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OXYGEN AND HYDROGEN ISOTOPE PARTITIONING BETWEEN
WATER LIQUID AND VAPOR AT ELEVATED TEMPERATURES

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ABSTRACT

Oxygen and hydrogen isotope fractionation factors (α^O_{l-v} and α^D_{l-v}) between liquid water and water vapor have been calculated from vapor pressure ratio measurements and equations of state over the temperature range of 0 to 370°C. These data are compared to the liquid-vapor fractionation factors determined by direct mass spectral measurements. The values for α^D_{l-v} derived from the vapor pressure ratios are in close agreement with the experimental mass spectral measurements from 0 to 300°C when fugacity coefficient and molar volume corrections are used. Deviations from the direct measurements above 0 to 300°C are due to inadequacies in either (1) the magnitude of the molar volume correction for D_2O near the critical point, (2) the assumption of ideal mixing of the isotopic gases and liquids, and/or (3) the selection of 1.91 as the disproportionation factor for the formation of HDO. On the other hand, the α^O_{l-v} values derived from vapor pressure data (no fugacity or molar volume corrections) agree closely with low-temperature direct measurement data, pass through some of Bottinga's (1968) high temperature results, and extrapolate smoothly to $\alpha^O_{l-v} = 0$ at the critical temperature as is required by thermodynamics. This behavior coupled with the fact that Bottinga's (1968) oxygen isotope results exhibit a large scatter, indicates that liquid-vapor oxygen isotope fractionation factors based on vapor pressure measurements should be applied to high-temperature geothermal systems rather than the direct mass spectral data.

INTRODUCTION

Boiling of a homogeneous aqueous phase occurs as the fluid rises in a hydrothermal system and experiences a decrease in pressure. The boiling process induces a temperature decrease and, typically, a pH increase which causes minerals to precipitate (Drummond and Ohmoto, 1985). During boiling, the initially homogeneous aqueous phase separates into several phases including vapor or gas (e.g. CO_2, H_2S), liquid and minerals (e.g., quartz, calcite). An isotopic fractionation occurs when vapor separates from hot water because of differences in the partial pressure of

the various isotopic compounds (e.g., HDO, $H_2^{16}O, H_2^{18}O$). Therefore, in order to use the oxygen and hydrogen isotope composition of the water to (1) determine the origin(s) of the deep aquifer fluid and/or (2) apply isotope geothermometers involving D/H or $^{18}O/^{16}O$ exchange reactions with water, the equilibrium isotopic composition of the deep fluid (altered by boiling) must be calculated by taking into account the liquid-vapor phase separation.

The equilibrium isotope fractionation factors between water and vapor have been determined using three different methods: (1) direct mass spectrometric measurements of sampled vapor equilibrated with coexisting water, (2) calculations based on vapor pressure differences measured between vapor and liquid, and (3) quantum mechanical treatment of spectroscopic data on liquid and vapor (see O'Neil, 1986, for a review of the various approaches, particularly 1 and 3). Although the overlap in fractionation factors determined by these methods is respectable, errors have been generated due to difficulties in either (1) sampling or (2) assumptions made during the calculations. The purpose of this communication is twofold: first, to describe the methodology required in calculating the fractionation factors between liquid water and water vapor based on vapor pressure ratio measurements and improved equations of state, and second, to compare these results with directly measured isotopic fractionation factors. From this comparison, we will be in a better position to evaluate the quality of fractionation factors used to estimate deep fluid isotope compositions. We will point out the limitations of each approach and demonstrate, at the very least, that the vapor pressure isotope calculations for oxygen may be more accurate than the existing measured liquid-vapor isotope fractionations.

