NOTE

Direct measurements of D/H and $^{18}$O/$^{16}$O fractionation factors between vapor and liquid water in the temperature range from 10 to 40°C

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Vapor phase was separately collected without liquid condensate by raising the temperature of the container of vapor phase by 7°C higher than that of the interface of vapor-liquid equilibrium. D/H and $^{18}$O/$^{16}$O measurements were done for the identical aliquot of vapor samples in equilibrium with the liquid water in the temperature range from 10 to 40°C.

The empirical relationships between $\alpha_D$, $\alpha_{^{18}O}$ and the temperature of equilibration were obtained to be,

$$10^3 \ln \alpha_D = 2.408 \times 10^6 T^{-2} + 6.455 \times 10^4 T^{-1} - 168.7,$$
$$10^3 \ln \alpha_{^{18}O} = 5.9702 \times 10^6 T^{-2} - 3.2801 \times 10^4 T^{-1} + 52.227.$$

INTRODUCTION

Since the estimation of vapor pressure from the density measurement of a variety of isotopic water molecules was made by Waul and Urey (1935), a number of experimental studies on hydrogen and oxygen isotopic fractionations between vapor and liquid water has been done. These studies may be classified into two groups; (1) measurements of vapor pressure of isotopic molecules over liquid phase (e.g., for $\alpha_D$, Jones, 1968, and for $\alpha_{^{18}O}$; Szapiro and Steckel, 1967, Jakli and Staschewski, 1977) (2) measurements on D/H and/or $^{18}$O/$^{16}$O of both vapor and liquid (e.g., for $\alpha_D$, Merlivat et al., 1963, and Majoube, 1971, and for $\alpha_{^{18}O}$, Majoube, 1971).

With respect to the latter, the major trouble is that the collection of vapor at the same temperature as that of the vapor-liquid equilibrium is impossible because the collected vapor phase contains always some amount of liquid condensate.

In the present study, the isotopic fractionation factors ($\alpha_D$ and $\alpha_{^{18}O}$) between vapor and liquid near room temperature were measured through collection of vapor in a sampler held at higher temperature than that of the vapor-liquid equilibrium.

EXPERIMENTAL

Apparatus and experimental procedure

The vapor collection system is shown in Fig. 1. The system consists of a double thermostat. The temperature of the vapor-liquid equilibrium was fixed by circulating water through thermostat A at the temperature of T, and the equilibration vessel and the vapor sampler were immersed in thermostat B at the temperature of $T'$. The temperature difference ($T' - T$) was set to 7°C and was sufficient to avoid condensation of vapor in the vapor sampler in the temperature range in this study.

Pure water of ca. 5ml in the equilibration vessel was frozen at the dry ice-ethanol temperature and then evacuated together with the vapor sampler. In order to ensure the degassing of the liquid phase, freezing - evacuation - melting cycle was repeated several times. When the evacuation was completed, the system was immersed in thermostat B and the equilibration...
Fig. 1. The vapor collection system consists of double thermostat. The vapor sampler (V) is kept at the temperature 7°C higher than that of the equilibration vessel (E) in the two thermostats (A and B). L is liquid water and S stopcock.

vessel was connected to thermostat A. The volume of the vapor sampler was variable so as to collect about 10mg of water in each run at different equilibration temperatures.

The system was kept in the thermostat for 20 to 50 hours. When the vapor-liquid equilibrium was established, stopcock (S) (Fig. 1) was closed to separate the vapor sampler from the rest. The vapor sample was frozen by liq. N₂ immediately after the separation of the vapor sampler. The sampling of vapor was repeated seven times at the same equilibration temperature. The liquid phase was sampled and stored in capillaries.

Isotopic analysis Isotopic analyses of hydrogen and oxygen for milligram quantities of water have been established by Bigeleisen et al. (1952) for hydrogen through uranium reduction and by O'Neil and Epstein (1966) for oxygen through decomposition of water by BrF₅. However, the combination of two methods for the analysis of D/H and ¹⁸O/¹⁶O of an aliquot of water is impossible.

