Enrichment of the Heavy Water by Thermal Diffusion.

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(Received October 13, 1941.)

Introduction. It has been shown(1)(2) that heavy water which contains deuterium can be concentrated at the colder part in the thermal diffusion apparatus devised by Clusius and Dickel(3). On the other hand, it has been also shown definitely by one of the present authors(4) that the degree of the separation of salt solutions is changed by the addition of another salt, and that the separation of the added salt is also affected inversely at the same time. These results suggest that the isotopic composition of ordinary water may be shifted if it is treated in a thermal diffusion apparatus, especially in the case of salt solutions. The object of the present research is to study the effect of isotopic separation of water caused by the addition of some inorganic substances ($1\ \mathrm{N}\ H_2SO_4$, $0.1\ \mathrm{N}$ KCl and $1\ \mathrm{N}\ Na_2SO_4$).

Experiments. *Apparatus*:—The thermal diffusion apparatus used is of the same type as that described in the paper published by one of the present authors(5). The length (h) of the column which has an equidistant annular space is 30 cm., the width (a) of the annular space is 0.78 ± 10 mm., and the temperatures of the colder and the hotter walls are $20° \pm 2°$C. and $76° \pm 1°$C. respectively. The volumes of the upper and the lower reservoirs are 12 and 4 c.c. respectively.

Procedures:—As the experimental procedures are almost the same as those described in ref. (5), the details are omitted here. Using a part of the sample, which was treated in the apparatus for the desired length of time, the concentrations of H_2SO_4 and KCl were determined volumetrically, while that of Na_2SO_4 gravimetrically. Another part of the sample was distilled twice under the reduced pressure at room temperature. In the case of H_2SO_4, however, the distillation was carried out after neutralisation by metallic zinc. The density change of the purified water thus obtained was measured by means of the usual float method(6). The accuracy of the density measurement was estimated to be $\pm 1\ \gamma$.

Experimental Results. The experimental results are summarised in Table 1, where separation ratio (n'/n) denotes the ratio of the concentration of the solute at the bottom reservoir to that at the top.

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(1) K. Clusius and G. Dickel, *Naturwiss.*, **27** (1939), 148.
(2) H. Korsching and K. Wirtz, *ibid.*, **27** (1939), 367.
(3) K. Clusius and G. Dickel, *ibid.*, **26** (1938), 546.
(4) K. Hirota, *Bull. Chem. Soc., Japan*, **16** (1941), 232; *J. Chem. Soc., Japan*, **62** (1941), 568; L. T. Gillespie and S. Breck, *J. Chem. Phys.*, **9** (1941), 370.
(5) K. Hirota, *J. Chem. Soc., Japan*, **62** (1941), 480; *Bull. Chem. Soc., Japan*, **16** (1941), 475.
(6) M. Harada, *J. Chem. Soc., Japan*, **56** (1935), 811.

Table 1. Summarised Experimental Results.

Sample Used (Conc.)	No. of Exp.	Time in Hours	Separation Ratio of the Solute	Density Increase at the Bottom Reservoir in γ
Pure Water (Twice Distilled Water)	15	4	—	2
	3	7	—	0.5
	1	16	—	3
	2	24	—	−0.5
	4	43	—	1
H_2SO_4 (1 N)	8	5	1.5	1.5
	7	12	2.2	4
	6	24	2.7	8
	5	48	3.0	8
KCl (0.1 N)	11	8	1.0_7	8
	10	17	1.1_4	4
	9	24	1.1_4	6
	12	47	1.1_2	7
Na_2SO_4 (1 N)	13	7	1.3_7	2
	14	24	1.6_6	16

As seen in the table, the density differences of pure water, H_2SO_4 and KCl solutions seem to become constant in 48 hours, i.e., 0 γ for pure water, 8 γ for H_2SO_4 and 7 γ for KCl. In the case of Na_2SO_4, however, the data are not sufficient to arrive at a definite conclusion.

It is possible that the density increase is caused by the isotopic shift during the distillation of pure water as well as of the solutions. This effect is, however, negligibly small at least in the case of KCl solution in which the degree of the separation of the solute is small, while in the case of H_2SO_4 there remains some ambiguity, because the separation of the solute is large, and an isotopic shift may also occur in the process of the neutralisation.

