should affect the distribution very slightly and then only on account of the "salting out" effect. If, on the other hand, the ionized portion were distributed, the presence of the highly ionized salt would affect the distribution very greatly. In very dilute solutions Hantzsch and Sebaldt have found that ammonium chloride has almost no effect. Dawson and McCrae have, however, shown that the effect is measurable, the distribution ratio at 20° decreasing by 0.88 for each mol. of salt per liter of solution. The nitrate and sulfate also lower the distribution ratio, while the bromide increases it. The following table (III) gives the results of experiments on the distribution of ammonia between chloroform and a solution of ammonium chloride containing about 3 mols. per liter. At each concentration of ammonia the distribution ratio is very close to that found in the absence of ammonium chloride.

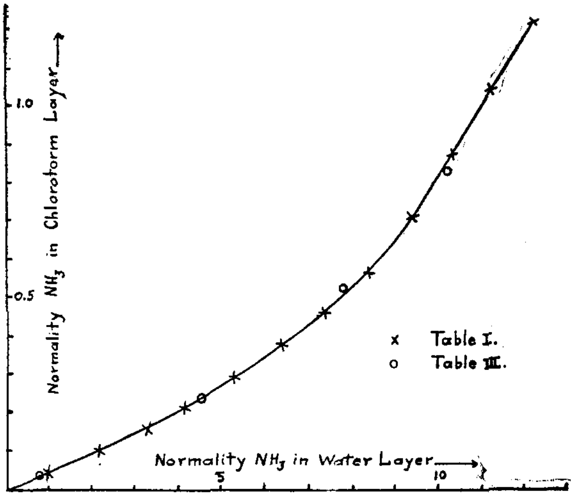

Table III.

Normality NH_3 in water layer (NH_4Cl—3N).	Normality NH_3 in $CHCl_3$ layer calc.	Normality NH_3 in $CHCl_3$ layer obs.
0.84	0.037	0.037
4.32	0.226	0.228
7.72	0.494	0.512
10.16	0.837	0.820

In this paper it has been shown that at 25° the distribution ratio for ammonia between water and chloroform varies with the concentration, from about 24 in dilute solution to about 10 in concentrated solution. The presence of ammonium chloride affects the distribution very slightly.

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ACTION OF THE OXIDES OF LEAD ON POTASSIUM TARTRATE.

By Francis C. Krauskopf.

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The solvent action of solutions of normal alkali tartrates on litharge was discovered and studied in detail by Kahlenberg and Hillyer.[1] Later some of the physical properties of these double tartrate solutions were investigated by Kahlenberg.[2] This solubility of litharge in solutions of normal alkali tartrates and the apparent insolubility of red lead and brown lead in the same solvents indicated that by this means red lead or brown lead might be obtained free from litharge, and that the amount of litharge in samples of red lead and brown lead might be determined. In attempting to work out the conditions of these separations and determinations it was found that both minium and lead dioxide are after all appreciably soluble in solutions of normal tartrates.

The following questions then arose: (1) Do red lead and brown lead dissolve in the tartrate solutions as such, or are they first reduced to litharge which then dissolves? (2) Is oxygen evolved during the solution of the higher oxides of lead, or is there an oxidation of the tartrate? (3) If the higher oxides are reduced to litharge by oxidizing the tartrate, would it not be possible by the addition of some mild oxidizing agent to prevent this reduction and so still use the method above suggested to effect a separation of the oxides?

That oxygen was not liberated from either minium or lead dioxide on solution in alkali tartrate was easily shown by the following experiments: A gas buret, C (Fig. 1), was connected to a flask, B, by means of the condenser A. A solution of potassium tartrate was boiled in the flask for several hours with about 10 grams of red lead, and the whole apparatus was allowed to cool to the original temperature. About one-third of the red lead had dissolved and the residue had undergone no apparent change. When this residue was treated with dilute acid, no carbon dioxide was given off, indicating that none of the tartrate had been oxidized to carbonate. The water in the gas buret regained its original height when the apparatus cooled, showing that no oxygen had been evolved. A repetition of the experiment produced the same results. When lead dioxide was used in place of minium no evolution of oxygen could be

