Booth and Pierce.[9] While the earlier workers simply mixed alcoholic solutions of beryllium nitrate and benzoylacetone, the present method involves neutralization of the benzoylacetone in the presence of beryllium ion. The reaction proceeds with the dilution of the alcoholic solution by a considerable volume of water, thus facilitating crystallization of the water-insoluble product.

Five grams of benzoylacetone (0.032 mole) in 20 ml. of 95% ethanol is added to a solution of 3.3 g. of beryllium(II) nitrate 4-hydrate (0.016 mole) in 35 ml. of 95% ethanol. Thirty milliliters of 1 *N* aqueous sodium hydroxide (0.030 mole) is added dropwise to the solution while it is stirred rapidly. As the sodium hydroxide is added, crystals begin to form. After addition is complete, the solution is allowed to stand 30 minutes and then filtered. The product is washed with small amounts of alcohol and water and then dried at 110°. After recrystallization from benzene and again drying at 110°, the melting point is 210°. Booth and Pierce reported 211°. *Anal.* Calcd. for $[Be(C_{10}H_9O_2)_2]$: C, 72.45; H, 5.47. Found: C, 72.67; H, 5.58.

Partial Resolution with *d*-Quartz.—Partial resolution of bis-(benzoylacetono)-beryllium was attained by shaking 25 ml. of a benzene solution of the complex with powdered quartz for 15 minutes. The quartz was removed by filtration and the rotation read at the sodium D line using a Schmidt and Haensch Polarimeter (No. 9143). The readings given represent from six to ten settings of the instrument and are compared with a benzene blank.

Concn., %	Quartz, g.	α
0.2	1	$+0.011 \pm 0.003$
2.0	2	$+0.026 \pm 0.002$
2.0	2	$+0.019 \pm 0.004$

The racemization of the complex is slow enough to allow adequate verification of the observed rotation.

Time, hr.	Initial	1.5	5	9
α	+0.019	+0.020	+0.013	0.000

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[9] H. S. Booth and D. G. Pierce, *J. Phys. Chem.*, **37**, 59 (1933).

DEPARTMENT OF CHEMISTRY AND
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The Preparation and Properties of Tin(II) Chlorofluoride

BY WM. H. NEBERGALL, GINO BASEGGIO AND JOSEPH C. MUHLER

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In connection with investigations concerning methods of preparing tin(II) fluoride[1] for use as an anticariogenic agent,[2] crystallin tin(II) chlorofluoride was found to be formed when hydrofluoric acid was added to a concentrated aqueous solution of tin(II) chloride.

Subsequent studies showed tin(II) chlorofluoride to be very effective in reducing the acid solubility of powdered human dental enamel as well as the incidence of experimental dental caries in rats.[3] Moreover the results of a clinical study involving the topical application of tin(II) chlorofluoride solutions to the erupted permanent teeth of school children[4] indicate that this compound is even more effective in reducing the incidence of new dental caries than tin(II) fluoride when solutions of the two compounds are administered at the same fluoride level.

The work reported herewith will make it possible for those who may wish to study the anticariogenic activity of tin(II) chlorofluoride to prepare samples of this compound for their own use.

Experimental

The Preparation of Tin(II) Chlorofluoride from Tin(II) Chloride and Hydrofluoric Acid.—Tin(II) chloride dihydrate, 112.8 g. (0.5 mole), was weighed into a 200-ml. polyethylene beaker and 15 g. of oxygen-free, boiling water was added to dissolve the salt. With an atmosphere of oxygen-free nitrogen maintained above the solution, it was heated to 55° on a steam-bath, and 22.5 g. (0.55 mole) of 49.6% hydrofluoric acid was slowly added to the solution. Crystals of the product formed when the mixture was allowed to cool to room temperature. The supernatant liquid was decanted and the crystals were washed three times with 95% ethanol; the alcohol was decanted after each washing. The product was dried in an evacuated desiccator over a 1:1 mixture of anhydrous calcium chloride and potassium hydroxide. The yield of the product was 21.8 g. (25%).

Anal. Calcd. for $SnClF$: Sn, 68.53; F, 10.97. Found: Sn, 68.7, 68.3, 68.5; F, 10.7, 10.7, 10.8.

