 g. TH_2	8 cc. NH_3	4 g. manganese sulphate	in 100 cc.	193
(38)	The same exposed to the air for a few minutes				167
(39)	4 g. TH_2	8 cc. NH_3	0.1 g. manganese sulphate after exposure	in 100 cc.	183
(40)	4 g. TH_2	8 cc. NH_3	0.02 g. ferric chloride	in 100 cc.	210
(41)	4 g. TH_2	8 cc. NH_3	0.3 g. nickel sulphate	in 100 cc.	202
(42)	4 g. TH_2	8 cc. NH_3	0.1 g. cobalt nitrate	in 100 cc.	189
(43)	4 g. TH_2	8 cc. NH_3	4 g. citric acid	in 100 cc.	192
(44)	4 g. TH_2	16 cc. NH_3	4 g. citric acid	in 100 cc.	194
(45)	4 g. TH_2	8 cc. NH_3	4 g. cane-sugar	in 100 cc.	508
(46)		8 cc. NH_3	4 g. cane-sugar	in 100 cc.	314
	Difference between (45) and (46) due to 4 g. TH_2				194

THE RELATION BETWEEN THE ROTATION AND CONCENTRATION OF TARTARIC ACID IN AMMONIACAL SOLUTION.

(47)	1 g. TH_2	8 cc. NH_3	in 100 cc.	48
(48)	2 g. TH_2	8 cc. NH_3	in 100 cc.	95.5
(49)	3 g. TH_2	8 cc. NH_3	in 100 cc.	145.5
(50)	4 g. TH_2	8 cc. NH_3	in 100 cc.	193.5

Effect of Ammonia and Ammonium Chloride on the Rotation of Cane-Sugar.

(51) 8.17 g. cane-sugar .... in 100 cc. 647
(52) 8.17 g. cane-sugar 8 cc. NH_3 .... in 100 cc. 641

The Same in More Dilute Solution.

(55) 2 g. cane-sugar .... in 100 cc. 155
(56) 2 g. cane-sugar 4 cc. NH_3 .... in 100 cc. 155
(57) 2 g. cane-sugar 8 cc. NH_3 .... in 100 cc. 156
(58) 2 g. cane-sugar 16 cc. NH_3 .... in 100 cc. 161

Consequently more than 4 cc. free ammonia in 100 cc. should be avoided.

(59) 2 g. cane-sugar 4 cc. NH_3 8 g. ammonium chloride in 100 cc. 155

Note : 8 g. ammonium chloride are equivalent to about 16 cc. ammonia : hence, the ammonium chloride has much less influence than the equivalent of ammonia.

Effect of Ammonia and Ammonium Chloride on the Rotation of Inverted Sugar.

A solution of 16.34 g. cane-sugar in 100 cc. was inverted according to Clerget's method, 50 cc. being heated with 5 cc. concentrated hydrochloric acid to 70° for ten minutes and made up to 100 cc. On adding ammonia, the solution turned gradually a bright yellow color, but during the change of color the reading did not appear to alter. (Temperature = 19°.)

(60) 20 cc. of the solution .... made up to 25 cc. 145.5
(61) 20 cc. of the solution 2 cc. NH_3 .... made up to 25 cc. 147.5
(62) 20 cc. of the solution 5 cc. NH_3 .... made up to 25 cc. 138

The Same in More Dilute Solution. (Temperature = 18°.)

(63) Inverted sugar equivalent to 1.634 g. cane-sugar, 5 cc. concentrated hydrochloric acid in 100 cc 40
(64) Inverted sugar equivalent to 1.634 g. cane-sugar, 5 cc. concentrated hydrochloric acid, 8 cc. NH_3 40
(65) Inverted sugar equivalent to 1.634 g. cane-sugar, 5 cc. concentrated hydrochloric acid, 16 cc. NH_3 37
(66) Inverted sugar equivalent to 1.634 g. cane-sugar, 5 cc. concentrated hydrochloric acid, 6.8 cc. NH_3 39

Note : 5 cc. hydrochloric acid are equivalent to about 4 cc. ammonia so that these experiments show that a greater *excess* than 2 cc. in 100 cc. or 1 cc. in 50 cc. should be avoided.

Effect of Magnesium Sulphate on the Rotation of Sugar and Tartaric Acid.

(67) A solution was made up containing in 100 cc. the following :
14.4 g. sodium bicarbonate, 7.6 g. tartaric acid, 5 g. citric acid, and 4.2 g. sugar.
25 cc. of this solution, 2 cc. ammonia, 1.5 cc. concentrated hydrochloric acid made up to 50 cc 347

25 cc. of this solution, 2 cc. ammonia, 1 cc. hydrochloric acid, 5 g. magnesium sulphate made up to 50 cc 315

The same amount of magnesium sulphate, with ammonium chloride to prevent precipitation, has practically no effect on sugar alone.

