

by using a thermometer graduated to  $0.1^\circ$ , 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.<sup>3</sup> 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,<sup>4</sup> 2.9045 g./cc. at  $15^\circ$ , and the value selected for the International Critical Tables, 2.890 at  $20^\circ$ , 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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**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 given<sup>1</sup> 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  $0.1^\circ$  below the freezing point, the liquid at the same time being continuously stirred. Under these conditions the melting point is  $-0.89^\circ$ . The melting point  $-0.89^\circ$  differs from that previously found by  $0.90^\circ$ , 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  $0^\circ$  so that a minimum of decomposition occurred. Pyrex glass was found to be most suitable but only one out of a

<sup>3</sup> Buffington and Latimer, *THIS JOURNAL*, **48**, 2305 (1926).

<sup>4</sup> Perkin, *J. Chem. Soc.*, **45**, 533 (1884).

<sup>1</sup> *THIS JOURNAL*, **42**, 2548 (1920).

large number of dilatometers could be used successfully, as too much decomposition was evident in the others. The value 1.4649 found for the density at  $0^\circ$  agrees within 1 part in 1500 with the previous<sup>1</sup> determinations 1.4633.

In a dilatometer slight decomposition often occurs as is evidenced by the formation of minute bubbles. The following method is then recommended. The dilatometer is connected as indicated in the diagram by means of a rubber tube "B" to one end of an open manometer having an adjustable mercury reservoir A. The reading of the meniscus of the dilatometer is taken at atmospheric pressure,  $p_1$ , and then the mercury is rapidly raised so that the enclosed gas in the dilatometer and connecting tubing is compressed to a pressure  $p_2$  given by the manometer. The meniscus then gives a reading  $R_2$  at the pressure  $p_2$  as compared to the reading  $R_1$  at the pressure  $p_1$ . The volume  $v$  of the oxygen produced in the decomposition of the peroxide is given by  $v = K(R_1 - R_2) \div (1 - p_1/p_2)$ , where  $K$  is the volume of the unit length of the capillary of the dilatometer. As an example, in an inferior dilatometer (5cc. capacity), three sets of meniscus readings were made at twenty-minute intervals and the volumes of the bubbles in the liquid estimated by the above method as 0.0086, 0.0156 and 0.0214 cc. With these corrections the densities calculated for each of the three sets of observations agreed within 1 part in 7000.

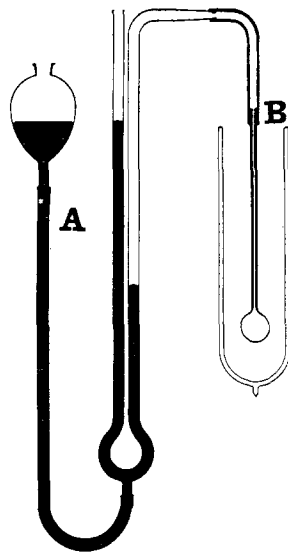


Fig. 1.

It was found that for concentrated aqueous solutions of peroxide containing up to 5% of water, the density could be accurately expressed by the equation  $D = 0.9486 + .005163 A$ , where  $A$  is the per cent. by weight of hydrogen peroxide.

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