Suzuki and Itoh (1974) proposed a new method of simultaneous analysis of D/H and ¹⁸O/¹⁶O for milligram quantities of water, in which the modified CO₂-H₂O exchange in the gas phase at 1,400°C with Pt catalyst was followed by the reduction of H₂O with hot uranium metal. We applied Suzuki and Itoh method for samples of 15, 20 and 40°C. This method, however, was found unsatisfactory in terms of precision.

We applied the method for D/H and ¹⁸O/¹⁶O analyses by Kishima and Sakai (1980)* to the vapor sample. The results on α_D and α_¹⁸O at 10, 25, 30 and 35°C were obtained by this method. Hydrogen and oxygen isotopic ratios are given as per mil deviation from those of the standard by

$$\delta(\%o) = \left( \frac{R}{R_{standard}} - 1 \right) \times 10^3 \quad (1)$$

where, R represents the values of D/H or ¹⁸O/¹⁶O ratios.

The isotopic fractionation factor between vapor and liquid phase is defined by the relation

$$\alpha = \frac{R(I)}{R(v)} = \frac{1 + 10^{-3}\delta(I)}{1 + 10^{-3}\delta(v)} \quad (2)$$

where, R(I) and R(v) are isotopic ratios of liquid and vapor, respectively.

The standard deviation in repeated measurement for samples at a fixed temperature were ± 1.0‰ for δ_D, ± 0.15‰ for δ_¹⁸O by Suzuki and Itoh method, and ± 0.10‰ for δ_¹⁸O by Kishima and Sakai method.

*A revised method of CO₂-H₂O equilibration (Epstein and Mayeda, 1953) for milligram quantities of water samples, in which both CO₂ and H₂O (liq.) were enclosed in a small pressurized equilibration vessel. CO₂ was extracted for δ¹⁸O analysis. The water sample was then recovered and submitted to the δD analysis. The D/H ratio of the sample was found to be preserved throughout the procedure of the oxygen isotope analysis. The quantity of water sample was measured volumetrically after converting the vapor into hydrogen gas by uranium reduction, and the water quantity was used for material balance calculation.
Table 1. Fractionation factors between vapor and liquid in the temperature range from 10 to 40°C

<table>
<thead>
<tr>
<th>t°C</th>
<th>αD-obs.</th>
<th>10^3lnαD-obs.</th>
<th>10^3lnαD-calc.</th>
<th>α18O-obs.</th>
<th>10^3lnα18O-obs.</th>
<th>10^3lnα18O-calc.†</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1.0935</td>
<td>89.4</td>
<td>89.3</td>
<td>1.01093*</td>
<td>10.87</td>
<td>10.85</td>
</tr>
<tr>
<td>15</td>
<td>1.0886</td>
<td>84.9</td>
<td>84.3</td>
<td>1.01032**</td>
<td>10.27</td>
<td>10.30</td>
</tr>
<tr>
<td>20</td>
<td>1.0812</td>
<td>78.1</td>
<td>79.5</td>
<td>1.00981*</td>
<td>9.76</td>
<td>9.81</td>
</tr>
<tr>
<td>25</td>
<td>1.0775</td>
<td>74.7</td>
<td>74.9</td>
<td>1.00940*</td>
<td>9.36</td>
<td>9.37</td>
</tr>
<tr>
<td>30</td>
<td>1.0736</td>
<td>71.0</td>
<td>70.4</td>
<td>1.00908*</td>
<td>9.04</td>
<td>8.99</td>
</tr>
<tr>
<td>35</td>
<td>1.0695</td>
<td>67.2</td>
<td>66.1</td>
<td>1.00870*</td>
<td>8.67</td>
<td>8.66</td>
</tr>
<tr>
<td>40</td>
<td>1.0630</td>
<td>61.1</td>
<td>62.0</td>
<td>1.00835**</td>
<td>8.32</td>
<td>8.36</td>
</tr>
</tbody>
</table>

* KISHIMA and SAKAI method.
** SUZUKI and ITOH method.
† Calculated values are obtained by equation (3) or (4) in the text.

RESULTS AND DISCUSSION

The results of αD and α18O determinations are presented in Table 1 against temperature for the temperature range from 10 to 40°C. Each point represents the average value of several analyses.

