Relative Volatility of H_2O^{16}/H_2O^{18} and Equilibration Time for Fractional Distillation of Water[*]

By Sadahiro SAKATA and Noriyoshi MORITA

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Introduction

In a previous experiment[1], fractional distillation of water was accomplished with a packed column under total reflux by continuously supplying at the top of the column the same volume of fresh normal water as that of the distillate, and the relative volatility of light- to heavy-oxygen water was calculated from the concentration of heavy oxygen in the still water by assuming the same number of theoretical plates as that determined from concentration of heavy hydrogen and by using 1.026 for the relative volatility of H_2O/HDO. In the kind of fractionation applied there, the equilibration time for hydrogen isotopes was about twice that for oxygen isotopes and, therefore, the apparent value of the relative volatility of light- to heavy-oxygen water diminished gradually as the fractionation proceeded toward equilibrium. Extrapolating our experimental results, we concluded that the correct value lies between 1.0043 and 1.0040.

For further confirmation of the result,

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[1] S. Sakata and N. Morita, This Bulletin, **29**, 284 (1956).

another kind of experiment was made with a packed column where equilibrium of fractional distillation between waters in the still and in the condenser was obtained. The effect of the concentration of H_2O^{17} upon the concentration of H_2O^{18} was taken into consideration. The mean value of the relative volatility of H_2O^{16}/H_2O^{18} was proved to be 1.0039 with a possible error of ±0.0002.

Experimental Procedure and Results

Distillation apparatus is shown diagramatically in Fig. 1. The column, 250 cm. in height, was made of 50 mm. copper tube with 1 mm. wall thickness. It was packed with heli-pack type packings, size 5×5×3 mm., made from 0.3 mm. copper wire. The volume of the still was 2.0 l. and that of condenser was 5.0 l.

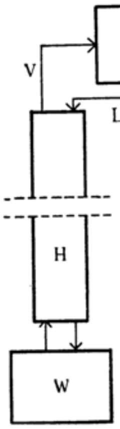

Fig. 1. Fractionation Apparatus.

At the beginning of each series of experiments, 1.5 l. of normal water was poured into the still and 5.0 l. into the condenser. The still was heated externally with an electric furnace, and the column hold-up of water after boiling-up was judged to be about 100 cc. from the decrease of water in the still. The uncertainty of the hold-up does not seriously alter the conclusions given later. The through-put was determined from the quantity of condensate obtained during a short given interval and was calculated to be 3.3 cc./min. or 200 cc./hr.

TABLE I

RESULTS, SERIES-1

Duration days	Excess in Density Still γ	Condenser γ
0.0	0.0	—
5.0	15.9	—
10.0	19.5	—
17.0	19.4	—
33.0	20.7	−6.0
D	7.1	−1.8
	$n+1=19.4_1$	
O^{18}	13.0	−4.0
(O^{17}	0.6	−0.2)
	$\alpha=1.0038_3$	
51.0	21.9	−5.0
D	7.3	−1.5
	$n+1=18.9_2$	
O^{18}	13.9	−3.3
(O^{17}	0.7	−0.2)
	$\alpha=1.0039_7$	

TABLE II

RESULTS, SERIES-2

Duration days	Excess in Density Still γ	Condenser γ
0.00	0.0	—
1.00	5.2	—
2.00	9.0	—
3.10	12.7	—
4.23	14.8	—
5.90	16.9	—
8.00	19.9	—
11.00	21.5	—
15.00	23.6	—
18.00	24.1	—
23.14	23.8	−7.5
D	7.8	−2.6
	$n+1=22.9_2$	
O^{18}	15.3	-4.6_9
	$\alpha=1.0038_0$	
27.00	24.2	−7.1
D	7.3	−2.6
	$n+1=22.0_8$	
O^{18}	16.1	-4.3_0
	$\alpha=1.0040_2$	

