sumption of an *aci*-form is based entirely on methods of the classical theory of electrolytes and therefore without any real basis.

The "intermediate" form of von Halban and Eisenbrand[13] is identical with the undissociated molecule. The difference between the absorption spectra of the molecule in aqueous solution and in hexane, which led to the assumption of a second form, must be explained by strong interaction between the molecules; the assumption of a hydrogen bond is, of course, very obvious. Indeed, Dalmon and Freymann[24] by determining the infrared absorption at the frequency of the hydrogen vibration furnished definite evidence of the formation of a hydrogen bond in the range between 80 and 100% HNO_3, *i. e.*, in the range where less than one water molecule is available per molecule of the acid. Another factor interfering with the interpretation of ultraviolet spectra, the presence of nitrogen pentoxide in anhydrous acid, is supported by the Raman spectra of Susz and Briner and of Chédin.

These difficulties, encountered in the derivation of degrees of ionization from extinction coefficients have been pointed out by von Halban and Eisenbrand. Nevertheless, considering the satisfactory agreement shown in Fig. 1, and the success of Fromherz' measurements[25] on moderately strong electrolytes, more information can be expected from this source.

From Fig. 1 one must expect that the concentration of the ions is already very low at 18 moles of HNO_3 per liter, corresponding to the composition $HNO_3 \cdot H_2O$. Association by hydrogen bonds and formation of nitrogen pentoxide explain the surprisingly quick decrease of the ionization with increasing concentration.

The rapid increase of the partial molal heat contents[26] of nitric acid above $c = 3$ corresponds to the decrease of the ionization as indicated by Fig. 1. We intend to discuss the thermodynamic properties on a later occasion.

The authors wish to thank Professor G. N. Lewis for illuminating discussions.

Summary

1. A characteristic Raman spectrum represents a sufficient and under certain conditions necessary criterion of the existence of undissociated molecules and intermediate or complex ions.

2. According to this criterion, alkali nitrates and a number of other uni-univalent salts are completely ionized. Ion pairs are not to be classified as undissociated molecules.

3. The degrees of ionization of nitric acid have been determined by a method previously suggested.

4. The thermodynamic ionization constant of nitric acid is $K = 21$. Earlier crude estimates of the order of magnitude of the ionization constant are compared with the present result.

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(24) R. Dalmon and R. Freymann, *Compt. rend.*, **211**, 472 (1940).

(25) H. Fromherz and Kun Hou Lih, *Z. physik. Chem.*, **A153**, 321 (1931); H. Fromherz, *ibid.*, **153**, 376 (1931). *Cf.* also E. Rabinowitch and W. H. Stockmayer, THIS JOURNAL, **64**, 335 (1942).

(26) *Cf.* the values calculated (ref. 9a) from the data of G. Becker and W. A. Roth, *Z. physik. Chem.*, **A174**, 104 (1935).

PULLMAN, WASHINGTON RECEIVED FEBRUARY 5, 1943

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN]

The Preparation and Properties of Potassium Thiogermanate and Thiogermanic Acid[1]

BY HOBART H. WILLARD AND C. W. ZUEHLKE

Germanium sulfide may be classified among the least soluble sulfides, it being quantitatively precipitated from solutions 6 N in hydrogen ion concentration. In 1886 Winkler[2] showed that germanium sulfide is not precipitated, however, from weakly acid solutions and he postulated the existence of a stable thiogermanate as an explanation of this behavior. Abrahams and Müller[3] utilized this property as the basis of a separation of arsenic from germanium. They showed that arsenic is quantitatively precipitated as the sulfide from a solution which is less than 0.09 N in hydrogen ion concentration, while germanium remains in solution under these conditions. Schwarz and Giese,[4] noting the solubility of germanium sulfide in alkali sulfides, isolated $Na_6Ge_2S_7$ and $K_6Ge_2S_7$

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(1) From a dissertation submitted by C. W. Zuehlke to the Graduate School of the University of Michigan in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry.

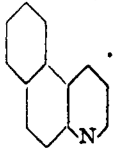
(2) Winkler, *J. prakt. Chem.*, [2] **34**, 220 (1886).

(3) Abrahams and Müller, THIS JOURNAL, **54**, 86 (1932).

(4) Schwarz and Giese, *Ber.*, **63**, 779 (1930).

and thereby demonstrated the existence of a thiogermanate stable in alkaline media. They did not investigate the properties of this ion in the acid range, or whether it is responsible for the failure of germanium sulfide to precipitate from weakly acid solution.

The *p*H of a 0.02 *M* solution of germanium dioxide was found to change rapidly from 6.8 to 1.8 upon being treated with hydrogen sulfide. Although a stream of carbon dioxide will rapidly remove hydrogen sulfide dissolved in water, such treatment was found to be much less effective when used to remove the hydrogen sulfide dissolved in a solution of germanium dioxide. These facts indicate that hydrogen sulfide and germanium dioxide, in aqueous solution, combine to form a thiogermanic acid of considerable stability and comparable to the mineral acids in strength.

