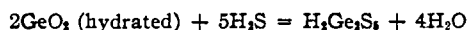


neutralization with sulfuric acid to the methyl red endpoint. The gelatinous oxide was filtered and washed thoroughly on the filter. The moist oxide was then suspended in 25 ml. of absolute alcohol and treated with hydrogen sulfide. The reaction required about one hour for completion.



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 ether 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, $\text{K}_2\text{Ge}_2\text{S}_5$, was prepared and the existence of a number of its hydrates was indicated.

3. Solid thiogermanic acid, $\text{H}_2\text{Ge}_2\text{S}_5$, 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. FELSING¹ AND GEORGE M. WATSON²

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}

(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*, **63**, 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).

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 Crafton⁷ 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_D^{20} 1.36857 (1.36864)⁷; normal boiling point, 49.71 ± 0.02° (49.731).⁷

Pitzer⁹ 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.

(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).

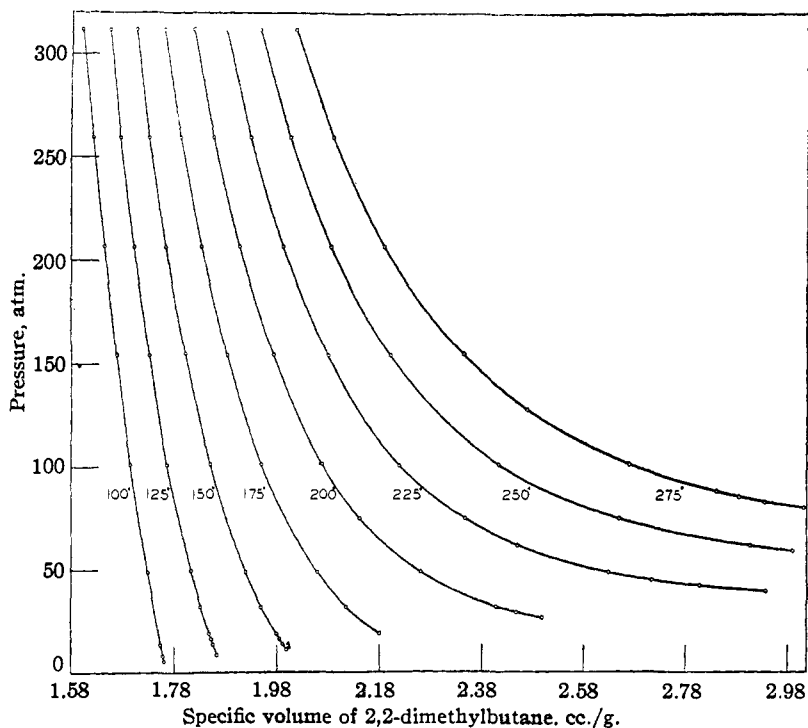


Fig. 1.

Discussion of Results.—The density data are believed to be accurate to 1.10 to 0.2%. The uncertainty in the measurement of pressure is less than 0.03%, in the determination of mass less than 0.01%, and in the measurement of volume from 0.05 to 0.10%. Temperature measurements are correct at least to 0.01°.

No attempt was made to determine the densities of the liquid at its own vapor pressure with the

TABLE I

COMPRESSIBILITY OF LIQUID 2,2-DIMETHYLBUTANE

Molecular weight, 86.172. Pressures are in normal atmospheres. Temperatures are on the International Temperature Scale.^a

| Temperature, °C. | 100.00 | 125.00 | 150.00 | 175.00 |
|-----------------------|--------|--------|--------|--------|
| Pressures, atm. | cc./g. | cc./g. | cc./g. | cc./g. |
| 10.00 | 1.757 | 1.861 | | |
| 15.00 | 1.753 | 1.854 | 1.989 | |
| 20.00 | 1.749 | 1.847 | 1.977 | 2.173 |
| 30.00 | 1.743 | 1.835 | 1.954 | 2.123 |
| 35.00 | 1.739 | 1.830 | 1.944 | 2.104 |
| 40.00 | 1.736 | 1.824 | 1.934 | 2.088 |
| 45.00 | 1.733 | 1.819 | 1.926 | 2.073 |
| 50.00 | 1.730 | 1.814 | 1.918 | 2.059 |
| 55.00 | 1.726 | 1.809 | 1.910 | 2.046 |
| 60.00 | 1.723 | 1.804 | 1.902 | 2.033 |
| 100.00 | 1.696 | 1.768 | 1.852 | 1.952 |
| 150.00 | 1.670 | 1.734 | 1.806 | 1.888 |
| 200.00 | 1.647 | 1.706 | 1.768 | 1.840 |
| 250.00 | 1.627 | 1.681 | 1.737 | 1.800 |
| 300.00 | 1.606 | 1.659 | 1.711 | 1.768 |

| Temperature, °C. | 200.00 | 225.00 | 250.00 | 275.00 |
|-----------------------|--------|--------|--------|--------|
| Pressures, atm. | cc./g. | cc./g. | cc./g. | cc./g. |
| 10.00 | | | | |
| 15.00 | | | | |
| 20.00 | | | | |
| 30.00 | | 2.438 | | |
| 35.00 | 2.372 | 4.000 | | |
| 40.00 | 2.327 | 2.920 | 6.128 | |
| 45.00 | 2.288 | 2.716 | 4.480 | 6.682 |
| 50.00 | 2.256 | 2.608 | 3.592 | 5.592 |
| 55.00 | 2.228 | 2.530 | 3.185 | 4.596 |
| 60.00 | 2.204 | 2.471 | 2.977 | 3.984 |
| 100.00 | 2.070 | 2.222 | 2.418 | 2.662 |
| 150.00 | 1.980 | 2.068 | 2.212 | 2.360 |
| 200.00 | 1.914 | 2.001 | 2.097 | 2.205 |
| 250.00 | 1.866 | 1.939 | 2.020 | 2.107 |
| 300.00 | 1.827 | 1.891 | 1.960 | 2.033 |