Two series of experiments were done, the results of which are tabulated in Tables I and II. During each series of experiments, samples of about 15 cc. were taken from the still at intervals of several days and their total excess densities due to both heavy oxygen and heavy hydrogen were measured as compared with normal water. After equilibrium of fractionation was reached, two samples of water, one from the still and the other from the condenser, were taken. The total excess densities of these samples were measured first and then the heavy oxygen content of each of these samples was determined by electrolyzing the sample and combining the evolved oxygen with standard hydrogen[2]. As will be seen from the experimental procedure, the excess density of water taken from the condenser is negative. The density due to H_2O^{17} was separated from the density due to total heavy oxygen water by calculation on the assumptions that the relative volatility of H_2O^{16}/H_2O^{18} was 1.0039 and of H_2O^{16}/H_2O^{17} was $\sqrt{1.0039}$, and that the concentrations

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2) N. Morita and T. Titani, This Bulletin, **11**, 414 (1936).

of H_2O^{18} and H_2O^{17} in normal water were respectively 224.7 and 21.9 in γ unit[3,4]. The number of theoretical plates $n+1$ was calculated from the excess densities due to heavy hydrogen of the samples as determined by subtracting the densities due to heavy oxygen from the total excess densities and by using $\sqrt{1.052}$ as the relative volatility of H_2O/HDO and 0.000147 (15.8γ) as the atomic fraction of deuterium in normal water. Using this number of theoretical plates, the relative volatility α of H_2O^{16}/H_2O^{18} was calculated from the excess densities due to H_2O^{18} of the two samples, Δs_w for the water from the still and Δs_p for the water from the condenser, by the equation

$$(224.7+\Delta s_w)/(224.7+\Delta s_p)=\alpha^{n+1} \qquad (1)$$

Two sets of measurements were made for each series of experiments. Four values of α in Table I and II give a mean value $\alpha=1.0039_1$. If we assume an error of $\pm 0.1\gamma$ for each value of measured excess densities due to deuterium and that due to O^{18}, the largest possible error in α is ± 0.00014. Although the error of each value of excess densities may be larger than $\pm 0.1\gamma$, the deviation of each calculated value of α from the mean value was rather small, and we concluded ± 0.0002 to be the possible error of the mean value.

Relation of Simultaneous Concentration of Heavy Oxygen and Heavy Hydrogen

Harbert[5] assumed Fenske's relation for each pair of components of a multicomponent system at equilibrium under total reflux. Normal water consists of nine components, as is shown in Table III. Mole fraction of each component in Table III was calculated by using values[3,4] of atomic fraction of isotopes, i.e. H=0.999853, D=0.000147, O^{16}=0.997640, O^{18}=0.001981 and O^{17}=0.000379, as well as by using the equilibrium constant for hydrogen isotopes $[HOD]^2/[HOH][DOD]=3.87$ and by assuming no isotopic effect for oxygen isotopes. As we can consider that these components in water constitute an ideal solution, we can apply Harbert's equation for equilibrium

TABLE III

COMPOSITION OF NORMAL WATER

No.	Formula	Mole fraction
1	HHO^{16}	$99.73467\cdot 10^{-2}$
2	HHO^{18}	$19.80418\cdot 10^{-4}$
3	HHO^{17}	$3.78889\cdot 10^{-4}$
4	HDO^{16}	$29.32616\cdot 10^{-5}$
5	HDO^{18}	$5.82326\cdot 10^{-7}$
6	HDO^{17}	$1.11409\cdot 10^{-7}$
7	DDO^{16}	$22.28229\cdot 10^{-9}$
8	DDO^{18}	$4.42456\cdot 10^{-11}$
9	DDO^{17}	$0.84650\cdot 10^{-11}$

$$x_{jw}=\alpha_{1j}^{n+1}x_{jp}\Big/\sum_{i=1}^{9}\alpha_{1i}^{n+1}x_{ip} \qquad (2)$$

where x is concentration in mole fraction, suffix i or j indicates any one component in these nine components, suffix w indicates water in still, suffix p indicates water in condenser, and α_{1j} is the relative volatility of the most volatile component H_2O^{16} to j's component. As will be seen from Eq. (2), any two components show Fenske's relation because the denominator of the equation is common for all components and because for a pair of components j and j′ there exists a relation $\alpha_{1j'}/\alpha_{1j}=\alpha_{jj'}$.

