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division on the drum was found to be equal to 0.0106% of deuterium oxide. The drum readings were corrected for the familiar change in the fringe colors with drum setting. In the case of the 40-mm cell it was found that the fringes are symmetrical at a reading of 55 divisions and again at intervals of 50 divisions. Thus from 55 to 105 the color match is made one fringe too high and the number of divisions (14) between the fringes must be subtracted from the reading.²

Samples of less than 20% concentration were measured with a 40-mm. cell. Higher concentrations can be handled by accurately diluting a small amount with ordinary water. Shorter cells such as the 10-mm. one with a 9-mm. inset giving a 1-mm. layer will handle the highest concentrations. The minimum quantity for the 40-mm. cell is 1.5 cc. and for the others the amount is correspondingly smaller. The precision of measurement is proportional to the length of cell, that for the 40-mm. chamber being about 0.02%. However, our present calibration for drum readings between 1500 and 3000 is not this precise.

Some precautions are necessary in preparing and handling the samples. A large bottle of redistilled water served as a standard. This was checked frequently by redistillation. Moderately concentrated samples for analysis were distilled in a small glass apparatus directly into the cell. Concentrated samples were distilled in a vacuum apparatus and drained into the cell through a tip on the end of the receiver. In the vacuum distillation the air can be removed by shaking during a preliminary freezing. Care must be observed to keep concentrated samples in water-free air to prevent serious dilution.

(2) See Gans and Bose, Z. Instrumentenk., 36, 137 (1916); L. H. Adams, This Journal, 37, 1181 (1915), for a discussion of this phenomenon.
DEPARTMENT OF CHEMISTRY

 COLUMBIA UNIVERSITY
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THE REFRACTIVE INDEX OF H_2O^{18} , AND THE COMPLETE ISOTOPIC ANALYSIS OF WATER

Sir:

In order to determine the validity of several additive laws in mixtures of $H^{1}H^{1}O$ and $H^{2}H^{2}O$ it has been necessary to dilute $H^{2}H^{2}O$ with different amounts of ordinary water. The density of these mixtures and the refractive index, as well as the dependence of the latter upon temperature and wave length, have been determined. The complete results are contained in a paper which has been sent by one of us to the *Physical Review*.

The volumes proved to be not quite additive. When x, which is the mole fraction of H²H²O, or the atom fraction of H², is 0.50, the molal

volume is 0.05% greater than is calculated from linearity, and when x = 0 the partial molal volume of H²H²O is 0.2% greater than when x = 1.

If Δs is the difference in specific gravity at 25° between a given sample and ordinary water, we find that

$$x = 9.579 \ \Delta s - 1.03 \ (\Delta s)^2 \tag{1}$$

but for less refined work we may write

$$\Delta s = 0.1056 \ x \tag{2}$$

Here we have assumed the value Δs equals 0.1056 for pure H²H²O given by Lewis and Macdonald [THIS JOURNAL, 55, 3057 (1933)]. If this value is found later to correspond to a different mole fraction than 100% it will suffice to multiply the x given by Equation (1) by that new mole fraction.

The refractive index is found to be linear with the mole fraction. If Δn is the difference in refractive index at 25° between a given sample and ordinary water

$$\Delta n = -0.00449 x \tag{3}$$

(This is the value for white light as used in an interferometer. The coefficient of x for sodium light is -0.00445.)

From a sample of water containing about 0.5% 0¹⁸, and of normal isotopic composition with respect to hydrogen, we have found an approximate value for the refractive index of H₂O¹⁸. The effect of this isotope is of the opposite sign from that of H², namely

$$\Delta n = 0.0008 \ y \tag{4}$$

where y is the increase in mole fraction of H_2O^{18} , or the atom fraction of O^{18} , over its value in ordinary water. Ordinarily O^{17} will be too little concentrated to be considered.

We therefore have a remarkably simple method of finding the complete isotopic composition of any sample of water whose density and refractive index have been determined. The equations are

 $\begin{array}{cccc} x &= 1.370 & \Delta s &- 190.5 & \Delta n & (5) \\ y &= 7.692 & \Delta s &+ 180.9 & \Delta n & (6) \\ \hline \\ Department of Chemistry & Gilbert N. Lewis \\ University of California & Daniel B. Luten, Jr. \\ Berkeley, California & Received November 24, 1933 & Published December 14, 1933 \\ \hline \end{array}$

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