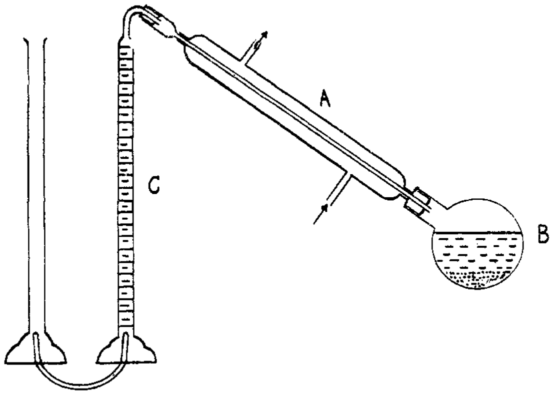

Fig. 1.

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[1] *Am. Chem. J.*, 16, 94 (1894).

[2] *Z. physik. Chem.*, 17, 577 (1895).

detected, but on continued boiling the residual lead dioxide was found to be mixed with a large amount of white residue. This residue gave off carbon dioxide readily when treated with dilute acid, which indicated an oxidation of the tartrate to carbonate.

When litharge dissolves in potassium tartrate it causes a certain definit change in the rotatory power of the tartrate solution, depending on the amount of lead oxide dissolved.[1] If red lead is first reduced to litharge which then dissolves the amount of change in rotation caused by any given amount of red lead should be the same as that caused by a chemically equivalent amount of litharge. If these changes in rotation were not the same, it would be still further proof that the red lead dissolves as red lead and that the potassium tartrate does not first reduce the red lead to litharge.

Four hundred grams of tartaric acid were just neutralized by potassium hydroxide and the solution made up to one liter. This solution in a 200 mm. tube had a rotation of +35.76° at 20°. Minium does not dissolve as readily as litharge in the tartrate solution, and it is hard to get the last traces of a sample of minium to dissolve. Again, the amount of minium that dissolves in a given time varies with the amount of oxide in contact with the solution. Accordingly various amounts of minium were weighed out into 200 cc. flasks, and to each sample there was added 50 cc. of the tartrate solution. The flasks were closed with corks to prevent evaporation, and kept in a water bath at 50° for four days. The flasks were shaken frequently to hasten the solution.

At the end of this time the rotation of the solution above the lead oxide was determined. The lead oxide was filtered off by means of a Gooch crucible, washed, dried at 180° and weighed. The amount of lead oxide dissolved was thus determined. From the filtrate the lead was precipitated by means of hydrogen sulfide, the lead sulfide filtered off, the tartrate solution evaporated to its original bulk (50 cc.) and its rotation again determined in order to see if any change had occurred in the tartrate solution.

Similar experiments were made using a potassium tartrate solution of approximately one-half the concentration of the original. This solution had a rotation of +17.60° in a 200 mm. tube.

The red lead used in the above experiments was from a Merck sample marked chemically pure. It was digested for a short time with dilute potassium tartrate solution to remove any small amounts of litharge, washed well and dried at 180° to constant weight. 1.8749 grams of this dried sample when ignited gave 1.8307 grams of litharge. According to theory it should give 1.8311 grams.

The litharge used was a chemically pure preparation of Merck's.

The following tables show the results of these experiments.

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[1] *Z. physik. Chem.*, **17**, 577 (1895).

TABLE I.

Changes in rotation of a solution of normal potassium tartrate upon the addition of red lead and of litharge. Rotation of original tartrate solution + 35.76°.

No.	Pb_3O_4 in 50 cc. Grams.	Rotation.	(A). Diminution of rotation.	Rotation with lead removed.	PbO in 50 cc. Grams.	Rotation.	(A'). Diminution of rotation.	Rotation with lead removed.	A—A'.
1	0.3600	35.05°	0.71°	35.61°	0.3576	35.32°	0.44°	35.69°	0.29°
2	0.5930	34.35	1.41	35.70	0.5791	34.90	0.86	35.72	0.61
3	0.6512	34.16	1.60	35.67	0.6361	34.76	1.00	35.70	0.60
4	0.8463	33.60	2.16	35.62	0.8267	34.41	1.35	35.68	0.81
5	1.2842	32.40	3.36	35.57	1.2546	34.36	1.40	35.75	1.96

TABLE II.