In addition to the fractionation by distillation, we must consider the following exchange reaction of hydrogen isotopes as a possible cause of change in concentration of components

$$\underset{k}{HOH}+\underset{l}{DOD}=\underset{m}{2HOD} \qquad (3)$$

From Harbert's equation we can write

$$x_{mw}/x_{kw}=\alpha_{km}^{n+1}(x_{mp}/x_{kp})$$

$$x_{mw}/x_{lw}=\alpha_{lm}^{n+1}\ (x_{mp}/x_{lp})$$

where suffixes k, l and m indicate components as shown under Eq. (3). Then

$$x_{mw}^2/x_{kw}\cdot x_{lw}=(\alpha_{km}\cdot\alpha_{lm})^{n+1}(x_{mp}^2/x_{kp}\cdot x_{lp})$$

When vapor pressures of pure components are written as P_k, P_l and P_m we have the relation

$$\alpha_{km}\cdot\alpha_{lm}=P_k\cdot P_l/P_m^2$$

Therefore when P_m is geometrical mean of P_k and P_l, $\alpha_{km}\cdot\alpha_{lm}$ becomes unity, and we have the relation

$$x_{mw}^2/x_{kw}\cdot x_{lw}=x_{mp}^2/x_{kp}\cdot x_{lp}$$

Thus we can conclude that when either the water in the still or in the condenser is in isotopic equilibrium, the other is also in isotopic equilibrium and the exchange reaction shown in Eq. (3) has no effect on change in concentration of components of water under fractional distillation.

Fig. 2 shows the calculated values of fractional concentration of each component of water which is in equilibrium with normal water versus the number of theoretical plates of a fractionation column. In this calculation we assumed the relative volatility of H_2O^{16} to each component to

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

4) I. Kirshenbaum, "Physical Properties and Analysis of Heavy Water", McGraw-Hill Book Co., N. Y. (1951).

5) W. D. Harbert, *Ind. Eng. Chem.*, **37**, 1162 (1945).

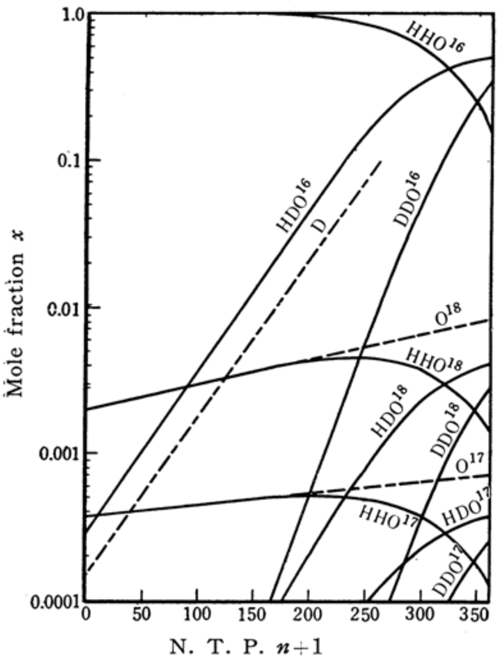

Fig. 2. Change of concentration with N. T. P.

TABLE IV

RELATIVE VOLATILITY

HHO^{16}	HDO^{16}	DDO^{16}
1.0000	$\sqrt{1.052}$	1.052
HHO^{17}	HDO^{17}	DDO^{17}
$\sqrt{1.0039}$	$\sqrt{1.0039 \cdot 1.052}$	$1.052\sqrt{1.0039}$
HHO^{18}	HDO^{18}	DDO^{18}
1.0039	$1.0039\sqrt{1.052}$	$1.0039 \cdot 1.052$

be as shown in Table IV. As are shown by dotted lines in the Fig. 2, the logarism of atomic fraction of D, O^{18}, and O^{17} in the range as shown in the Figure each shows a linear relation with $n+1$.

