

The Coefficient of Expansion of Bromoform.—Our attention was called by Professor Hildebrand to the fact that the only determination of the coefficient of expansion of bromoform to be found in the literature, that of Thorpe,¹ was evidently made with impure material, since its melting point was recorded as 2.5° instead of the more recent value² of 7.7°. We accordingly undertook a redetermination of this coefficient.

The bromoform used was purified by washing with sodium carbonate solution and then with water, drying for seventy-two hours over anhydrous calcium chloride and distilling three times under a pressure of about 20 mm. The melting points after each distillation were, respectively, 7.65, 7.70, 7.70°, as determined by a standardized thermometer graduated to 0.1°, which was immersed in the melting solid contained in a jacketed test-tube.

The coefficient of expansion was determined from the density at a series of temperatures ranging from 9 to 50°. A Pyrex pycnometer was used, having a volume of approximately 150 cc.

Beginning at 9°, and then at a series of successively higher temperatures, the pycnometer was immersed in a water-bath until temperature equilibrium was reached. The temperature of the bath was obtained

TABLE I

DATA AND RESULTS

Temp., °C.	Density, g./cc.	Specific volume	Molal volume
9.32	2.9187	0.34261	86.597
9.96	2.9178	.34273	86.626
13.93	2.9067	.34403	86.955
14.92	2.9048	.34426	87.014
15.00 ^a	2.9043	.34431	87.027
18.73	2.8938	.34556	87.343
19.90	2.8918	.34581	87.404
20.00 ^a	2.8912	.34588	87.423
23.21	2.8822	.34696	87.696
24.92	2.8787	.34737	87.801
25.00 ^a	2.8780	.34746	87.823
27.92	2.8700	.34843	88.069
29.93	2.8656	.34897	88.203
32.43	2.8581	.34989	88.436
34.93	2.8525	.35057	88.608
38.65	2.8419	.35187	88.938
40.02	2.8393	.35219	89.019
42.71	2.8317	.35315	89.259
47.04	2.8201	.35459	89.625
50.27	2.8117	.35565	89.893

^a These values were calculated from Equation (1).

¹ Thorpe, *Proc. Roy. Soc. (London)*, **24**, 283 (1876).

² International Critical Tables, Vol. I.

by using a thermometer graduated to 0.1° , which was compared with one recently calibrated by the Bureau of Standards. The filled pycnometer was weighed at each temperature and the density, given in Table I, was calculated from these weights. The coefficient of cubical expansion of Pyrex glass used was that recently obtained by Buffington and Latimer.³ All weights were reduced to vacuum.

No recent determination of the density of bromoform has been made and those in the literature are not in close agreement. However, that of Perkin,⁴ 2.9045 g./cc. at 15° , and the value selected for the International Critical Tables, 2.890 at 20° , agree well with our values.

The following empirical equation for the variation of specific volume with temperature was obtained by the method of least squares from the data in Table I.

$$V_t = 0.24204 [1 + 0.00090411 (t - 7.7) + 0.0000006766 (t - 7.7)^2] \quad (1)$$

The values calculated by the aid of this equation differ by not more than three units in the last decimal place from the experimental points.

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CHEMICAL LABORATORY OF THE
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA

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ALBERT SHERMAN
JACK SHERMAN

The Freezing Point and Density of Pure Hydrogen Peroxide.—The above constants are of importance as criteria of the purity of peroxide. The freezing point as previously given¹ was taken when complete solidification took place, and the freezing bath was kept at a temperature several degrees below the freezing point of the peroxide. This gave too low a value, since the rate of crystallization of hydrogen peroxide is slow and the liquid has a great tendency to supercool. By a sufficient number of crystallizations a sample of peroxide was obtained which remained at a constant temperature during the whole process of solidification. The precaution necessary is to maintain the cooling bath at a temperature less than 0.1° below the freezing point, the liquid at the same time being continuously stirred. Under these conditions the melting point is -0.89° . The melting point -0.89° differs from that previously found by 0.90° , and this large difference must be ascribed to the slow rate of solidification which was not taken into account in the former work.

Special precautions were taken with regard to the dilatometer in the measurement of the density at 0° so that a minimum of decomposition occurred. Pyrex glass was found to be most suitable but only one out of a

³ Buffington and Latimer, *THIS JOURNAL*, **48**, 2305 (1926).

⁴ Perkin, *J. Chem. Soc.*, **45**, 533 (1884).

¹ *THIS JOURNAL*, **42**, 2548 (1920).