Same as Table I using a tartrate solution approximately half as concentrated, having a rotation of +17.60.

No.	Pb_3O_4 in 50 cc Grams.	Rotation.	(A). Diminution of rotation.	Rotation with lead removed.	PbO in 50 cc. Gram.	Rotation.	(A'). Diminution of rotation.	Rotation with lead removed.	A—A'
1	0.2486	16.84°	0.76°	17.55°	0.2427	16.98°	0.62°	17.56°	0.14°
2	0.3811	16.55	1.05	17.58	0.3730	16.73	0.87	17.56	0.18
3	0.4689	16.35	1.25	17.58	0.4580	16.61	0.99	17.59	0.26
4	0.5392	16.22	1.38	17.60	0.5265	16.49	1.11	17.58	0.27

From the above tables the following facts are evident: (1) The rotation of potassium tartrate solutions is diminished by the addition of either litharge or red lead. (2) This diminution increases as the concentration of the oxide in the solution increases. (3) In all cases when the lead is removed the rotation of the tartrate solution returns to practically its original value. (4) The diminution of rotation caused by any amount of minium is in all cases slightly greater than that caused by a chemically equivalent amount of litharge.

Summary.

The results of this investigation may be summarized as follows:

1. Because of the appreciable solubility of both minium and lead dioxide in solutions of normal potassium or sodium tartrate, it is impossible to determin the amount of litharge in a sample of either of these oxides by extraction with such solutions.

2. When minium or lead dioxide dissolves in potassium tartrate solution no evolution of oxygen occurs.

3. When lead dioxide dissolves in potassium tartrate solutions an oxidation of the tartrate occurs with concomitant precipitation of lead carbonate, while red lead dissolves without appreciable oxidation of the tartrate.

4. Red lead dissolved in normal potassium tartrate solution gives slightly greater diminution of the rotation than a chemically equivalent amount of litharge, indicating that red lead is not reduced to litharge before dissolving.

To Professor Kahlenberg who suggested this work the author wishes to express thanks for kind and helpful criticism.

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NOTES.

The Distribution of Hydrogen Sulfide in a Large Laboratory and the Use of Aluminium Stopcocks.—The problem of supplying hydrogen sulfide to a large number of students working in a chemical laboratory, when the work is being done at a number of points widely separated, is usually a more or less difficult one. Any ideas that will simplify this condition may be of interest to those in charge of large laboratories. The hydrogen sulfide system which was installed in the new chemical laboratory at the University of Michigan a little more than a year ago has been working so satisfactorily that a brief description of the essential features will be given.

The generators are placed in a small room located in the attic, so as to be above the level of all rooms in which hydrogen sulfide is used. The hydrogen sulfide generator room adjoins the attic storeroom which is reached by means of an elevator, so that supplies of ferrous sulfide and hydrochloric acid may be easily taken up. The hydrogen sulfide generator room is supplied with a small exhaust fan operated by an independent motor, and the waste pipe for carrying away the spent solution from the hydrogen sulfide generators connects directly with the main sewer outside the building. These two devices prevent the escape of gas into the attic or into the rest of the building through the water waste risers. There are two generators installed, one to supply the hydrogen sulfide, the other being held in reserve for use when it is necessary to clean or fill the first. The generators used are substantially like the one described by A. W. Browne and M. F. Mehling in THIS JOURNAL, 28, 838 (1906).

The main generating bottle has been modified by the addition of one tubular at the top and of one opposit the bottom tubular. The extra top tubular is closed with a solid rubber stopper and is used for introducing fresh ferrous sulfide without the necessity of disturbing the glass connections.

As the amount of work done in this laboratory calls for the use of 500 kilos of ferrous sulfide per year, it is necessary to add ferrous sulfide about once a week and hydrochloric acid almost daily. On account of the large amount of ferrous sulfide used, a certain amount of finely divided, insoluble material tends to accumulate in the bottom of the generator. By introducing a rapid stream of water through the bottom tubular opposit the spent acid discharge, any finely divided material can be flushed out and the ferrous sulfide kept clean and active.