3. Iodine in alkaline media has been shown to produce azo- and nitroso-benzenesulfonamides. These products are of bacteriological interest.

4. The bacteriological and roentgenological properties of these substances are under investigation.

NEW YORK, N. Y. RECEIVED MAY 29, 1937

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

The Densities of Mixtures of Light and Heavy Water

BY L. G. LONGSWORTH

In the preparation of some H_2O–D_2O mixtures for use in a series of transference measurements with such mixtures as solvents, it was observed that the mole fraction of D_2O in the solvent computed from the weights of H_2O and D_2O deviated by as much as 0.5% from the value obtained with the aid of the relation

$$N_{D_2O} = 9.377\ \Delta S - 1.01\ \overline{\Delta S^2} \qquad (1)$$

in which

$$\Delta S = 1 - d^{25}{}_{25} = 1 - \frac{n^{25}{}_4}{0.99707_4}$$

This equation is due to Lewis and Luten[1] and modified by Baker and La Mer.[2] It seemed desirable therefore to redetermine the densities of these mixtures as a function of the mole fraction, N_{D_2O}, of deuterium oxide.

The starting material was a sample of heavy water having a specific gravity of 1.10700. Accepting the value of 1.10790[3] as the specific gravity of pure D_2O the value of N_{D_2O} for this sample may be taken tentatively as 0.10700/0.10790 = 0.9916_6. Weighed quantities of this and ordinary water were mixed and the density of the resulting liquid was determined. This process was repeated until N_{D_2O} had been decreased to 0.2 in steps of 0.2.

The density measurements were made with the aid of a pycnometer similar to that described by Smith and Wojciechowski.[4] The volume of the pycnometer was 8.5 ml. and the capillary neck, marked with a single graduation, had an internal diameter of 1.4 mm. The pycnometer was filled with the aid of a hollow stainless steel needle. The pycnometer was then placed in a thermostat at 25.00° and the position of the meniscus relative to the graduation was observed to 0.001 cm. with a traveling microscope. Weighings were then made with a duplicate pycnometer as counterpoise. An air density of 0.0012 was used in the reduction of the weights to vacuum.

The results are given in Table I. This table also includes the density of D_2O-free water and the value of N_{D_2O} for natural water from the work of Johnston[5] and Tronstad, Nordhagen and Brun.[6] The values of ΔS, column 4, are, in contrast to those of equation (1), referred to the density of *D_2O-free water.* The atomic weights used were O = 16.0000, H = 1.00756, D = 2.01309, as given by Urey and Rittenberg.[7] The oxygen isotope ratio was assumed to be normal in all H_2O–D_2O mixtures. It will be noted that the atomic weight of hydrogen has been given a correction for the deuterium normally present.

TABLE I

THE DENSITIES AND MOLAL VOLUMES OF MIXTURES OF H_2O AND D_2O

1 Material	2 N_{D_2O}	3 d_4^{25}	4 ΔS	5 ΔS calcd.	6 $V - V_a$, ml.
D_2O[3]	1.00000	1.10466	0.10792	0.10790	0.0000
Starting material	0.99166	1.10376	.10702	.10701	.0001
Dilution 1	.82358	1.08570	.08891	.08892	.0005
Dilution 2	.61023	1.06279	.06593	.06593	.0003
Dilution 3	.40243	1.04044	.04351	.04351	.0001
Dilution 4	.20192	1.01884	.02185	.02185	.0000
Natural water[5]	$.00017_8$	0.99707_4	$.00001_9$	$.00001_9$	.0000
H_2O[5,6]	.00000	$.99705_5$	.00000		.0000

It is of considerable interest that H_2O–D_2O mixtures form a perfect solution, almost within the experimental error, as tested by the absence of a volume change on mixing. Identifying H_2O and D_2O with the subscripts 1 and 2, respectively, a perfect solution conforms to the relation[8]

$$V_a = N_1v_1 + N_2v_2 \qquad (2)$$

in which V_a is the volume of a mole of solution

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[1] Lewis and Luten, THIS JOURNAL, **55**, 5061 (1933).

[2] Baker and La Mer, *J. Chem. Phys.*, **3**, 406 (1935).

[3] Selwood, Taylor, Hipple and Bleakney, THIS JOURNAL, **57**, 642 (1935).

[4] Smith and Wojciechowski, *Rocsniki Chem.*, **16**, 104 (1936).

[5] Johnston, THIS JOURNAL, **57**, 484 (1935).

[6] Tronstad, Nordhagen and Brun, *Nature*, **136**, 515 (1935).