Discussion. To check the above results, the separation ratios of the solutes in this research were compared with those in ref. (5), in which an apparatus with such dimentions as $h = 94$ cm. and $a = 0.15$ cm. was used. As shown there, in these apparatus the separation ratios at the stationary state can be expressed as:

$$\ln \frac{n'}{n} = C \cdot D' \frac{h}{a^4} ,$$

where D' is the thermal diffusion constant and C is the constant which depends only on the kind of the solution. The ratios of the logarithm of the separation ratios of this experiment ($\ln(n'/n)_{\mathrm{II}}$) to those in ref. (5) ($\ln(n'/n)_{\mathrm{I}}$) were calculated in each solution, and it was found that these values agree fairly well with the theoretical value (4 ± 1). This is shown in Table 2.

Table 2. Comparison of the Separation Ratios.

		(*)	n'/n	$\ln(n'/n)$	$\frac{\ln(n'/n)_{II}}{\ln(n'/n)_{I}}$
H_2SO_4	(1 N)	II	3	1.1	$5._2$
	(1 N)	I	1.23	0.21	
KCl	(0.1 N)	II	1.1_3	0.1_2	3±1
	(1 N)	I	1.04	0.4	
Na_2SO_4	(1 N)	II	1.6_6	0.5_3	$4._1$
	(1 N)	I	1.14	0.13	

(*) I and II denote the values in the previous research (ref. 5) and those of the present one, respectively.

Next, the density increase of pure water will be discussed. The separation ratio of pure water containing about 30% of deuterium was 1.09_3, according to Korsching and Wirtz⁽²⁾, who used an apparatus with $h = 10$ cm. and $a = 0.25$ mm. From these dimensions, D' values of D_2O was calculated to be $5\times10^{-10}\,\dfrac{\text{cm}^2}{\text{sec. deg}}$ by the formula (1) as described in ref. (5), taking the ordinary diffusion constant of D_2O at 35°C. as 3.9×10^{-5} cm.^{2}/sec.⁽⁷⁾ Assuming that D' value of the water, containing heavy oxygen, is same as the above, the density increase due to both heavy hydrogen and heavy oxygen in our experiment was calculated to be 0.6 γ.⁽⁸⁾ This estimated value conforms to our experiment in the case of pure water where no separation was found within our experimental errors. The separations in the solutions, however, are large as compared with the above calculation.

As the mechanism of the separation of the solute is not clear at present, we cannot account definitely for the reason why the enrichment of the heavy water occurs in the case of the solutions. Here, a plausible explanation was tried as follows: In solutions, the zero-point energies in the vibration between ions and solvated water are different in various water molecules which are different in molecular weight. Owing to this, isotopic shift might occur between solvated water molecules and the non-solvated in the sense that the solvated become richer in heavier isotopes. Therefore, in the thermal diffusion column, the enrichment of heavy water and that of the solute occur at the same time, as is observed in our experiments.

This argument holds in the same way whether the density increase is due to deuterium or to heavy oxygen, and the present authors consider that it will be mainly caused by the latter. If the density increase is assumed to be the result of the deuterium, the separation ratio of the

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(7) W. J. C. Orr and J. A. V. Butler, *J. Chem. Soc.*, **1935**, 1273.

(8) The natural contents of heavy hydrogen and heavy oxygen in water are 1/5800 and 1/500, which correspond to 18~19γ and 200γ as density. [H. L. Johnston: *J. Am. Chem. Soc.*, **57** (1935), 484; S. H. Manian, H. C. Urey, W. Bleakney: *ibid.*, **56** (1934), 2601.]

deuterium will take an improbably large value (1.4), which is much larger than the separation ratio of the solute itself in KCl solution.

In conclusion, the authors express their sincere thanks to Dr. S. Sato, the Director of the Laboratory, for the permission of the publication of this paper, and the senior author also to Dr. R. Yoshimura, the Chief of the Department of Inorganic Chemistry, for their encouragement throughout this research.

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Railway Company, Dairen.