DIRECT ISOTOPE MEASUREMENT METHOD

The fractionation factors (α^O and α^D) describing the partitioning of oxygen and hydrogen isotopes between pure water liquid (containing low levels of ^{18}O and deuterium) and water vapor have been measured experimentally by several laboratories (Bottinga, 1968; Merlivat et al.,

1963, Majoube, 1971). These data are plotted as the data points in Figs. 1 and 2 as a function of temperature, and also summarized in Table 1, where

$$\alpha_{\ell-v} = R_\ell/R_v$$

$$(R = D/H \text{ or } {}^{18}O/{}^{16}O) . \tag{1}$$

Here R is the concentration ratio of the isotopic molecules (HDO/H_2O or $H_2{}^{18}O/H_2{}^{16}O$) in the liquid (R_ℓ) or the vapor (R_v). In the delta notation,

$$10^3 \ln\alpha^O_{\ell-v} \simeq \delta^{18}O_{\ell\text{-standard}} - \delta^{18}O_{v\text{-standard}} \tag{2}$$

$$10^3 \ln\alpha^D_{\ell-v} \simeq \delta D_{\ell\text{-standard}} - \delta D_{v\text{-standard}} \tag{3}$$

where

$$\delta_{\text{sample-standard}} = \left[\left(\frac{R_{\text{sample}}}{R_{\text{standard}}}\right) - 1\right]10^3 . \tag{4}$$

The quantity $\delta_{\text{sample-standard}}$ represents the permil deviation of the isotopic ratio of a substance from that of a standard reference material. Analytically, differences in the isotopic ratios of two substances of approximately 0.1 permil in $^{18}O/^{16}O$ and 1.0 permil in D/H are distinguishable by mass spectrometry.

The isotopes of hydrogen and oxygen are present in different proportions in water vapor and liquid water at equilibrium. At ambient temperatures, there is an appreciably higher concentration of the heavy isotopes, deuterium and ^{18}O, in the liquid phase, but this difference between phases becomes less as temperatures increase (Figs. 1 and 2). Above approximately 221°C (cross-over), deuterium becomes concentrated into the vapor phase. In general, the agreement between the measured D/H fractionation factors from various sources is relatively good. Greater scatter is noticeable at the higher temperatures (see Truesdell et al., 1977, for a more detailed comparison of both oxygen and hydrogen isotope experimental data). Bottinga (1968) claims an error of approximately ±0.3 permil for oxygen. Inspection of Fig. 1 indicates that there is a large scatter in Bottinga's (1968) oxygen data (130-330°C), much greater than observed by Majoube (1971) for lower temperature experiments. This scatter and associated enrichment in ^{18}O relative to the vapor pressure method (solid line--Fig. 1) suggest that a small contamination of the vapor by the liquid phase may have occurred during sampling. The larger error in mass spectral measurements of hydrogen isotopes (±1 permil) probably masks this contamination problem.

VAPOR PRESSURE ISOTOPE METHOD

The fractionation of isotopes between a mixture of two condensed isotopic molecules and their coexisting vapor is given by

$$\ln\alpha_{\ell-v} = \ln\frac{Q_\ell}{Q_v} - \int_V^{V'} \frac{\partial \ln Q_\ell}{\partial V} dV \tag{5}$$

where Q is the partition function ratio of the isotopic molecules in each phase, V is the molar volume of the condensed phase (prime denotes light isotope--^{16}O or H), and $\alpha_{\ell-v}$ is the equilibrium isotope fractionation factor between liquid (ℓ) and vapor (v) (Bigeleisen, 1963; Jancso and Van Hook, 1978; Jakli and Van Hook, 1981). The first term on the right of Equation (5) is equivalent to the fugacity ratio of the pure substances along the liquid-vapor curve at the temperature of interest, assuming that the isotopic gases mix ideally. The second term accounts for changes in molar volume of the condensed phase due to mixing of the isotopic molecules and can be approximated by $(V - V')^2/2 \beta VRT$, where β is the isothermal compressibility coefficient (Bigeleisen, 1963; Jancso and Van Hook, 1978). Thus, for oxygen isotope fractionation between $H_2O(\ell)$ and H_2O (v), Equation (5) can be formulated as

$$\ln\alpha^O_{\ell-v} \simeq \ln\frac{P_{H_2{}^{16}O}}{P_{H_2{}^{18}O}} + \frac{\ln\gamma_{H_2{}^{16}O}}{\ln\gamma_{H_2{}^{18}O}} - \frac{\left(V_{H_2{}^{18}O} - V_{H_2{}^{16}O}\right)^2}{2\beta_{H_2{}^{18}O} V_{H_2{}^{18}O} RT} \tag{6}$$

where P is the vapor pressure of the pure isotopic substance ($H_2{}^{18}O$) and γ is the fugacity coefficient.