An insoluble derivative of this thio acid was prepared by treating a germanium dioxide solution with hydrogen sulfide followed by precipitation with 5,6-benzquinoline, . An analysis of the product gave the molar ratios

Moles of base per mole of germanium	1.06
Moles of sulfur per mole of germanium	2.44

Although these ratios are not exact, they indicate a formula of $B_2Ge_2S_5$ (where B represents the base) derived from the corresponding acid, $H_2Ge_2S_5$.

The Preparation of Potassium Thiogermanate

A very concentrated solution of potassium germanate was prepared by treating 3 g. of germanium dioxide[5] with 3 g. of potassium hydroxide dissolved in 10 ml. of water.

$$GeO_2 + 2KOH = K_2GeO_3 + H_2O$$

The hydrated oxide was reprecipitated by neutralization with 3.5 ml. of glacial acetic acid yielding a viscous suspension of the oxide in a minimum quantity of water.

$$K_2GeO_3 + 2HAc = GeO_2 + 2KAc$$

Hydrogen sulfide was found to react rapidly with germanium oxide in this form to yield a colorless and somewhat viscous solution of potassium thiogermanate.

$$2GeO_2 \text{ (hydrated)} + 5H_2S + 2KAc = K_2Ge_2S_5 + 2HAc + 4H_2O$$

All attempts to precipitate the very soluble salt from the resulting solution failed. The addition of 100 ml. of acetone caused the immediate separation of two layers. The upper acetone layer was found to contain most of the excess potassium acetate and acetic acid, while the lower aqueous layer consisted of a very concentrated solution of potassium thiogermanate.

The addition of 50 ml. of absolute alcohol to this concentrated solution caused the immediate deposition of fine crystalline plates of potassium thiogermanate. The mother liquor was decanted, the product was washed with alcohol, and dried in a current of dried air. Analysis of this product gave the results listed.

Anal. Found (moles × 10^3 per gram): S, 1.153, 1.156, 1.154, 1.154; Ge, 0.4629, 0.4620, 0.4598; K, 0.4619, 0.4610, 0.4633. Using the average value of potassium as a reference of 2.000, the following molar ratios are obtained: K, 2.000; S, 4.995; Ge, 1.997; H_2O (by difference), 2.748.

The figure for the water content indicates that the product obtained in this manner probably consists of more than one crystal modification. Products of varying degrees of hydration were obtained by changing the conditions of precipitation. The addition of 25 ml. of 95% alcohol to the aqueous extract prepared from 3 g. of germanium dioxide did not cause immediate precipitation. A product obtained by cooling this solution to 0° contained 3.705 moles of water per mole of salt. When crystallization was allowed to proceed from this solution at room temperature large glassy rods with tapered ends were formed slowly over a period of twelve hours. This product was found to contain 6.974 moles of water per mole of salt. In addition to the heptahydrate a number of other crystal modifications undoubtedly exist.

The solid deteriorates rapidly in contact with air, becoming coated with a chalky deposit which may be free sulfur, germanium dioxide, or both. The salt is extremely soluble in water to yield a slightly acid solution (*p*H 6.2) which has a pronounced odor of hydrogen sulfide. The solution contains a sufficient concentration of sulfide ion to precipitate zinc sulfide and the metallic sulfides less soluble than zinc sulfide. The more soluble sulfides represented by cobalt, nickel, etc., are not precipitated.

The Preparation of Thiogermanic Acid

It was shown in the preceding section that the reaction of germanium dioxide with hydrogen sulfide indicates the possible formation of the $Ge_2S_5^{=}$ ion. Since free thiogermanic acid is a strong acid, the corresponding potassium salt is formed in the presence of potassium acetate. When this reaction is carried out in an unbuffered solution the hydrogen ion concentration increases until a normality of 0.09 is reached which corresponds to a limiting concentration of thiogermanic acid. Further reaction produces germanium sulfide.

Ethyl alcohol, being of a less polar nature than water, was found to repress the ionization of the free thio acid, thereby allowing a much higher limiting concentration of the acid. Although germanium dioxide is less soluble in alcohol than in water its reaction with hydrogen sulfide will, nevertheless, proceed but at a diminished rate dependent upon the concentration of the alcohol present. The anhydrous oxide proved to be essentially inert, and accordingly it was necessary to dissolve and reprecipitate the oxide in hydrous form before use.

