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R. H. Crist, G. M. Murphy, and H. C. Urey

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# The Use of the Interferometer in the Isotopic Analysis of Water

R. H. Crist, G. M. Murphy and H. C. Urey, *Department of Chemistry, Columbia University*

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A method of analysis of mixtures of protium and deuterium oxides is presented. It consists in calibrating the apparent difference in indices of refraction of natural water and that containing higher concentrations of deuterium oxide, as obtained by a Zeiss water interferometer, against the corresponding differences in specific gravities. It is found that these two quantities are not proportional. The precision of measurement in the neighborhood of an experimentally determined specific gravity in a 40.06 mm cell is 0.01 percent.

IN the present state of our knowledge concerning the properties of the oxides of the two isotopes of hydrogen, the measurement of concentrations is of prime importance. For the most part methods of analysis are based upon differences in specific gravity of natural water and the sample. The float method[1] is a measurement of the temperature of a water bath that will just buoy up a vessel containing the sample for analysis, and depends upon the temperature coefficient of specific gravity. In another method the principle of the Cartesian diver is used so that the density of the water is determined in terms of the external gas pressure.[2] It has been found that the index of refraction of heavy water is considerably different from that of ordinary water.[3] This makes possible the use of the very precise interferometric methods for the determination of these differences. However, there are a number of indeterminate errors so that the measurements of $\Delta n$ are not absolute. In order to utilize them for the purpose of analysis, it suffices to calibrate the instrument carefully by means of the specific gravities. When this is effected, the precision of the measurement and ease of operation make its use very desirable. The instrument we have used is the Zeiss water interferometer.[4]

This instrument has been employed frequently in the analysis of aqueous solutions and the reader is referred to the literature for general information.[5] Light from a tungsten lamp is passed through a cell with two chambers, the one containing ordinary water and the other the sample. The difference in the indices of refraction of the two liquids is compensated by turning a glass plate in the standard beam. This glass compensator is adjusted by a lever which is raised by means of a lifting screw to which a drum and scale are attached. A geometrical analysis of the light path as the compensator is changed shows that the length of path is not proportional to the reading on the drum. It has been found that

$$\Delta p = ax - bx^2,$$

where $\Delta p$ is the change in light path and $x$ the drum reading and $a$ and $b$ are constants to be determined for the instrument in use.[6]

Further, there is a periodic shift of the zero point due to the fact that the indices of refraction of the solution, the water standard, and the compensator are different for the different colors of light. As a result, the true fringe may have colored edges or may be so diffuse because of other colors falling over the area that recognition or measurement is impossible. As the compensator is turned, neighboring fringes will be found

[1] Lewis and MacDonald, J. Chem. Phys. **1**, 341 (1933).

[2] Gilfillan and Polanyi, Zeits. f. physik. Chemie **A166**, 254 (1933).

[3] Washburn, Smith and Frandsen, J. Chem. Phys. **1**, 288 (1933).

[4] Crist, Murphy and Urey, J. Am. Chem. Soc. **55**, 5061 (1933); Lewis and Luten, J. Am. Chem. Soc. **55**, 5061 (1933).

[5] Gans and Bose, Zeits. f. Instrumentenk. **36**, 137 (1916); L. H. Adams, J. Am. Chem. Soc. **37**, 1181 (1915); W. Barth, Zeits. f. wiss. Phot. **24**, 145 (1926); Geffcken and Kruis, Zeits. f. physik. Chemie **B23**, 175 (1933).

[6] Adams, J. Wash. Acad. Sci. **5**, 267 (1915).

more satisfactory, and if one is selected, an error of whole fringe units is made. Therefore, appropriate corrections must be applied.

## CALIBRATION OF THE COMPENSATOR

The compensator and scale are calibrated by using monochromatic light, the field now consisting of alternate light and dark bands throughout the whole range. If the light in one beam is retarded the fringes will be shifted and a particular fringe in the field can no longer be identified unless the change has been made very slowly and this fringe followed by continuous adjustment of the compensator. This can be done by filling both chambers of the cell with water and then adding a solution very slowly to the one chamber. The new position of the fringe corresponds to a definite number of fringes from the original setting. In order to find the number of fringes corresponding to the different positions of the drum, the usual procedure has been to take readings for every ten fringes and consider the average fringe width as that corresponding to the average position on the drum. In this way the fringe width or fringes per drum division are found for the whole range of the drum. A relation between the number of fringes and the drum reading is then sought.[7] In our case, the equations

$$N_G = 0.07402x - 2.67 \times 10^{-6}x^2 \quad (\lambda = 5461) \quad (1)$$

$$N_Y = 0.06850x - 2.49 \times 10^{-6}x^2 \quad (\lambda = 5890) \quad (2)$$

where $N$ represents the number of fringes and $x$ the drum setting, were accurate to 0.10 fringe up to 2500 divisions. However, when the individual fringes were measured, very much larger errors were found and were traced to a fault in the screw. This was not properly lined up, with the result that the tip described a small circle. When the line through the lever arm is perpendicular to the screw, no error results, but below and above this position, it is obvious that errors will be made. A plot of the number of fringes as a running number against the lower scale divisions for successive revolutions of the drum shows a minimum in the curve which should be a straight line. At the upper part of

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[7] For a variety of functions proposed, see Adams, Gans and Bose, Barth, reference 5.