[7] Urey and Rittenberg, *J. Chem. Phys.*, **1**, 137 (1933).

[8] J. H. Hildebrand, "Solubility of Non-Electrolytes," Reinhold Publishing Corp., New York, 1936, 2d edition, p. 58.

and v the molal volume of a pure component. The actual molal volumes, V, of the solutions are given by the relation

$$V = (N_1M_1 + N_2M_2)/d \qquad (3)$$

in which M is a molar weight and d the observed density. The expansions on mixing, $V - V_a$, recorded in column 6 of the table are zero almost within the limits of precision of the density determinations, *i. e.*, $\pm 1 \times 10^{-5}$. Consequently, if this expansion is assumed to be negligible, equations (2) and (3) may be combined to give the following simple relation between N_{D_2O} and ΔS

$$N_{D_2O} = \alpha\Delta S/(1 - \beta\Delta S) \qquad (4)$$

in which

$$\alpha = M_1/M_2(1 - d_1/d_2) = 9.235$$
$$\beta = [M_2d_1/d_2 - M_1]/M_2(1 - d_1/d_2) = 0.0309.$$

Evaluation of α and β from the data of Table I by the method of least squares gives $\alpha = 9.2351$ and $\beta = 0.0327$, and since these constants reproduce the densities within the experimental uncertainties, as is shown by a comparison of columns 4 and 5, their use is recommended.

The author wishes to thank Dr. D. A. MacInnes for many helpful suggestions in connection with this work.

Summary

The densities at 25° of a series of mixtures of light and heavy water have been determined. Contrary to the conclusion of earlier workers the components mix without appreciable change of volume. This fact is used in obtaining a new formula relating the composition of the mixtures to their densities.

NEW YORK, N. Y. RECEIVED JUNE 4, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF SMITH COLLEGE]

The Potential of the Ag(s), AgI(s), I^- Electrode[1]

BY JESSIE Y. CANN AND ALICE C. TAYLOR

The purpose of this investigation was to determine, by means of electromotive force measurements, the potential of the Ag(s), AgI(s), I^- electrode.

A search of the literature revealed that the results obtained for the value of this electrode were not concordant.[2]

Method and Apparatus

In this investigation the cell

Ag(s), AgCl(s), *m* KCl(aq.), *m* KI(aq.), AgI(s), Ag(s)

with flowing junction, was measured. Two pieces of apparatus were used: (1) that of MacInnes and Yeh,[3] and (2) that of Cann and Mueller,[4] suggested by the work of Randall and Cann.[5] In each case care was taken to prevent the flow of liquid over the electrodes.[6]

The cell was placed in the usual oil thermostat, regulated at 25°, and measurements were made with a shielded Leeds and Northrup Type K potentiometer.

Materials

All solutions were made up by weight, moles per 1000 g. of water in vacuum, from high grade "analyzed" salts and conductivity water. Care was taken to remove all traces of oxygen by bubbling an inert gas through the solutions.

The Ag(s), AgCl(s) spiral electrodes were made according to the method of Randall and Young.[7]

The Ag(s), AgI(s) spiral electrodes were made by two different methods: first, electrolytically following the general method of Randall and Young,[7] electrolyzing the reduced silver spirals in a 0.05 normal solution of hydriodic acid, with a current of 0.005 ampere, for two hours; and, second, by heating to 650°, the silver spirals covered with a paste of one part silver iodate and nine parts silver oxide, for ten minutes in accordance with the second method of Owen.[2e] Both sets of electrodes were protected, as much as possible, from light. After being washed in distilled water, each set was short-circuited together for some hours. Immediately before being introduced into the cell

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(1) The experimental part of this paper is a portion of a thesis submitted by A. C. Taylor in partial fulfilment of the requirements for the degree of Master of Arts at Smith College.

(2) (a) Noyes and Freed, THIS JOURNAL, **42**, 476 (1920); (b) Gerke, *ibid.*, **44**, 1684 (1922); (c) Pearce and Fortsch, *ibid.*, **45**, 2852 (1923); (d) Hass and Jellinek, *Z. physik. Chem.*, **162**, 153 (1932); (e) Owen, THIS JOURNAL, **57**, 1526 (1935).

(3) MacInnes and Yeh, *ibid.*, **43**, 2563 (1921).

(4) Cann and Mueller, *ibid.*, **57**, 2525 (1935).

(5) Randall and Cann, *ibid.*, **52**, 589 (1930).

(6) Carmody, *ibid.*, **54**, 210 (1932); Cann and LaRue, *ibid.*, **54**, 3456 (1932).

(7) Randall and Young, *ibid.*, **50**, 989 (1928).