Isotopic Self-Exchange Reactions of Water: Evaluation of the Rule of the Geometric Mean in Liquid−Vapor Isotope Partitioning

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Deviations from the random distribution of hydrogen isotopes among isotopic species of liquid and vapor water (the rule of the geometric mean) were critically assessed theoretically and experimentally from the triple to critical point of water. A third-order polynomial equation of the classical near-critical expansion was used to accurately describe the liquid−vapor isotope fractionation of H_2O and D_2O on the basis of their equations of state. It was found that experimental data for the enthalpy of mixing of H_2O-D_2O can be used to calculate accurately the deviation from the rule of the geometric mean in liquid and vapor water, $\ln(K_{D(v)}/K_{D(l)})$. A new equation obtained in this study shows that the value of $\ln(K_{D(v)}/K_{D(l)})$ smoothly decreases from +0.009 to 0 with increasing temperature from the triple to critical temperature of water. In contrast, the equation available in the literature and that derived from mass spectrometric measurements of liquid−vapor partitioning of H_2O and HDO show complex behavior, including maximum, minimum, and crossover.

1. Introduction

Isotopic self-exchange reactions of water in gaseous and liquid phases have been studied by a number of investigators over the past several decades. The deviation from the rule of the geometric mean is one of the main features of these reactions. It is well-known that the disproportionation reaction (i.e., $H_2O + D_2O \leftrightarrow 2HDO$) in the liquid and gaseous phases does not obey the rule of the geometric mean ($K_D \neq 4$). In addition, the equilibrium hydrogen isotope fractionation factor between liquid and gaseous water for $HDO-H_2O$ deviates from the square root of that for D_2O-H_2O. Although a number of experimental studies have been conducted, our understanding of the disproportionation reactions at elevated temperatures is still very limited. Furthermore, the formalism for expressing deviations from the rule of the geometric mean in the literature is valid only at low temperatures as discussed below. Here, we reexamine these reactions from the triple to critical point of water along the liquid−vapor boundary.

2. Liquid−Vapor Partitioning of Hydrogen Isotopic Water

Liquid−vapor partitioning of hydrogen isotopic water molecules (H_2O, HDO, and D_2O) has been investigated by two different experimental techniques. One is mass spectrometric determinations of HDO/H_2O ratios of natural abundances ($HDO/H_2O \approx 0.000\,30$) between coexisting liquid and vapor phases. These measurements directly provide the equilibrium constant of the following reaction, assuming ideal mixing of H_2O-HDO

$$K_{L-V(HDO)}:\ H_2O_{liquid} + HDO_{vapor} \leftrightarrow HDO_{liquid} + H_2O_{vapor} \tag{1}$$

Many investigators have determined the value of $K_{L-V(HDO)}$ over a wide range of temperatures. The most comprehensive work is that of Horita and Wesolowski,[1] who reported a global equation that described eq 1 from the triple to critical temperature of the solvent H_2O (Figure 1).

The other technique makes use of the differences in the saturated vapor pressures of pure isotopic waters (H_2O and D_2O), i.e., vapor pressure isotope effects (VPIE). Bigeleisen[2,3] derived an equation that relates VPIE determined from two pure isotopic species separately and the equilibrium constant of the following reaction at infinite dilution of one isotopic species (D_2O) in another (H_2O)

$$K_{L-V(D_2O)}:\ H_2O_{liquid} + D_2O_{vapor} \leftrightarrow D_2O_{liquid} + H_2O_{vapor} \tag{2}$$

$$-\ln K_{L-V(D_2O)} = \left(\frac{PV_g}{RT} - \frac{PV_l}{RT}\right)\ln\frac{P*}{P} \tag{3}$$

where P and $P*$ are the saturation vapor pressures for solvent (H_2O) and solute (D_2O), respectively. V_g and V_l are the molar volumes of gas and liquid phases of the solvent, respectively. R is the universal gas constant, and T is absolute temperature (K). From eq 3, we can calculate the liquid−vapor fractionation factor between D_2O and H_2O using VPIE, which is available from the literature[4] or can be calculated from the equation of state (EOS) of H_2O and D_2O.[5,6] Japas et al.[7] provided a more rigorous derivation of eq 3. Japas et al.[7] and Alvarez et al.[8] also accurately described near-critical asymptotic behavior using the classical near-critical expansion

$$T \ln K_{L-V}/(\rho_l - \rho_{cr}) = A_0^a + A_1^a(T - T_{cr}) \tag{4}$$

where K_{L-V} is the liquid−vapor equilibrium constant, ρ_l and ρ_{cr} are liquid and critical densities (mol/m^3), A_0^a and A_1^a are coefficients, and T_{cr} is the critical temperature, all for pure solvent H_2O along the liquid−vapor boundary. They showed