Equilibration Time

Urey and others[6,7] showed that the velocity of enrichment of a less-volatile component in a column is the greater, the nearer the plate is to the still, so that a stationary state sets in first at the lower part of the column. They, therefore, assumed that at a given moment shorter than equilibration time, the lower part of the column reaches the stationary state determined by Fenske's equation, while the upper part has the composition of the initial mixture. By applying the assumption to our experiment and assuming the upper part of the column to have the composition of the water in the condenser, the mean concentration $\bar{\eta}$ of a less-volatile component in the column is shown by

$$\bar{\eta}=\{x_{\mathrm{W}}+\alpha x_{\mathrm{P}}(\ln[x_{\mathrm{W}}]/x_{\mathrm{W}}-1)\}/n\alpha\ln\alpha \qquad (4)$$

where x_{W} is the concentration of a less-volatile component in the still at a given moment, x_{P} is that in the condenser, and x with square brackets shows a value at equilibrium.

Additionally we assume, as was done by Urey and others, that the vapor which enters into the condenser is in one-plate equilibrium with the refluxing water, and then we have the following relation by a material balance in a short interval $\mathrm{d}t$

$$x_{\mathrm{P}}L\mathrm{d}t-(x_{\mathrm{P}}/\alpha)V\mathrm{d}t=W\mathrm{d}x_{\mathrm{W}}+H\mathrm{d}\bar{\eta} \qquad (5)$$

where V is the molar vapor velocity, L is the reflux velocity, W is the still hold-up, and H is the column hold-up. Under total reflux $L=V$, and at any moment from material balance we have $Wx_{\mathrm{W}}+Px_{\mathrm{P}}=(W+P)x_0$, where P is the condenser hold-up and x_0 is the fractional concentration of the less-volatile component in normal water. By setting $W/P=a$, $W/L=b$, and $H/L=c$, and substituting Eq. (4) into Eq. (5), we have

$$\begin{aligned}\mathrm{d}t=&\left(\frac{\alpha}{\alpha-1}\right)\left[b+\frac{c\{1+\alpha a(1-\ln[x_{\mathrm{W}}])\}}{n\alpha\ln\alpha}\right]\\&\times\frac{\mathrm{d}x_{\mathrm{W}}}{\{(1+a)x_0-ax_{\mathrm{W}}\}}\\&+\left(\frac{\alpha}{\alpha-1}\right)\frac{ca\ln x_{\mathrm{W}}\mathrm{d}x_{\mathrm{W}}}{\{(1+a)x_0-ax_{\mathrm{W}}\}n\ln\alpha}\\&-\left(\frac{\alpha}{\alpha-1}\right)\frac{c\mathrm{d}x_{\mathrm{W}}}{(n\ln\alpha)x_{\mathrm{W}}}\end{aligned} \qquad (6)$$

Integration of Eq. (6) with a constriction that $x_{\mathrm{W}}=x_0$ at $t=0$ and with the relation $(1+a)x_0-ax_{\mathrm{W}}=x_{\mathrm{P}}$ gives