EFFECT OF ALKALI AND ACID ON THE ROTATION OF TARTARIC ACID IN THE PRESENCE OF AMMONIUM MOLYBDATE.

(68)	3 g. TH_2 3.33 cc. NH_3	in 100 cc.	145
(69)	3 g. TH_2 45 cc. NH_3	in 100 cc.	147
(70)	3 g. TH_2 3.33 cc. NH_3, about 4 g. ammonium molybdate	in 100 cc.	1501
(71)	3 g. TH_2 45 cc. NH_3, about 4 g. ammonium molybdate	in 100 cc.	152
(72)	3 g. TH_2 3.33 cc. NH_3, about 4 g. ammonium molybdate, about 4 cc. concentrated nitric acid	in 100 cc.	1147
(73)	3 g. TH_2 3.33 cc. NH_3, about 4 g. ammonium molybdate, about 12 cc. concentrated nitric acid	in 100 cc.	445
(74)	0.64 g. KHT (impure), 0.65 cc. NH_3, 4 g. ammonium molybdate, 4 cc. normal acetic acid	in 100 cc.	297
(75)	0.64 g. KHT (impure), 0.65 cc. NH_3, 4 g. ammonium molybdate, 20 cc. normal acetic acid	in 100 cc.	337
(76)	0.64 g. KHT (impure), 0.65 cc. NH_3, 4 g. ammonium molybdate, 40 cc. normal acetic acid	in 100 cc.	355

THE NON-EFFECT OF ALUMINUM AND IRON SALTS, PHOSPHORIC ACID, AND SODIUM CARBONATE ON THE ROTATION OF TARTARIC ACID IN THE METHOD OF GROUP III.

In the following experiments the mixtures were treated according to the directions given under Group III.

(77)	0.1 g. KHT	65.5
(78)	0.1 g. KHT	66.5
(79)	0.1 g. KHT, 0.2 g. alum	65.5
(80)	0.1 g. KHT, 0.2 g. alum, 0.2 g. calcium acid phosphate	66.5
(81)	0.1 g. KHT, 0.1 g. sodium bicarbonate	66.5
(82)	Similar results were obtained using 0.2, 0.05, and 0.025 g. of KHT.	
(83)	0.2 g. KHT	130
(84)	0.2 g. KHT, 0.02 g. ferrous sulphate, 0.01 g. ferric chloride	130

The last two are earlier experiments and were made with solutions different from those described in the paper. For this reason the numbers are lower than those given below for 0.2 g. KHT, but the two readings show that iron has no influence.

EXPERIMENT TO TEST THE SOLUBILITY OF CALCIUM TARTRATE AND THE EFFECT OF STARCH.

The following were treated according to the method III.

(85)	0.2 g. KHT	134
(86)	0.1 g. KHT, 0.138 g. CaT (=0.1 g. KHT), 0.2 g. alum, 0.3 g. phosphate cream of tartar substitute containing starch	133

THE ROTATION DUE TO INVERTED STARCH IN COMMERCIAL CREAM OF TARTAR SUBSTITUTES AND BAKING-POWDERS.

In the following experiments 8 g. of the sample and 8 cc. of concentrated ammonia were made up to 100 cc. (Note : Samples of corn starch, when treated in this way, gave filtrates which were practically inactive.)

	Description.	Brand.	Starch. Per cent.	Rotation.
(87)	Superphosphate substitute	....	26	8.3
(88)	Superphosphate substitute	....	13	10.4
(89)	Phosphate baking-powder	Q.	37	3.3
(90)	Alum baking-powder	H. C.	50	15.8
(91)	Alum baking-powder	J.	52	18.3
(92)	Alum-phosphate baking-powder	B. R.	48	2.9
(93)	Alum-phosphate baking-powder	W. S.	49	8.3
(94)	Alum-phosphate baking-powder	W. S.	49	11.0
(95)	Alum-phosphate baking-powder	W. S.	49	11.3
(96)	Alum-phosphate baking-powder	C.	46	—0.2
(97)	Alum-phosphate baking-powder	G. S.	52	5.4
(98)	Alum-phosphate baking-powder	G. S.	52	5.6
(99)	Alum-phosphate baking-powder	W. E.	50	14.8
(100)	Alum-phosphate baking-powder	S. C.	51	10.4
(101)	Alum-phosphate baking-powder	U.	50	3.5

EXPERIMENTS TO SHOW THAT THE ROTATION OF INVERTED STARCH IS NOT INCREASED BY MOLYBDATE.

(102) 4 g. phosphate substitute, 8 cc. NH_3 to 100 cc 4

(103) 0.5 g. phosphate substitute, treated by molybdate method.... 0

(104) A solution of inverted starch was prepared by treating starch with sulphuric acid and removing the latter by barium carbonate. This solution was diluted so that :

20 cc. and 8 cc. NH_3 made up to 100 cc. gave.................. 9

5 cc. of the same solution treated by molybdate method........ 2

RELATION BETWEEN AMOUNT OF TARTARIC ACID AND THE ROTATION IN THE MOLYBDATE METHOD.