## TABLE I.

| $x$ | Fringe width | $x$ | Fringe width |
|-----|-----|-----|-----|
| 110.2 | 14.0 | 2525.7 | 15.7 |
| 124.9 | 14.7 | 2541.8 | 16.1 |
| 139.0 | 14.1 | 2558.2 | 16.4 |
| 152.3 | 13.3 | 2575.2 | 17.0 |
| 165.2 | 12.9 | 2592.9 | 17.7 |
| 178.6 | 13.4 | 2509.0 | 16.1 |
| 192.0 | 13.4 | 2524.9 | 15.9 |
| 206.0 | 14.0 | | |

the scale the line is curved upward; at the midpoint it is straight. This is illustrated in Table I. Maximum errors of 0.15 fringe are possible because of this fault in construction. It may be possible that other workers have overlooked this source of error. In order to eliminate the difficulty, it was necessary to read the position of every fringe throughout the range of the compensator. These readings can be duplicated to 0.2 division or 0.013 fringe if the proper procedure is followed to eliminate back lash in the screw, which amounted to 1.5 divisions.

## THE SKIPPING OF FRINGES

This phenomenon is conveniently observed if water is put into both chambers of the cell and a solution very slowly run into the one. The achromatic band will shift but it can be kept in view by the adjustment of the compensator. As the electrolyte is added, it is observed that the fringe is no longer achromatic but the edges become increasingly colored until this fringe has the same appearance as the neighboring fringe. With further addition of electrolyte, this neighboring fringe becomes achromatic so that an error of one full fringe is made if this fringe is selected as it must be in actual practice.

The frequency of this shift can be calculated if all the necessary data concerning the indices of refraction are available. For potassium chloride solutions it has been found by experiment to occur every 280 divisions, and for mixtures of protium and deuterium oxides, every 50 divisions. The correction in the latter case is thus almost one-third of the total reading. In order to determine where the changes actually take place, a sample of heavy water with a reading of 2300 was very slowly diluted with ordinary water and the positions noted at which pure

achromatic fringes were observed, and again where there were two entirely similar fringes. In making these observations, it is necessary that the eye be always in a position at which the dark reference bands are free from color. From these data, Table II was constructed. In the

TABLE II.

| Number of fringes skipped | Scale reading | Fringe width sodium $D$ line | Total correction |
|---|---|---|---|
| 1 | 35 | 14.63 | 14.63 |
| 2 | 85 | 14.68 | 29.31 |
| 3 | 135 | 14.74 | 44.05 |
| 4 | 185 | 14.79 | 58.84 |
| 5 | 240 | 14.85 | 73.69 |

third column are listed the fringe widths for sodium light. In the second column are the scale readings around which two similar fringes will be found, the higher fringe being the one read. If, for example, this were at 190 divisions, then the true fringe would be at $190-58.8=131.2$. The ratio of this corrected scale reading over the difference in specific gravity will give a constant that can be used for approximate work. Because of the inaccuracies in the screw it is desirable to use another method.

From the calibration of the compensator, using green light ($\lambda$5461), it is found that the scale readings are related to the fringes as follows:

$$0 \text{ to } \quad 1.8 = \ 0.131 \text{ fringes}$$
$$1.8 \text{ to } 178.6 = 13.000 \quad \text{``}$$
$$178.6 \text{ to } 190 \ = \ 0.850 \quad \text{``}$$
$$\overline{190 \text{ div.} = 13.980 \quad \text{``}}$$

Now from the ratio of the constants of Eqs. (1) and (2),

$$N_Y = 0.926 N_G \qquad (3)$$

so that the number of yellow fringes would be $0.926 \times 13.98 = 12.94$ and this is in error by 4 fringes, as noted in column 1 of Table II. Thus 190 divisions correspond to 8.94 fringes of yellow light. This number is related to the difference in the indices of refraction of the water and the sample by

$$\Delta n = N\lambda/2L, \qquad (4)$$

where $N$ is the number of fringes and $L$ the length of the cell.

## CALIBRATION OF THE CELLS

The solutions for analysis were distilled twice from alkaline permanganate under atmospheric pressure and at least three times *in vacuo*. Considerable care must be observed in this latter operation to prevent spattering. The water after being frozen to evacuate the vessel is then melted in a stream of warm water with shaking. In this way the bubbles of air escape without spattering. The receiver bulb is provided with a tip which is filed and broken in the vessel to which the sample is transferred. The distillations were carried out by cooling the receiving bulb in solid $CO_2$ and the distilling bulb kept at about 35°C. Under these conditions, distillation took place without ebullition.