$$\begin{aligned}t=&\left(\frac{\alpha}{\alpha-1}\right)\left[b+\frac{c\{1+\alpha a(1-\ln[x_{\mathrm{W}}])\}}{n\alpha\ln\alpha}\right]\frac{1}{a}\ln\frac{x_0}{x_{\mathrm{P}}}\\&+\left(\frac{\alpha}{\alpha-1}\right)\left(\frac{c}{n\ln\alpha}\right)\left[-\ln\frac{x_{\mathrm{P}}}{a}\ln x_{\mathrm{W}}+\ln\frac{x_0}{a}\ln x_0\right.\\&+\ln\left(\frac{1+a}{a}x_0\right)\ln\frac{x_{\mathrm{W}}}{x_0}+\left(\frac{a}{1+a}\right)\left(1-\frac{x_{\mathrm{W}}}{x_0}\right)\\&\left.+\frac{1}{2^2}\left(\frac{a}{1+a}\right)^2\left(1-\frac{x_{\mathrm{W}}^2}{x_0^2}\right)+\cdots\cdots\right]\\&+\left(\frac{\alpha}{\alpha-1}\right)\left(\frac{c}{n\ln\alpha}\right)\ln\frac{x_0}{x_{\mathrm{W}}}.\end{aligned} \qquad (7)$$

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

[7] A. E. Brodsky and O. Ch. Scarre, *Acta Phys. Chim. U. R. S. S.*, **10**, 729 (1939).

Introducing in Eq. (7) the values applied in the experiments, i.e. $a=W/P=(1.5-0.1)/5.0=0.28$, $b=W/L=(1.5-0.1)/0.2=7$ hrs., and $c=H/L=0.1/0.2=0.5$ hr., and setting $n+1=20$, we obtain equilibration time 144 hrs. (6.0 days) for HDO and 147 hrs. (6.1 days) for H_2O^{18}. The values of x_W and x_P at equilibrium are calculated from the material balance relation, $Wx_W+Px_P=(W+P)x_0$, and from Fenske's equation for low concentration, $x_W/x_P=\alpha^{20}$. The time necessary for equilibration for HDO is almost equal to that for H_2O^{18}, which is in marked contrast to the previous experiment[1].

If we neglect the column hold-up, c in Eq. (7) vanishes, and the relation reduces to a simple equation

$$t=\{\alpha/(\alpha-1)\}(b/a)\ln(x_0/x_P) \qquad (8)$$

Eq. (8) gives equilibration time 135 hrs. for HDO and 113 hrs. for H_2O^{18}. In this case the latter is a little shorter than the former. They are not, however, so far different from those obtained above from Eq. (7).

The assumption made in Eq. (5) becomes incorrect as the fractionation approachs equilibrium. In this respect Jackson and Pigford mentioned in their recent paper[8] that at a range of very small concentration of a less-volatile component, such as we have treated, the time necessary to reach 90% of equilibrium from initial concentration is about twice the value of equilibration time as calculated by such an equation submitted by Urey and others. Taking this fact into consideration calculated values are nearly coincident with our experimental values.

Discussion

As has already been mentioned, an error $\pm0.1\gamma$ each in excess densities due to deuterium in still and that in condenser combined gives, for our experimental conditions a maximum deviation of ±0.45 in $n+1$, and this error combined with an error of $\pm0.1\gamma$ each in excess densities due to O^{18} in still and that in condenser makes an error of ±0.00014 in the relative volatility α of H_2O^{16}/H_2O^{18}. In addition to this, an error of 0.001 in the relative volatility A of H_2O/HDO gives an error of $(\Delta n/n)=0.038$, and this error results in an error of 0.00015 in α (increases when A increases). For example, if we apply Schutz and Zmachinsky's value[9,4] $A=1.0295$ in place of $\sqrt{1.052}$, α becomes 1.0044_8.

As concerns the relative volatility of light- to heavy-oxygen water at 100°C., Watson gave a short summary in his recent paper[3]. In his paper he introduced data from Lewis and Cornish[10], Wahl and Urey[11], and Riesenfeld and Chang[12], giving values of 1.0056–1.0060, 1.003 and 1.0046, respectively, as the relative volatility. Watson also introduced the studies of Brodsky and Scarre[7] and Hayter[13] which gave 1.0055 and 1.0056, and he himself concluded 1.0056 as the most probable value.