Five grams of germanium dioxide was dissolved in a potassium hydroxide solution and reprecipitated by

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(5) The authors wish to express their appreciation to the Eagle Pitcher Lead Co., who supplied a part of the germanium dioxide used in this work.

neutralization with sulfuric acid to the methyl red endpoint. The gelatinous oxide was filtered and washed thoroughly on the filter. The moist oxide was then suspended in 25 ml. of absolute alcohol and treated with hydrogen sulfide. The reaction required about one hour for completion.

$$2GeO_2 \text{ (hydrated)} + 5H_2S = H_2Ge_2S_5 + 4H_2O$$

The alcoholic solution of thiogermanic acid was dried over anhydrous magnesium sulfate, cooled to 0° and saturated with hydrogen sulfide. Two hundred ml. of reagent ethyl ether saturated with hydrogen sulfide at 0° was added, which caused the immediate separation of a dense second phase containing an extremely high concentration of the thio acid. This concentrated solution proved to be very unstable at room temperature but decomposed only slowly at 0°. The heavy layer was separated as rapidly as possible from the supernatant ether and was treated with anhydrous ethyl acetate, also saturated with hydrogen sulfide at 0°. This treatment with ethyl acetate served to extract the last amounts of solvent, causing the thiogermanic acid to solidify slowly. It was found helpful to decant the ester and to treat with fresh portions frequently. The final portion of ethyl acetate was decanted and the product was dried in a current of dry air.

In spite of the precautions taken to prevent the loss of hydrogen sulfide, the products obtained in this way were found to be contaminated to some extent with germanium oxide. An analysis of the best product prepared gave a ratio of 2.424 moles of sulfur per mole of germanium. Assuming the contaminant to be germanium dioxide solely this ratio corresponds to a composition of 98.55% thiogermanic acid and 1.45% germanium dioxide.

Thiogermanic acid is a white amorphous solid, extremely soluble in water to yield a strongly acid solution having a pronounced odor of hydrogen sulfide. Treatment with the mineral acids causes a deposit of germanium sulfide.

Summary

1. The probable existence of a thiogermanate ion, $Ge_2S_5^{=}$, in acid solution was indicated by preparing its derivative with 5,6-benzquinoline.

2. Potassium thiogermanate, $K_2Ge_2S_5$, was prepared and the existence of a number of its hydrates was indicated.

3. Solid thiogermanic acid, $H_2Ge_2S_5$, was prepared, but due to its instability pure specimens could not be obtained.

ANN ARBOR, MICHIGAN RECEIVED JUNE 4, 1943

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

The Pressure–Volume–Temperature Relations of 2,2-Dimethylbutane

BY W. A. FELSING[1] AND GEORGE M. WATSON[2]

There has been in progress in this Laboratory a systematic program of determining certain physical properties of selected pure hydrocarbons. Among the properties determined have been the compressibilities,[3] heat capacities,[4] and heats of vaporization.[5] This investigation deals with the pressure–volume–temperature relation of one of the hexanes, 2,2-dimethylbutane, at eight temperatures: at 25° intervals beginning with 100° and including 275°. No data over this range have been found for this hydrocarbon in the literature.

Method and Apparatus.—All measurements were made with the dead-weight piston gage and accessory equipment, described elsewhere.[3,6]

Material Used.—The sample of 2,2-dimethylbutane used in this investigation was prepared by synthesis from acetone by a method similar to that employed and described by Brooks, Howard and Crafton[7] and also described elsewhere.[8] The following comparison of its physical constants with recorded values indicates its purity: density, g./cc. at 20°, 0.64899 (0.64902)[7]; at 25°, 0.64433 (0.64432)[7]; refractive index, $n^{20}\text{D}$ 1.36857 (1.36864)[7]; normal boiling point, 49.71 ± 0.02° (49.731).[7]

Pitzer[9] has estimated the critical pressure and critical temperature to be 30 atmospheres and 490°K., respectively.

The Experimental Data.—The experimental data are presented graphically in the accompanying figure, in which specific volumes (cc./g.) are presented as functions of the pressure at different constant temperatures. From such large scale graphs, the specific volumes at each temperature were read off at rounded pressures; these values are given in Table I.

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(1) Present address: Underwater Sound Laboratory, Harvard University, Cambridge, Massachusetts.

(2) Present address: General Tire and Rubber Company, Akron, Ohio.

(3) (a) Kelso with Felsing, THIS JOURNAL, 62, 3132 (1940); (b) Kelso with Felsing, *Ind. Eng. Chem.*, 34, 161 (1942); (c) Felsing and Watson, THIS JOURNAL, 64, 1822 (1942); (d) Felsing and Watson, *ibid.*, 65, 780 (1943).

(4) (a) Dailey with Felsing, *ibid.*, 65, 42 (1943); (b) Dailey with Felsing, *ibid.*, 65, 44 (1943).

(5) Lemons with Felsing, *ibid.*, 65, 46 (1943).

(6) Beattie, *Proc. Am. Acad. Arts Sci.*, 69, 389 (1934).

(7) Brooks, Howard and Crafton, *Bur. Standards J. Research*, 24, 33 (1940).

(8) Kelso, Wash, Horeczy, Shive with Felsing, THIS JOURNAL, 63, 2273 (1941).

(9) Pitzer, *ibid.*, 63, 2413 (1941).