^a Burgess, *Bur. Standards J. Research*, 1, 635 (1928).

piston gage. Rather, the measurements were made at one to two atmospheres above the vapor pressures. The data for 100° to and including 200° are on the *liquid* sample; those for 225° and above represent gaseous densities only.

Acknowledgment.—The authors wish to acknowledge with thanks the grants received from the University of Texas Research Institute for equipment and research assistance.

Summary

1. The pressure-volume-temperature relations of 2,2-dimethylbutane have been determined at

25° intervals from 100° to and including 275° at pressures ranging from one or two atmospheres above the vapor pressures to approximately 300 atmospheres.

2. The data are presented tabularly and graphically, the specific volumes in cc./g. being related to the pressures at different temperatures.

AUSTIN, TEXAS

RECEIVED JUNE 15, 1943

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

The Volume of Mixing and the Thermodynamic Functions of Benzene-Carbon Tetrachloride Mixture¹

By SCOTT E. WOOD AND JAMES P. BRUSIE

The study of binary liquid mixtures by means of vapor pressures gives the change of the thermodynamic functions on mixing at constant pressure, whereas the theory gives the change of these functions on mixing at constant volume. The relationship between these functions for the two processes of mixing involves the volume of mixing.² It is therefore important to determine the volumes of mixing at several temperatures in order to determine how these functions change with temperature. This has been accomplished for benzene-carbon tetrachloride mixtures by measuring the volume of mixing at 30° and the coefficient of expansion from 15 to 75° over the whole range of composition.

Apparatus and Procedure.—The apparatus used for the expansion measurements is essentially that of Burlew.³ The design of the dilatometer was changed to that in Fig. 1b for greater ease of filling. The volume was about 5 cc., approximately 3 cc. being allowed for the solutions and 2 cc. for the mercury. During operation the tip of the capillary was always immersed below the surface of the mercury contained in the small receiving cups. Great difficulty was encountered in removing the last bubble of air from the tip of the capillary when joining the mercury in the capillary and in the cup. Many times the bubble seemed to cling to the tip and reënter the capillary when the dilatometer was cooled. This was overcome by grinding one side of the tip at a 45° angle up to the edge of the bore, as shown in cross-section in Fig. 1b.

It was determined that noticeable amounts of mercury evaporated from the collecting cups during the course of a run. Therefore a second cup of approximately the same size was always placed beside the collecting cup in order to determine this loss. At the end of each run the dilatometer was again weighed which together with the weight of the mercury in the receiving cups gave a measure of the loss of mercury by evaporation. This loss agreed to about 10% of the loss of mercury from the control cups.

The dilatometers were filled at room temperature under vacuum in the same manner as described by Burlew.³ However, since the density of the liquid mixtures was unknown, it was necessary to weigh both the mercury and solution in the dilatometer. All weights were recorded to ± 0.01 mg. and were consistent to ± 0.03 mg. They were corrected to vacuum. After the capillary had been dried the dilatometer was placed in the steel cylinder with a receiving cup in position. The mercury was then joined by gently heating the steel cylinder. Each series of measurements was started at 15°. The dilatometer was held at the desired temperature for one hour at the end of which time the two cups were replaced by another set and the temperature was raised. The temperature of the oil-bath was held to $\pm 0.005^\circ$.

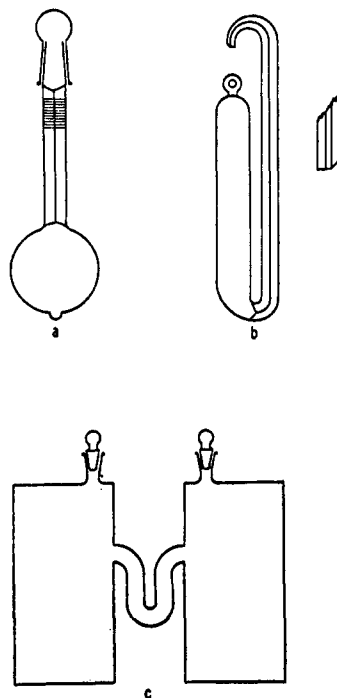


Fig. 1.—Apparatus.

The dilatometers were calibrated by a series of measurements with water at 10° intervals from 15 to 85°. The density of water in grams per cubic centimeter was com-

(1) This contribution contains material taken from a thesis by James P. Brusie presented to the Graduate School, Yale University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, February, 1943.

(2) G. Scatchard, *Trans. Faraday Soc.*, **33**, 160 (1937).

(3) J. S. Burlew, *THIS JOURNAL*, **62**, 690 (1940).