The equivalent expression for hydrogen isotope exchange must be modified to account for the disproportionation reaction, $H_2O + D_2O = 2 HDO$. Van Hook (1972) has experimentally investigated the vapor pressure isotope effect for hydrogen in water and finds that the disproportionation ratio, $\ln(P_{H_2O}/P_{D_2O})/\ln(P_{HDO}/P_{H_2O}) = 1.91$ over the range 0-100°C using data from Majoube (1971). Thus, Equation (5) is recast as:

$$1.91 \ln\alpha^D_{\ell-v} \simeq \ln\frac{P_{H_2O}}{P_{D_2O}} + \ln\frac{\gamma_{H_2O}}{\gamma_{D_2O}} - \frac{\left(V_{D_2O} - V_{H_2O}\right)^2}{2\beta_{D_2O} V_{D_2O} RT} \tag{7}$$

The second term in Equations (6) and (7) corrects the vapor pressure ratio for gas imperfection, whereas the third term corrects for the change in molar volume of the heavy isotopic molecule due to the dilution in the light isotopic medium.

The first term in Equation (6) was evaluated from a regression equation given by Jancso and Van Hook (1974), and the results are plotted in Fig. 1 and listed in Table 1. Data are unavailable to reliably calculate the second and third terms in Equation (6) at elevated temperatures, although these factors are likely to be insignificant due to the minor effects of ^{18}O substitution on the vibrational and bonding properties