Properties of Sn(II) Chlorofluoride.—Tin(II) chlorofluoride crystallizes as colorless prisms which melt at 185–190°. The compound dissolves in water (55% at 25°) to give solutions which are essentially clear initially; within an hour a white precipitate is formed due to hydrolysis of the salt. A 4% solution (the concentration used in topical application[4]) was found to have a *p*H of 2.0 immediately after preparation and also after standing for two hours.

X-Ray Powder Diffraction Data for Tin(II) Chlorofluoride.—In the following table are listed the interplanar spacings ("d") and the relative line intensities found to be characteristic of SnClF.

5.09 VS	2.68 M	2.27 M	1.61 M	1.39 W
3.89 VS	2.63 VW	2.19 M	1.58 M	1.34 W
3.35 VS	2.53 W	2.02 S	1.48 W	1.25 VW
3.07 M	2.44 W	1.90 M	1.45 W	1.24 VW
2.95 S (diffuse)	2.34 M	1.76 S	1.43 W	1.23 W

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[1] Wm. H. Nebergall, Joseph C. Muhler and Harry G. Day, THIS JOURNAL, **74**, 1604 (1952).

[2] C. L. Howell, C. Gish, R. Smiley and J. C. Muhler, *J. Amer. Dent. Assoc.*, in press.

[3] J. C. Muhler and H. G. Day, *J. Dent. Res.*, in press.

[4] C. L. Howell and J. C. Muhler, *Science*, **120**, 316 (1954).

The Orthobaric Density of Pure Nitric Acid[1]

BY S. ALEXANDER STERN AND WEBSTER B. KAY

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In the course of an investigation of the thermal decomposition of pure nitric acid, it became necessary to know accurately the orthobaric density of the pure acid between 0 and 32°. The "International Critical Tables"[2] tabulate values of the density of pure nitric acid between 5 and 30° based on a compilation of data published previous to 1927. More recent measurements, however, do not agree well with these data. Consequently, it was decided to measure the liquid density of pure nitric acid at a series of temperatures in this temperature range.

Materials.—Pure nitric acid was prepared by the reaction of 100% sulfuric acid on anhydrous potassium nitrate at 0° and under high vacuum. The nitric acid formed was collected in a container kept at the temperature of liquid nitrogen. The total acidity of the samples obtained in this manner was found, by volumetric analysis, to vary between 99.95 and 100.05%. No trace of NO_2 or of SO_3

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[1] This paper is based upon work performed under contract Number AF 33(038)-10381 with W.A.D.C., Wright-Patterson Air Force Base, Ohio.

[2] "International Critical Tables," Vol. III, McGraw-Hill Book Co., New York, N. Y., 1928, p. 59.

could be detected. The freezing point of nitric acid was found to be −41.60 ± 0.05°, in good agreement with the results of Forsythe and Giauque[3] (−41.59°) and of Dunning and Nutt[4] (−41.62°).

Apparatus and Procedure.—The orthobaric density of nitric acid was measured with a pycnometer constructed by blowing a bulb of about 3-cm.^{3} capacity on the end of a 1-mm. bore capillary tube. A similar but much smaller bulb was blown on the other end of the capillary to serve as a reservoir for the expansion of the liquid at higher temperatures. The volumes of the bulbs and the volume/mm. of the capillary, from a reference line etched on the capillary, were very carefully determined by calibration with mercury.

The pycnometer was sealed directly to the high vacuum line of the nitric acid generator and was filled with pure nitric acid by condensing the vapors in the bulb, which was cooled with a mixture of carbon tetrachloride and Dry Ice. The pycnometer was then sealed off from the line at a previously prepared mark and was immersed in a water-bath whose temperature was held constant within ±0.02°. As soon as temperature equilibrium was attained, the height of the acid meniscus above the reference line was measured with a cathetometer reading to 0.05 mm. These observations were repeated at approximately 2–4° intervals up to about 33°. The total volume occupied by the liquid sample at each temperature was then calculated, a correction being applied for the complement of the acid meniscus.

The temperature was measured with a precision mercury thermometer and read with the aid of the cathetometer telescope to within 0.02°. The thermometer was compared over the entire range against a platinum resistance thermometer which had previously been tested at the U. S. Bureau of Standards.

At the termination of the observations, the pycnometer was dried and weighed with calibrated weights. The tip of the pycnometer was then broken off, the nitric acid completely removed and the empty pycnometer plus the tip dried and weighed. The weight of the nitric acid sample was obtained by difference. All weights were reduced to vacuum. The density was calculated from these data.

