first order type where inhibition by products causes the first order rate constant to decrease with increase of conversion. The activation energy, calculated from the temperature variation of the first order rate, is 65,000 cal.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF TRINITY COLLEGE]

Ternary Systems. VIII. Potassium Iodate, Iodic Acid and Water

BY STERLING B. SMITH

Some forty years ago Meerburg[1] conducted a phase rule investigation of the solubility relations in the ternary system, potassium iodate, iodic acid and water at 30°. Since that time potassium biiodate has been accepted as a primary standard for use in alkalimetric and iodimetric titrations.

Inasmuch as the purification of the biiodate by recrystallization from aqueous solution hinges upon the congruent solubility of this salt in water, Meerburg's work has been extended to cover a range of temperatures from 0 to 50°.

Experimental

Isotherms at 0, 25 and 50° have been completed by analyzing the solutions and residues obtained by rotating mixtures of the three components in a thermostat until equilibrium is established.

The procedure differed from that of Meerburg in that he warmed his original complexes to 50–60°, obtaining homogeneous solutions, and then slowly cooled them to the temperature of the investigation. The prepared mixtures were then rotated in a thermostat until equilibrium was established, often requiring several weeks.

In this work, the original complexes were prepared using the compounds which exist as solid phases after equilibrium has been established. This cut down to forty-eight hours the time required to establish equilibrium and also obviated the appearance of metastable solid phases.

The analytical procedure also differed slightly. Meerburg titrated his samples with standard thiosulfate solution in the presence of excess potassium iodide both before and after the addition of sulfuric acid. In this work the acid content was first determined by titration with standard alkali and total iodate determined in the same sample by titration with standard thiosulfate solution in the presence of excess potassium iodide and hydrochloric acid.

The experimental results are given in the following abbreviated table. Values are given only for the isothermally invariant points and the point of congruent solubility. The values at these invariant points are the average of two or more closely agreeing results, the solid phases being the same in each instance but present in widely different proportions.

Kolthoff and van Berk[2] in advocating the use of potassium biiodate as a standard substance in volumetric analysis stated that "it should not be dried at too high temperatures, as the iodic acid in the potassium biiodate loses its water of constitution and is transformed into the corresponding anhydride. When dried at 200°, this takes place quantitatively."

A series of drying experiments was run at 105 ± 3° to determine the loss in water when the biiodate was dried at the usual temperatures. It was found that the sample reached a constant weight at the end of three days. Analysis of the resultant product showed an iodine pentoxide content of 87.67%, corresponding to a theoretical value of 87.63% for the compound $2KIO_3 \cdot I_2O_5$.

TABLE I[a]

SOLUBILITY DATA

Point in figure	Solution % HIO_3	% KIO_3	Solid phases
		Temperature, 0°	
	None	4.51	KIO_3
	0.35	4.47	KIO_3, $KIO_3 \cdot HIO_3$
	1.30	1.68	$KIO_3 \cdot HIO_3$
	5.76	0.13	$KIO_3 \cdot HIO_3$, $KIO_3 \cdot 2HIO_3$
	73.69	.39	$KIO_3 \cdot 2HIO_3$, HIO_3
	73.56	None	HIO_3
		Temperature, 25°	
	None	8.39	KIO_3
	0.61	8.46	KIO_3, $KIO_3 \cdot HIO_3$
	.77	4.90	$KIO_3 \cdot HIO_3$
	7.68	0.61	$KIO_3 \cdot HIO_3$, $KIO_3 \cdot 2HIO_3$
	75.51	.42	$KIO_3 \cdot 2HIO_3$, HIO_3
	75.56	None	HIO_3
		Temperature, 50°	
A	None	13.21	KIO_3
B	1.34	13.58	KIO_3, $KIO_3 \cdot HIO_3$
S	3.74	4.64	$KIO_3 \cdot HIO_3$
C	11.02	1.85	$KIO_3 \cdot HIO_3$, $KIO_3 \cdot 2HIO_3$
D	78.72	1.17	$KIO_3 \cdot 2HIO_3$, HIO_3
E	78.78	None	HIO_3

[a] For supplementary tables order Document 2389 from the American Documentation Institute, 1719 N St., N. W., Washington 6, D. C., remitting 50¢ for microfilm or 50¢ for photocopies.

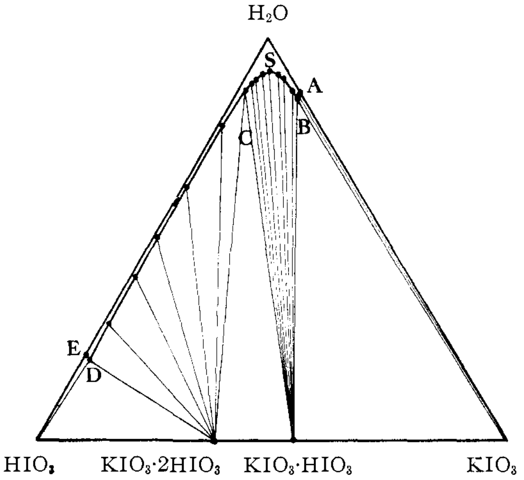

Fig. 1.—Temperature 50°.

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(1) Meerburg, *Chem. Weekblad*, **1**, 474 (1904); *Z. anorg. Chem.*, **45**, 324 (1905).

(2) Kolthoff and van Berk, THIS JOURNAL, **48**, 2799 (1926).