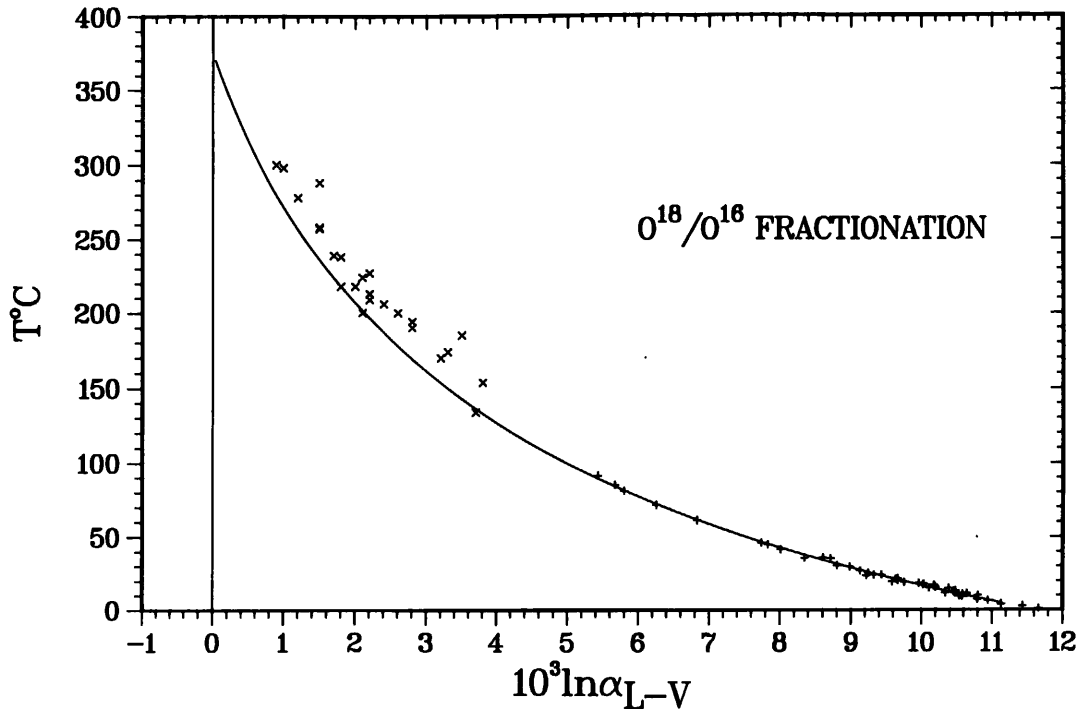
Figure 1. $^{18}O/^{16}O$ fractionation between pure water and vapor from 0 to 370°C. The solid curve is the vapor pressure ratio computed from the first term of Equation (6). Experimental data points are those of Majoube (1971:+) and Bottinga (1968:x). The $ln\alpha$ = 0.0 line is shown for reference.
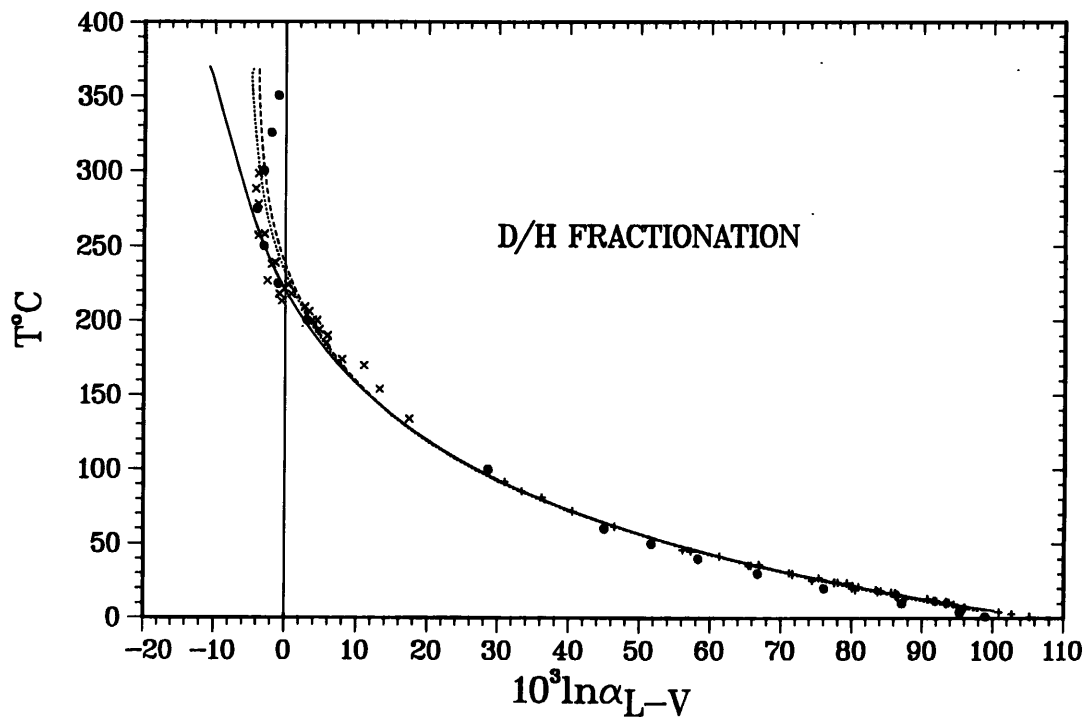
Figure 2. D/H fractionation between pure water liquid and vapor from 0 to 370°C. The solid curve is the vapor pressure ratio [1st term, Equation (7)], the dashed curve combines the vapor pressure and fugacity ratio terms [Equation (7)], and the dotted curve includes corrections due to condensed phase molar volume changes [1st, 2nd, and 3rd terms, Equation (7)]. The experimental points are those of Majoube (1971:+), Merlivat, et al. (1963:●) and Bottinga (1968:x). The $ln\alpha$ - 0.0 line is shown for reference.

Table 1. Activity coefficients of H_2O and D_2O vapor coexisting with liquid from 20-370°C computed from the equations of state, and D/H and $^{18}O/^{16}O$ isotope fractionations between water liquid and vapor computed from Equations (6) and (7) (see text). These data (a, b, c, g) are compared with experimental fractionation factors determined from mass spectral measurements (d, e, f, h, i).