At the highest temperature, a very small amount of decomposition occurred as indicated by a very pale yellow color appearing in the otherwise water-white liquid.

Results.—The density was found to vary linearly with the temperature over the range investigated, namely, 1.00–32.33°, and could be expressed by the equation

$$d(\text{g./cm.}^3) = 1.5492 - 0.00182t(^\circ\text{C.})$$

which was fitted by the method of least squares. The accuracy of the measurements is within ±0.0001 g./cm.^{3}. The experimental results are given in Table I.

TABLE I

THE ORTHOBARIC DENSITIES OF ANHYDROUS NITRIC ACID

Temp., °C. ± 0.05°	Density, g./cm.^{3} ± 0.0001	Temp., °C. ± 0.05°	Density, g./cm.^{3} ± 0.0001
1.00	1.5475	13.28	1.5249
1.74	1.5460	14.07	1.5234
2.61	1.5443	19.60	1.5136
4.20	1.5415	21.35	1.5105
9.52	1.5319	23.80	1.5059
10.50	1.5302	27.78	1.4989
10.90	1.5294	29.88	1.4948
12.70	1.5260	32.33	1.4905

A comparison of the values of the density as given by the equation with values reported in the literature is shown in Table II.

TABLE II

COMPARISON OF MEASURED DENSITIES OF PURE NITRIC ACID WITH LITERATURE VALUES

Temp., °C.	Literature	Density, g./cm.^{3} from eq. 1	Exptl. − lit.
0	1.54786[5]	1.5492	0.0013
0	1.5472[6]	1.5492	.0020
5	1.5402[7]	1.5401	− .0001
10	1.5310[7]	1.5310	.0000
12.5	1.5245[6]	1.5264	.0019
15	1.52150[5]	1.5219	.0004
15	1.5217[7]	1.5219	.0002
20	1.5129[7]	1.5128	− .0001
24.9	1.5033[8]	1.5039	.0006
25	1.5018[6]	1.5037	.0019
25	1.5040[7]	1.5037	− .0003
30	1.4952[7]	1.4946	− .0006

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(3) W. R. Forsythe and W. F. Giauque, THIS JOURNAL, **64**, 52 (1942).

(4) W. J. Dunning and C. W. Nutt, *Trans. Faraday Soc.*, **47**, 22 (1951).

(5) K. Mischtschenko, *Z. Prikladnoj Chim.*, **2**, 525 (1929).

(6) A. Klemenc and J. Rupp, *Z. anorg. Chem.*, **194**, 55 (1930).

(7) Reference 2.

(8) E. Briner, B. Susz and P. Favarger, *Helv. Chim. Acta*, **18**, 376 (1935).

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Spectrophotometric Evidence of Polymerization in Peroxytitanic Acid Solutions

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RECEIVED MAY 21, 1954

It has been well established through the work of Schaeppi and Treadwell[2] and others[3] that, in acid solution, titanic acid and hydrogen peroxide react in the one to one molar proportion to produce highly colored peroxytitanic acid. The color produced by this reaction has been the basis for many quantitative methods for the determination of titanium or peroxide in solution. It has been recognized by several workers that the light absorption of peroxytitanic acid solutions obeys Beer's law only at rather great dilutions, but a search of the literature has failed to reveal either a description of the nature of the deviations from the ideal behavior, or a satisfactory explanation of the cause for these effects.

In a general study of the flameproofing potentialities of titanium compounds we have investigated the absorption characteristics of peroxytitanic acid solutions in the concentration ranges where deviation from Beer's law is very pronounced. Some of our results are reported in this communication, and a possible explanation of the behavior of concentrated peroxytitanic acid solutions is advanced.

Experimental

Titanium sulfate solutions were prepared by adding a known weight of redistilled tetraisopropyl titanate to ice-cold 5 *N* sulfuric acid, shaking the chilled mixture until solution was complete, and diluting to the desired concentration. It was established in separate experiments that the analytically pure tetraisopropyl titanate could be handled with

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(2) Y. Schaeppi and W. D. Treadwell, *Helv. Chim. Acta*, **31**, 577 (1948).

(3) Several references are given in "Gmelin's Handbuch der anorganischen Chemie," 8th Ed., System No. 41, pp. 269–270.