The specific gravity determinations were made in duplicate with carefully calibrated pycnometers, the usual corrections being made for temperature and barometric pressure. The pycnometers held about 28 cc except in the case of the sample containing 17 percent deuterium, where a smaller pycnometer holding about 12 cc was used. Duplicate weighings agreed within 2 parts per 100,000 which represents about 0.02

TABLE III.

| Percent approx. | $\Delta s$ $\times 10^6$ | $x$ | $N$ | $N$ cor. | $\Delta s/N$ cor. |
|---|---|---|---|---|---|
| Cell I. $L=40.06$ mm | | | | | |
| 0.36 | 401 | 49.0 | 3.27 | 2.27 | 1767 |
| 1.20 | 1334 | 154.8 | 10.49 | 7.49 | 1781 |
| 2.18 | 2423 | 289.7 | 19.67 | 13.67 | 1772 |
| 4.41 | 4900 | 597.6 | 40.14 | 28.14 | 1741 |
| 14.66 | 16290 | 2103.4 | 133.33 | 92.33 | 1764 |
| 17.42 | 19356 | 2525.5 | 157.54 | 107.54 | 1800 |
| Cell II. $L=10.06$ mm | | | | | |
| 1.20 | 1334 | 43.5 | 2.90 | 1.90 | 7021 |
| 2.18 | 2423 | 65.5 | 4.45 | 3.45 | 7023 |
| 4.41 | 4900 | 149.5 | 10.11 | 7.11 | 6891 |
| 14.66 | 16290 | 498.9 | 33.63 | 23.63 | 6893 |
| 17.42 | 19356 | 595.4 | 40.00 | 28.00 | 6913 |
| 39.72 | 44133 | 1398.0 | 91.08 | 63.08 | 6996 |
| Cell III. $L=1.104$ mm | | | | | |
| 4.41 | 4900 | 12.0 | 0.82 | 0.82 | 5961 |
| 14.66 | 16290 | 52.6 | 3.52 | 2.52 | 6464 |
| 17.42 | 19356 | 59.1 | 3.98 | 2.98 | 6502 |
| 39.72 | 44133 | 131.5 | 8.89 | 6.89 | 6405 |

The second column is the difference in specific gravity of the sample and water at 25°C, the third is the reading on the drum of the interferometer, the fourth is the number of yellow fringes to which the drum reading corresponds, the fifth is this number of fringes less the number of fringes skipped as determined from Table II.

percent deuterium. No correction was made for possible increase of the oxygen isotopes.

The standard water was water redistilled from alkaline permanganate. A sample of this when distilled *in vacuo* showed no change when measured by the interferometer. All measurements are corrected to 25°C, the temperature coefficient of the scale readings being 0.4 percent per degree. Three cells were used with lengths 40.06, 10.01, 1.104 mm, respectively. The results are given in Table III. The last column shows that $\Delta n$ as determined by this instrument is not proportional to $\Delta s$. Furthermore, as is seen in Table IV, the ratios of the $\Delta n$'s for the same

TABLE IV. *Ratio of $\Delta n$'s for the cells.*

| Percent (approx.) | $N$(cor.)I/$N$(cor.)II. | $N$(cor.)II/$N$(cor.)III. |
|---|---|---|
| 1.20 | 3.942 | |
| 2.18 | 3.962 | |
| 4.41 | 3.958 | 8.648 |
| 14.66 | 3.907 | 9.376 |
| 17.42 | 3.840 | 9.396 |
| 39.72 | | 9.155 |
| 72 | | 9.000 |
| Measured ratio of the cells | 3.982 | 9.11 |

solutions in different cells are not constant. At one position in each set the ratio is close to the ratio of the length of cells obtained by actual measurement. This effect of the length of cells has also been observed by Brodskii and Shershever.[8]

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[8] Brodskii and Shershever, Zeits. f. physik. Chemie **A155**, 417 (1931).

In view of the variation in the value of $\Delta s/N$ and the non-proportionality of $\Delta n$ and $L$ it is necessary to plot $\Delta s/N$ against $N$ for each cell and to have a sufficient number of points so that interpolation can be made with the precision desired.

The precision of $\Delta s$ was shown to be $\pm 1 \times 10^{-6}$. The scale can be set to 0.5 divisions or about 0.03 fringes. The error introduced by using sodium for the tungsten light in correcting for the skipping is indeterminate but its magnitude can be estimated. There is no error if $N$ is a whole number of skip intervals, i.e., 50 divisions or about 3 divisions since it is then simply included in the value $\Delta s/N$. There is an error for any fraction of a skip interval. The error in the constant of Eq. (3) is of the order of one or two percent. Thus the error on the maximum of three fringes would then be but a few hundredths of a fringe. Therefore, it would seem that the error in the vicinity of an experimental specific gravity value would be within 0.06 fringe. For the 40 mm cell this would represent an error of 0.01 percent of deuterium oxide. For the other cells, the error is in proportion to the length.

This method of analysis is rapid, very precise and requires small samples. After a sample is prepared free from impurities, the analysis can be made in ten or fifteen minutes. The precision is as high as can be attained by careful pycnometer methods. The minimum quantities required for analysis using the 40, 10 and 1 mm cells are 1.5, 0.3 and about 0.05 cc, respectively.