T°C	γ_{H_2O}	γ_{D_2O}	$10^3 \ln\alpha^D_{l-v}$						$10^3 \ln\alpha^O_{l-v}$		
			a	b	c	d	e	f	g	h	i
20	0.998954	0.998914	82.0	82.1	80.8	81.6	76.0	81.5	9.74	9.75	9.54
40	0.997487	0.997543	62.8	62.7	62.2	62.5	58.3	61.3	8.20	8.17	8.17
60	0.994907	0.995121	47.8	47.7	47.3	47.6	45.0	46.4	6.93	6.98	7.03
80	0.998029	0.991187	36.1	35.9	35.7	35.9		36.1	5.87	5.88	6.07
100	0.984875	0.985274	26.9	26.7	26.6	26.7	28.6	27.8	4.98	4.99	5.24
120	0.976698	0.976905	10.8	19.6	19.5	19.4		21.5	4.23	4.53	4.53
140	0.966001	0.965941	13.1	14.1	13.9	16.4		16.3	3.09	3.91	3.91
160	0.952567	0.952010	9.4	9.8	9.6	11.7		11.7	3.03	3.37	3.37
180	0.936275	0.935116	5.7	6.3	6.1	7.3		7.4	2.55	2.90	2.90
200	0.917123	0.915317	2.6	3.6	3.3	3.5	3.0	3.5	2.13	2.48	2.48
220	0.895215	0.892759	0.04	1.4	1.1	0.4		0.1	1.76	2.10	2.10
240	0.870741	0.867640	-2.0	-0.18	-0.65	-1.9		-2.2	1.44	1.77	1.77
260	0.843938	0.840170	-3.7	-1.4	-2.0	-3.4		-3.6	1.15	1.46	1.46
280	0.815052	0.810547	-5.2	-2.3	-2.7	-4.2		-4.0	0.96	1.19	1.19
300	0.784283	0.778931	-6.5	-2.9	-3.5	-4.3	-3.0	-3.4	0.72	0.94	0.94
320	0.751721	0.745416	-7.8	-3.3	-4.1	-3.7		-2.2	0.46	0.72	0.70
340	0.717229	0.709948	-9.0	-3.6	-4.5	-2.6		-1.3	0.28	0.51	0.45
360	0.680205	0.672009	-10.1	-3.8	-4.8	-0.9		-0.5	0.11	0.32	0.19
370	0.660261	0.651379	-10.8	-3.7	-4.3	0.04			0.03	0.26	

(a) The $\ln\alpha_{l-v}$ value was computed using first term only, Equation (7).

(b) The $\ln\alpha^D_{l-v}$ value was computed using first and second terms, Equation (7).

(c) The $\ln\alpha^D_{l-v}$ value was computed using all three terms, Equation (7).

(d) Majoube (1971): 1000 $\ln\alpha$ = 24.44 $(10^6/T)$ - 76.248 $(10^3/T)$ + 52.612; 0-120°C.

(d) Bottinga and Craig (1968): 1000 $\ln\alpha$ = 559.69 - 808.06 $(10^3/T)$ + 372.81 $(10^6/T^2)$ - 54.41 $(10^9/T^3)$; 140-370°C.

(e) Merlivat et al. (1963) measured D/H fractionations.

(f) Truesdell et al. (1977), smoothed (D/H) data from various sources.

(g) The $\ln\alpha^O_{l-v}$ value was computed from first term, Equation (6).

(h) Majoube (1971); 0-120°C; 1000 $\ln\alpha$ = 1.137 $(10^6/T)$ - 0.4156 $(10^3/T)$ - 2.066; 0-120°C.

(h) Bottinga (1968) and Bottinga and Craig (1968): 1000 $\ln\alpha$ = 0.7664 $(10^6/T^2)$ + 1.2051 $(10^3/T)$ - 3.493 (after Friedman and O'Neil, 1977); 140-370°C.

(i) Truesdell et al. (1977), smoothed $(^{18}O/^{16}O)$ data from various sources, primarily Bottinga (1968).

of H_2O. The calculated vapor pressure ratios (Fig. 1) agree well with Majoube's (1971) fractionation factors (measured by mass spectrometry) because these data were incorporated into the regression equation given by Jancso and Van Hook (1974). The only oxygen isotope data available at temperatures above 100°C are those of Bottinga (1968). As noted earlier, there is a large amount of scatter in his results. The fact that the fractionation factors calculated from the vapor pressure ratios pass through a portion of Bottinga's (1968) data and extrapolate smoothly to $\ln\alpha_{\ell-v} = 0$ at the critical temperature suggests that the calculated quantities listed in Table 1 (column g) may be a better representation of the true $\alpha^0_{\ell-v}$ at temperatures above 100°C than the scattered experimental values. It is possible that the correction for gas nonideality and condensed phase molar volume changes would bring the computed curve more in line with Bottinga's (1968) measurements. However, these corrections are likely to be smaller than the analogous corrections involving hydrogen isotopes discussed below.