Chemical analysis of the original recrystallized product showed that oven drying may be omitted if the biiodate is washed with ethyl alcohol and air dried.

Summary

The results of this investigation show that the solubility relations in this system are the same over a range of temperatures as those found by Meerburg at 30° and confirm the fact that potassium biiodate can be recrystallized safely from aqueous solution.

In using potassium biiodate as a volumetric standard, care should be exercised in drying the sample. Either an alcohol-washed, air-dried sample should be used or a sample which has been dried sufficiently to convert the compound to the anhydride.

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[CONTRIBUTION FROM THE DEPARTMENT OF INORGANIC AND ANALYTICAL CHEMISTRY OF THE HEBREW UNIVERSITY]

The Structure and Behavior of Ferric Tartrate and Citrate Complexes in Dilute Solutions[1]

BY M. BOBTELSKY AND J. JORDAN

It is hard to find a problem of complex chemistry which has been studied with as much stubbornness as the behavior and structure of the various metallic tartrates and citrates. This is apparently due to the fact that these complexes are met with simultaneously in various fields of the natural sciences: analytical chemistry, both qualitative and quantitative, makes use of these complexes, though not to a sufficient extent; the properties of the various tartrates and citrates, their solubility and their behavior in the presence of alkali seem to be well suited for the analytical separation of metals without using hydrogen sulfide; oxy-complexes (especially the citrates of iron and of the alkaline earths) are of considerable interest in physiological chemistry, too.

The structure of tartrates and citrates of bivalent cations has been discussed in a previous paper.[1a] There, we have postulated formulas assuming that the organic (tartrate and citrate) radicals occupy *three* coördination positions, though some tartrates of bivalent cations have been prepared which crystallize with two molecules of water[2,3] (thus suggesting coördination number four for the tartrate radical). Apparently, the structure of the various complexes depends not only on the organic radical, but also on the cation concerned. Furthermore, a regrouping of the radicals may occur, while the complexes are neutralized by alkali.

In this paper we should like to discuss the complexes of a tervalent cation: we have chosen the ferric complexes, because they are the most important ones and are easily accessible to photometric, conductometric, potentiometric and polarographic research. Some "thermometric titrations"[4] were also carried out by us, to confirm results obtained by other methods.

It should be borne in mind that it is extremely difficult to crystallize out citrate or tartrate complexes of iron.[5] The citrates are very soluble and the tartrates are mostly precipitated as basic salts.[5,6,7] Even the structure of the well-known crystallized "green ferric citrate" is still controversial.[8,9] And, generally, there is no finally accepted view about the structure of the ferric citrate and tartrate complexes, though many papers have been published on this subject.[5–17]

Contrary to bivalent cations, tervalent iron forms complexes not only with trisodium citrate and disodium tartrate but even with *free* citric and tartaric acid. We have found that in the most stable complexes the molar ratio between iron and the tartrate or citrate radicals is $2Fe^{III}$: 3Cit (or 3Ta).[17a]

Experimental

Conductometric, photometric and **polarographic** measurements were carried out as described in the previous paper.[1]

Potentiometric titrations were made with a Hellige "electron-tube-potentiometer" using a bright platinum

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(1) This paper was presented before the Division of Physical and Inorganic Chemistry at the 110th Meeting of the American Chemical Society, Chicago, September, 1946.

(1a) M. Bobtelsky and J. Jordan, THIS JOURNAL, **67**, 1824 (1945).

(2) Fr. Bullnheimer and E. Seitz, *Ber.*, **33**, 817 (1900).

(3) S. U. Pickering, *J. Chem. Soc.*, **96**, 1409 (1909); **97**, 1837, 1851 (1910); **99**, 169 (1911); **101**, 174, 1614 (1912); **103**, 1354 (1913); **107**, 942, 955 (1915); **109**, 235 (1916).

(4) W. Swietoslawski, "Thermochemie" (Part VII of Ostwald-Drucker's Handbuch), p. 108 (1928).

(5) S. U. Pickering, *J. Chem. Soc.*, **103**, 1358 (1913); **105**, 644 (1914).

(6) W. Franke, *Ann.*, **486**, 242 (1931).

(7) Eliane Poulenc-Ferrand, *Compt. rend.*, **210**, 299 (1940).

(8) E. Belloni, *C. A.*, **15**, 839 (1921).

(9) W. D. Treadwell and E. Wettstein, *Helv. Chim. Acta*, **18**, 200, 981 (1935).

(10) C. Morton, *Chem. Zentr.*, **102**, II, 3569 (1931); **104**, I, 753 (1933).

(11) E. E. Wark and J. W. Wark, *Z. physik. Chem.*, **157**, 310 (1931).

(12) Shin'ichiro Hakomori, *Chem. Zentr.*, **99**, I, 1385 (1928).

(13) N. L. Galvez, *C. A.*, **32**, 7183 (1938).

(14) H. Grossmann and A. Loeb, *Z. physik. Chem.*, **72**, 93 (1910).

(15) Pariselle and Delsal, *Compt. rend.*, **198**, 83 (1934).

(16) Delsal, *J. chim. phys.*, **35**, 350 (1938).

(17) Yeu-Ki-Heng, *ibid.*, **33**, 356 (1936).

(17a) In this paper, the abbreviations "Cit" and "Ta" are generally used for citrate and tartrate and do not denote any particular acid or ion.