SHORT COMMUNICATIONS

On the Relative Volatility of Heavy- and Light-oxygen Water

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As concerns the relative volatility of heavy- and light-oxygen water at 100°C, M. H. Wahl and H. C. Urey[1] obtained a value of 1.003 by extrapolating their experimental values measured at four temperatures between 11.25 and 46.35°C, and this value has been accepted. Recently, H. E. Watson[2] analysed the results of his experiments on the concentration of light oxygen water and concluded that a value of 1.0056 is the most probable one for the relative volatility of H_2O^{16} and H_2O^{18}. He quoted for comparison the values between 1.0046 and 1.0062 which were obtained by several other authors. During our experiments on the concentration of heavy oxygen by the fractional distillation of water, we became aware of the fact that the degree of enrichment of the heavy oxygen was excessive as compared with that of the deuterium, so far as the value of 1.003 was used as the single plate fractionation factor for heavy oxygen. Therefore we attempted to verify the relative volatility by the following experiments.

A packed column is operated at total reflux under atmspheric pressure. Distillation is started with 4l of normal water in the pot. As distillation is continued, the same volume of normal water as that of distillate is refluxed at the top of the column. Thus, at intervals small quantities of water sample (about 30 cc. each time) are taken out of the pot and their contents in heavy oxygen and deuterium are measured separately. Assuming that the plate efficiencies are equal for isotopes of oxygen and hydrogen, and that the fractionation factor for H_2O/HDO is 1.0260, we can obtain the apparent fractionation factors each time of sampling for heavy oxygen water by applying Fenske equation. Some of the results obtained are tabulated in the accompanying table.

Duration of operation days	Excess density due to		Number of plates in Fenske eq. based on deuterium	Apparent fractionation factor for heavy oxygen
	deuterium r	heavy oxygen r		
24	14.9	36.2	25.9	1.0058
38	24.4	46.2	36.4	1.0052
46	25.9	49.4	37.8	1.0053
55	29.5	54.2	41.0	1.0053
63	32.2	56.1	43.3	1.0052
80	39.5	59.0	48.8	1.0048
88	41.3	59.4	50.0	1.0047
95	43.7	59.5	51.8	1.0045

As will be seen in the table, the apparent fractionation factor for oxygen isotope diminishes gradually as the fractionation proceeds toward equilibrium. This fact may indicate that the concentrations of heavy oxygen and deuterium in water do not proceed at the same rate, but that heavy oxygen reaches equilibrium earlier than deuterium. Time (t) necessary for equilibration can be calculated by the equation advanced by H. C. Urey, et. al.[3]:

$$t=\frac{H\left\{(1-N)\ln\frac{1-N}{1-N_0}+N\ln\frac{N}{N_0}\right\}}{wN(\alpha-1)k\ln\alpha}+\frac{h(N_0-N)}{wN(\alpha-1)}$$

Here, N and N_0 denote the mole fraction of the less-volatile component at the top and the bottom, H and h are the hold-up in the column and the pot, w is the through-put, α is the single plate fractionation factor, and k is the number of theoretical plates. Under our experimental conditions t's are calculated to be about 39 days for heavy oxygen and about 78 days for deuterium, i. e. the former reaches equilibrium twice as rapidly as the latter. The experimental results show a longer time than that mentioned for equilibration but their tendency is in accord with the prediction.

In conclusion, it is quite clear that the value of 1.003 obtained by Wahl and Urey is too low. However, the value of 1.0056 obtained by Watson seems too high because his calculation might be based on an incorrect plate number which was determined by the non-equilibrated concentration of deuterium.

Recently the following relation for the relative volatility and the temperature T in °K is presented[4]:

$$\log(pH_2O^{16}/pH_2O^{18})=3.20/T-0.00680$$

According to this equation, the relative volatility is 1.0041 for 100°C. Extrapolating our experimental results, we can also conclude that the correct value may lie between 1.0043 and 1.0040. In another experiment done under a larger through-put, we obtained a value of 1.0043.

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1) M. H. Wahl and H. C. Urey, *J. Chem. Soc.*, 3, 411 (1935).

2) H. E. Watson, *J. Appl. Chem.*, 3, 556 (1953).

3) H. C. Urey, J. R. Huffman, H. C. Thode, and M. Fox, *J. Chem. Phys.*, 5, 856 (1937).

4) I. Kirschenbaum, "Physical Properties and Analysis of Heavy Water", McGraw-Hill Book Co. Inc., New York, N. Y. (1951), p. 29.