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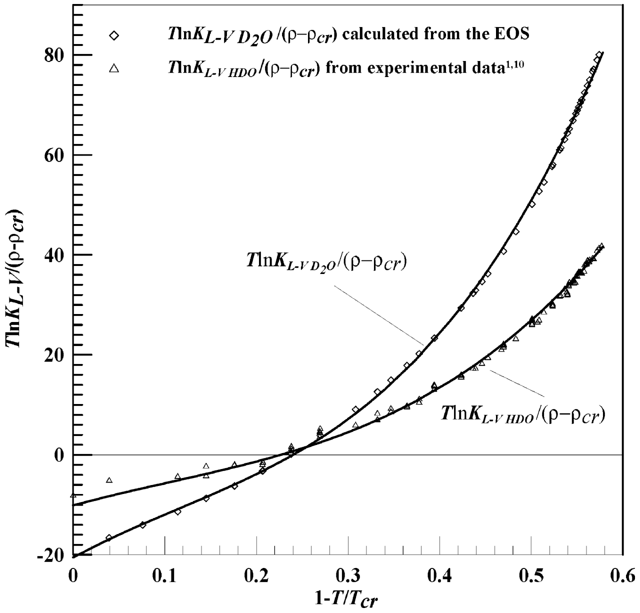

Figure 1. The third-order polynomial to represent the liquid−vapor hydrogen isotope fractionation (eq 5 and Table 1).

that the range where the term $RT \ln K_{L-V}$ varies linearly as a function of ρ_l extends approximately 20 K beyond the near-critical regions. To describe the liquid−vapor isotope distribution down to room temperature, we expanded eq 4, including the second- and third-power terms of $(1 - T/T_{cr})$

$$T \ln K_{L-V(D_2O)}/(\rho_l - \rho_{cr}) = A_0 + A_1(1 - T/T_{cr}) + A_2(1 - T/T_{cr})^2 + A_3(1 - T/T_{cr})^3 \quad (5)$$

where A_0, A_1, A_2, and A_3 are coefficients. Equation 5 provides the theoretical temperature dependence in the vicinity of the critical point. A different expression for $\ln K_D$ valid over all the range of existence of liquid water has been given by Japas et al.[7] We fitted the values of $K_{L-V(D_2O)}$ to eq 5, which were calculated from the EOS of H_2O and D_2O[5,6] using eq 3 (Table 1). Errors in EOS for D_2O[6] are much larger than those for H_2O.[5] Consequently, our results are not significantly affected if, instead of EOS for H_2O,[5] the current standard EOS by Wagner and Pruss[9] is used. Results of calculations are shown in a plot of $(1 - T/T_{cr})$ vs $T \ln K/(\rho_l - \rho_{cr})$ (Figure 1), which was used previously.[7] We also fitted extensive mass spectrometric data of $K_{L-V(HDO)}$ from room temperature to near the critical point obtained by Horita and Wesolowski[1] to eq 5 (Figure 1 and Table 1). As shown in Figure 1, the polynomial expansion of eq 5 provides a correct description for the temperature dependence of equilibrium hydrogen isotope fractionation in the range from room to the critical temperature.

3. Disproportionation Reaction of Hydrogen Isotopic Water

The two equilibrium constants $K_{L-V(HDO)}$ and $K_{L-V(D_2O)}$ are related by two disproportionation reactions in the vapor and liquid phases

$$K_{D(v)}:\ H_2O_{vapor} + D_2O_{vapor} \leftrightarrow 2HDO_{vapor} \quad (6)$$

$$K_{D(l)}:\ H_2O_{liquid} + D_2O_{liquid} \leftrightarrow 2HDO_{liquid} \quad (7)$$

through the relationship

$$K_{L-V(D_2O)} = K^2_{L-V(HDO)}\frac{K_{D(v)}}{K_{D(l)}} \quad (8)$$

This simple relationship holds for the entire range of isotopic composition ($0 \le D/(H + D) \le 1$). It is well-known that hydrogen isotope disproportionation reactions of eqs 6 and 7 do not obey the rule of the geometric mean (i.e., $K_{D(l)}, K_{D(v)} < 4$). In addition, the two constants are not equal ($K_{D(v)}/K_{D(l)} \neq 1$). Rolston and Gale[11] showed that the deviation of the ratio $K_{D(v)}/K_{D(l)}$ from unity is the reason for an unusual dependence of liquid water−H_2 isotope fractionation factor on deuterium contents in the system. Equation 8 can be rewritten as

$$\ln K_{L-V(D_2O)} = 2 \ln K_{L-V(HDO)} + \ln(K_{D(v)}/K_{D(l)}) \quad (9)$$

Van Hook[12,13] used an equation with a different formalism

$$\ln K_{L-V(D_2O)} = (2 - r)\ln K_{L-V(HDO)};$$

$$r = -\frac{\ln(K_{D(v)}/K_{D(l)})}{\ln K_{L-V(HDO)}} \quad (10)$$

On the basis of experimental data on vapor pressures and boiling and freezing points in the literature, Van Hook[12,13] reported a constant value of r (0.09 ± 0.03) over the temperature range from 233 to 473 K.