The following are the averages of the best agreeing results of several experiments : In each case the substances were treated as described under III.

(105) 0.2 g. KHT 133

(106) 0.1 g. KHT 66

(107) 0.05 g. KHT 32

(108) 0.025 g. KHT 16.2

TEST ANALYSES BY THE SEVERAL METHODS DESCRIBED.

(109) *Test Analysis, Group I* (*1*) *and* (*2*).—Separation of cream of tartar and calcium tartrate. A mixture was made up of 2 g. KHT and 0.2 g. CaT and treated as directed under Group I (2) 167

The same mixture treated according to I (1)............... 157

The mixture contains 0.798 g. tartaric acid as bitartrate and 0.058 g. tartaric acid as calcium tartrate, or total $TH_2 = 0.856$ g.

The amounts calculated from the rotations are :

Total TH_2, 0.865 g., TH_2 as bitartrate, 0.815.

(110) *Test Analysis, Group II (1).*—A mixture was prepared corresponding to the sodii cit. tartras effervescens of the B.P.

13.72 grams sodium bicarbonate
4.92 grams citric acid
7.30 grams tartaric acid
4.06 grams sugar

30.00

The whole was dissolved in cold water and made up to 100 cc. (sol. *A*).

25 cc. of this solution and 1 cc. NH_3 made up to 50 cc. gave $334'$ (*a*).

25 cc. of *A* required 4.2 cc. concentrated HCl to decolorize methyl violet.

25 cc. of *A* were heated with 4.2 + 2.5 cc. HCl to 70° for ten minutes, then methyl orange was added and 5 + 1 cc. NH_3. The solution, made up to 50 cc., gave a reading of..........(Temperature = 20°) $125'$ (*b*) from which the sugar $z = 3.97$ g.

From this the rotation of the uninverted sugar in the 100 cc. is

$$3.97 \times 79.7 = 317',$$

and therefore the rotation of the tartaric acid

$$x = 2 \times 334 - 317 = 351,$$

from which the weight of tartaric acid

$$y = 4 \times 0.00519 \times 351 = 7.28.$$

(111) *Test Analysis, Group II (2).*—"Effervescing magnesium sulphate" (B.P.) was prepared as follows :

20.0 grams magnesium sulphate
14.4 grams sodium bicarbonate
7.6 grams tartaric acid
5.0 grams citric acid
4.2 grams sugar

The analysis was carried out exactly as described in the account of this method in the text, 3. g. sodium phosphate being used to precipitate the magnesium.

The following readings were obtained :

(*c*) .... $68'$
(*d*) (Temperature = 18°) .... $13'$

from which

$$\text{the sugar, } z = \frac{10 \times (68 - 2 \times 13) \times 1.254}{142 - \frac{1}{2}t} = 3.96,$$

and the tartaric acid,

$$y = 4\,(680 - 79 \times 3.96)\,0.00519 = 7.62.$$

In both the above experiments, it must be admitted, the tartaric acid comes out better than should be expected from the error in the sugar.

(112) *Test Analysis, Group III.*—The following mixture was made up and analyzed by the method described under the above head. 0.5 gram were taken for analysis.

1.0 gram potassium bitartrate
1.0 gram calcium tartrate
0.5 gram alum
1.0 gram phosphate tartar substitute

This mixture contains 32.9 per cent. tartaric acid.
Amount found: 33.4 per cent. tartaric acid.

UNIVERSITY OF MANITOBA, } June, 1902.
UNIVERSITY OF TORONTO, }

[CONTRIBUTIONS FROM THE LABORATORIES OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

THE EQUIVALENT CONDUCTIVITY OF THE HYDROGEN ION DERIVED FROM TRANSFERENCE EXPERIMENTS WITH HYDROCHLORIC ACID.

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I. PURPOSE OF THE INVESTIGATION.

IN calculating the degree of dissociation of a weak acid from its conductivity, it is first necessary to determine in some indirect way the value of its molar conductivity that corresponds to complete dissociation. This has been commonly done by adding to the molar conductivity of its sodium salt at extreme dilution the difference between that of hydrochloric acid and that of sodium chloride. The results so obtained may, however, be in error by a considerable amount, by reason of the fact that impurities in the water make it impossible to determine accurately the conductivity of hydrochloric acid (or any other strong acid) at a dilution where the dissociation is substantially complete. The values ordinarily employed have been obtained, therefore, by estimating, with the help of the change in the observed conductivity with the dilution, the probable effect of the impurities, and by making allowance for this effect.

A second, independent method that might be applied to the calculation of the molar conductivity of completely dissociated hydrochloric acid is to divide the equivalent conductivity of the chlorine ion by the transference number of moderately dilute hy-