The empirical relationships between 10^3lnα and temperature are obtained as follows by the least square fitting:

\[ 10^3\ln\alpha_D = 1.408 \times 10^6T^{-2} + 6.455 \times 10^4T^{-1} - 168.7 \]  \hspace{1cm} (3),

\[ 10^3\ln\alpha_{18O} = 5.9702 \times 10^6T^{-2} - 3.2801 \times 10^4T^{-1} + 52.227 \]  \hspace{1cm} (4)*

\hspace{1cm} (283.15 ≤ T ≤ 313.15K).

In Figs. 2 and 3 our results are compared with those of some previous studies. As seen in Fig. 2, our result on αD is close to that of MAJOUBE (1971) at the higher temperature range, and is close to that of PUPEZIN et al. (1972) at the lower temperature range. The temperature dependence of αD given by the present study is similar to that of JONES (1968). As seen in Fig. 3, our result on α18O is close to that of MAJOUBE (1971). It is found that the isotopic fractionation factors from the measurements on D/H and 18O/16O of both vapor and liquid seem to be consistently higher than those based on the measurements of vapor pressure of isotopic molecules over liquid except for MERLIVAT et al. (1963).

There is a heat flow from the vapor phase to the liquid phase in our method because of the temperature difference between the two phases. In a closed system with temperature gradient, the density of an ideal gas in the system is different depending on the change in the temperature but the pressure is constant throughout the system. In order to check whether or not the vapor pressure of the vapor in the sampler is controlled by the temperature of vapor-liquid equilibrium, the amount of vapor in the sampler of known volume was measured to estimate the vapor pressure. This was done by measuring the amount of hydrogen gas manometrically after converting all the vapor in the sampler into hydrogen gas. The result is given in Table 2. As seen in Table 2, the calculated vapor pressures are close to or slightly higher than that of DORSEY (1940). Judging from the errors involved in measuring the volume of the sampler, the amount of H₂ gas and the temperature, we consider the estimated vapor pressure to agree well with the predicted values. It can be concluded that the vapor pressure is

*Equation (4) for oxygen isotope is given on the basis of differently weighted data; the data for 10, 25, 30 and 35°C (obtained by KISHIMA and SAKAI method) with the weight proportional to the reciprocal of standard deviation, ±0.10‰, and those for 15, 20 and 40°C (obtained by SUZUKI and ITOH method) with the weight proportional to the reciprocal of ±0.15‰.
controlled by the temperature of vapor-liquid equilibrium which is by 7°C lower than the vapor phase temperature.

It is inferred that the isotopic concentration gradient in our system can be neglected for the following reasons. As the temperature gradient exists in a narrow portion of the system and our system is closed for material transfer, the convection which gives rise to the thermal diffusion is quite difficult to occur.

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Table 2. Estimation of the vapor pressure in the vapor sampler

<table>
<thead>
<tr>
<th>Temperature of equilibration (°C)</th>
<th>Volume of vapor sampler (ml)</th>
<th>Amount of water vapor (m. mol)</th>
<th>( P_{H_2O} ) estimated (mmHg)</th>
<th>( P_{H_2O} ) DORSEY (1940) (mmHg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.0 ± 0.2</td>
<td>1,292 ± 2</td>
<td>0.651 ± 0.020</td>
<td>9.2 ± 0.3</td>
<td>9.21</td>
</tr>
<tr>
<td>25.0 ± 0.2</td>
<td>448 ± 2</td>
<td>0.586 ± 0.009</td>
<td>24.9 ± 0.4</td>
<td>23.76</td>
</tr>
<tr>
<td>30.0 ± 0.2</td>
<td>448 ± 2</td>
<td>0.754 ± 0.006</td>
<td>32.5 ± 0.3</td>
<td>31.83</td>
</tr>
<tr>
<td>35.0 ± 0.2</td>
<td>165 ± 2</td>
<td>0.370 ± 0.008</td>
<td>44.0 ± 1.1</td>
<td>42.18</td>
</tr>
</tbody>
</table>

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