Although the value 1.003 of Wahl and Urey was long accepted, it was not exact enough because it was a value which was extrapolated far from the measured values between 11.25 and 46.35°C., and this value seems much too low. Calculated values of 1.0056–1.0060 from Lewis and Cornish's data also seem inexact because their data were based on an uncertain number of the theoretical plates of their fractionation column. Increase in the assumed number of theoretical plates decreases the value of the relative volatility, and if we use a number around 50 instead of the 40 which they assumed, the value of the relative volatility of H_2O^{16}/H_2O^{18} becomes 1.004. Moreover, it is uncertain whether a true equilibrium of fractionation had been reached or not within such a short time as they applied to their experiments.

Brodsky and Scarre measured ratios of concentration of heavy hydrogen and heavy oxygen of water in a still to those of normal water by using a rotating column under total reflux by continuously supplying fresh normal water at the top of the column, as was done in our previous experiment[1]. In their calculation, howerer, they used a value of 17.9γ as the concentration of heavy hydrogen in normal water and a value of 171γ as that of heavy oxygen. The resultant values of the ratio under atmospheric pressure were 2.74 for hydrogen and 1.26 for oxygen. In place of the above values for natural abundance we use 15.8γ for heavy hydrogen and 224.7γ for O^{18}. Then the ratios reduce to 2.97 and 1.20, respectively. The

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[8] R. F. Jackson and R. L. Pigford, *Ind. Eng. Chem.*, **48**, 1020 (1956), Fig. 4.

[9] P. W. Schutz, SAM Report A-595, Apr. 12, 1943.

[10] G. N. Lewis and R. E. Cornish, *J. Am. Chem. Soc.*, **55**, 2616 (1933).

[11] M. H. Wahl and H. C. Urey, *J. Chem. Phys.*, **3**, 411 (1935).

[12] E. H. Riesenfeld and T. L. Chang, *Z. physik. Chem.*, **B33**, 127 (1936).

[13] A. J. Hayter, Ph. D. Thesis, London Univ., 1950.

ratio for heavy hydrogen, combined with $\sqrt{1.052}$ for the relative volatility of H_2O/HDO, gives $n+1=43.0$, and this value, combined with the ratio for heavy oxygen, gives 1.0042 for the relatives volatility of light- to heavy-oxygen water. If the density due to O^{17} be excluded, the value of the relative volatility will reduce to about 1.0040.

Hayter's experiment, on which Watson's conclusion was based, was done with a packed column with 2500 packings which effect 0.21 theoretical plate per one packing. This number of theoretical plates was based on the fractionation of the system of benzene and carbon tetrachloride. By their fractionation of water, they obtained numbers between 250–400 from the fractionation of hydrogen isotopes, and applying these values, they concluded a value of 1.0056 as the relative volatility of H_2O^{16}/H_2O^{18}. The reason for the discrepancy between this value and our present value is not immediately clear. It seems probable, however, that their experiment was not based on true equilibrium of hydrogen isotopes. They used a continuous method for the fractional distillation, and the decrease of plate efficiency by such productive distillation may be more prominent for hydrogen isotopes than for oxygen isotopes, as was pointed out by Cohen[14]. In order to make applicable a value of around 1.004 for the relative volatility, the number of theoretical plates must be about 560, a value which does not seem improbable. If we use $0.12\times2500=525$ as the number of theoretical plates, we obtain 1.0043 as the relative volatility.

In conclusion, we do not find any fact which seems inconsistent to any great degree with our present result. Thus, by applying values of the natural abundance of D, O^{18} and O^{17} in normal water which are respectively 15.8, 224.7 and 21.9 in γ unit and of the relative volatility of $H_2O/HDO=\sqrt{1.052}$, and by assuming that the plate efficiency of the fractionation column is identical for hydrogen and oxygen isotopes, we conclude 1.0039 ± 0.0002 as the relative volatility of H_2O^{16}/H_2O^{18}.

Department of Chemical Engineering
Faculty of Engineering, Nagoya
University, Chigusa-ku, Nagoya

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[14] K. Cohen, *J. Chem. Phys.*, **8**, 588 (1940).