All of the values on the right-hand side of Equation (7) can be calculated from the triple point to the critical point, using the equation of state of H_2O (Haar et al., 1984) and the newly formulated equation of state of D_2O (Hill et al., 1982). The fugacity coefficients (γ) along the liquid-vapor curve calculated from the equations of state for H_2O and D_2O are listed in Table 1. The γ's for H_2O agree precisely with those reported by Haas (1970) to 350°C. The vapor pressure ratios computed from these equations of state agree closely with directly measured differential vapor pressures summarized and critiqued by Jancso and Van Hook (1981). In Fig. 2, the solid curve is computed using only the vapor pressure ratios [first term--Equation (7)]. The $\alpha^0_{\ell-v}$ values computed from fugacity ratios [combination of the first and second terms on the right side of Equation (7)] are plotted as the dashed curve in Fig. 2. The dotted curve in Fig. 2 incorporates the molar volume correction to the partition function for dilution of liquid D_2O in liquid H_2O.

These three approximations to $\alpha^0_{\ell-v}$ are compared with experimentally measured D/H fractionations in Fig. 2 (Majoube, 1971; Bottinga, 1968; Merlivat et al., 1963). Since Van Hook (1972) selected the factor 1.91 in Equation (7) to fit Majoube's (1971) data, the excellent agreement between Majoube's results and the computed fractionations is expected. The fractionation computed using all three terms in Equation (7) represents the experimental measurements adequately from 0-300°C. The divergence between 200° and 300°C, approximately 2 permil, is considered within the combined analytical and experimental errors in the fractionations measured by mass spectrometry for D/H ratios. Above 300°C, the quantity computed in Equation (7) does not adequately represent the data of Merlivat et al. (1963). Merlivat's data extrapolate smoothly to $\ln\alpha_{\ell-v} = 0$ at the critical point as is thermodynamically required. The discrepancy is most likely due to one or more of the following:

(1) the approximation used to compute the molar volume correction near the critical point of D_2O, where the difference in molar volume between H_2O and D_2O is large, may be erroneous, (2) mixing of the isotopic gases and liquids may not be ideal at high vapor densities and temperatures, and/or the factor 1.91 may not be valid in this temperature range. Nevertheless, it is obvious that vapor pressure data for isotopically pure D_2O and H_2O give a reliable estimate of the D/H fractionation between vapor and pure water, particularly below 300°C.

CONCLUSIONS

An alternative approach to direct measurements for determining the isotopic fractionation between liquid water and water vapor has been described. This method utilizes the vapor pressure ratios of the isotopically pure substances, $H_2^{16}O$, $D_2^{16}O$, and $H_2^{18}O$. Abundant data (Jancso and Van Hook, 1974; Jakli and Van Hook, 1981; Haar, et al., 1984; and Hill et al., 1982) are available on the vapor pressures of these liquids from 0-370°C in the absence of dissolved species. Detailed numerical treatment of these data and their comparison with direct measurements indicate the following:

(1) Vapor pressure ratios can be recast into isotope fractionation factors for $^{18}O/^{16}O$ and D/H between pure water and water vapor if corrected for vapor nonideality and molar volume changes of the condensed phase. These corrections are more important for D/H fractionation.

(2) Once these calculations are made, the agreement between directly measured fractionation factors and those calculated from vapor pressure ratios is very good (±1 permil for D/H, ±0.2-0.4 permil for $^{18}O/^{16}O$), but only up to temperatures of between 250 and 300°C. No direct isotope measurements are available above approximately 325°C.

(3) The existing data used for vapor pressure isotope calculations cannot predict 0 permil (D/H) fractionation at the critical point as is required by thermodynamics.

(4) However, $\ln\alpha_{\ell-v}$ does extrapolate smoothly to 0 at the critical point from vapor pressure isotope calculations. The computed curve (Fig. 1) passes through some of Bottinga's (1968) data and, considering the scatter in his results, appears preferable, at least below 300°C. We recommend that the oxygen isotope fractionation factors between liquid water and water vapor derived from vapor pressure measurements be applied to geothermal systems.

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