Since values of both $K_{L-V(D_2O)}$ and $K_{L-V(HDO)}$ are now available over the entire range of the liquid−vapor boundary of water (Figure 1), one can re-examine the deviation from the rule of the geometric mean. A straightforward method is to obtain a polynomial equation for the value of $K_{L-V(D_2O)} - 2K_{L-V(HDO)}$ from the two equations of $K_{L-V(D_2O)}$ and $K_{L-V(HDO)}$ (Table 1). Unfortunately, this approach resulted in large uncertainties, because the deviation from the rule of the geometric mean, $K_{L-V(D_2O)} - 2K_{L-V(HDO)}$, is small compared to the two values of $K_{L-V(D_2O)}$ and $2K_{L-V(HDO)}$. An alternative approach is to use experimental data for the enthalpy of the disproportionation reaction ($H_2O + D_2O \leftrightarrow 2HDO$). From eqs 5 and 9, the deviation from the rule of the geometric mean can be expressed as

$$\ln K_{D(l)} - \ln K_{D(v)} = 2 \ln K_{L-V(HDO)} - \ln K_{L-V(D_2O)} = (\rho_l - \rho_{cr})/T[B_o + B_1(1 - T/T_{cr}) + B_2(1 - T/T_{cr})^2 + B_3(1 - T/T_{cr})^3] \quad (11)$$

Differentiation of eq 11 with respect to temperature, using the thermodynamic relationship $\Delta H = -RT^2(\partial/\partial T \ln K)_P$ gives

$$\Delta H_v - \Delta H_l = T^2 \frac{\partial}{\partial T}\{(\rho_l - \rho_{cr})/T[B_0 + B_1(1 - T/T_{cr}) + B_2(1 - T/T_{cr})^2 + B_3(1 - T/T_{cr})^3]\}_P \quad (12)$$

where ΔH_v and ΔH_l are enthalpies of reactions 6 and 7, respectively.

Simonson[14] measured the value of ΔH_l experimentally from 310 to 673 K and represented these experimental data by the following equation (Table 2):

$$\Delta H_l = -R\{q_1 + 3q_2/T^2 + q_3(\alpha T^2) - q_4 T\} \quad (13)$$

where $q_1 = -32.1072$ (K), $q_2 = 1.879\ 89$ (K^2), $q_3 = 1.529\ 02 \times 10^{-4}$, and $q_4 = -3.213\ 29 \times 10^{-2}$. α is the isobaric expansivity of H_2O, which can be calculated from the EOS of Kestin et al.[6] ΔH_v can be obtained from the reduced isotopic

TABLE 1: Results of Fitting of $K_{L-V(D_2O)}$ and $K_{L-V(HDO)}$ to Eq 5

	$10^3T \ln K_{L-V(D_2O)}/(\rho_l - \rho_{cr})$		$2 \times 10^3T \ln K_{L-V(HDO)}/(\rho_l - \rho_{cr})$		difference	
coefficient	value m^3 K/mol	error[a] (σ) m^3 K/mol	value m^3 K/mol	error[a] (σ) m^3 K/mol	value m^3 K/mol	error[a] (σ) m^3 K/mol
A_0	−20.114	0.112	−27.620	0.168	7.505	0.202
A_1	98.649	4.682	167.542	17.933	−68.893	18.534
A_2	−187.260	21.830	−331.779	175.635	144.520	176.987
A_3	551.540	46.790	640.072	164.371	−88.532	170.901

[a] Errors reflect uncertainties in the least-squares fitting.

TABLE 2: Comparison of Enthalpies of Reactions 6 and 7

	$10^2\Delta H_l/RT$		
T (K)	this study	Simonson (1990)	$10^2\Delta H_v/RT$
298.15	5.4249	5.4264	7.9182
323.15	5.0004	5.0489	7.0341
348.15	4.6262	4.6692	6.2538
373.15	4.2834	4.3014	5.5667
398.15	3.9623	3.9519	4.9621
423.15	3.6563	3.6234	4.4299
448.15	3.3611	3.3164	3.9609
473.15	3.0740	3.0302	3.5466
498.15	2.7942	2.7634	3.1800
523.15	2.5220	2.5145	2.8547
548.15	2.2598	2.2811	2.5654
573.15	2.0123	2.0604	2.3074
598.15	1.7889	1.8456	2.0768
623.15	1.6108	1.6075	1.8702

TABLE 3: Polynomial Coefficients in Eq 11 for Calculating the Deviation from the Rule of the Geometric Mean

coefficients	value 10^3 m^3 K/mol	error[a] (1σ) m^3 K/mol
B_0	0	0.09576
B_1	5.6938	0.14176
B_2	−18.7921	0.41563
B_3	35.2445	0.44635

[a] Errors reflect uncertainties from the least-squares fitting.

partition function ratio calculated by Bron et al.[15] or Richet et al.,[16] assuming ideal-gas behavior for vapor phase (Table 2). Thus, calculations of the left-hand and right-hand sides of eq 12 from 278 to 600 K with a 1 K step can provide a set of linear equations, which were then used to solve for the four unknown coefficients B_i by the least-squares method (Table 3). A good agreement in the value of ΔH_l between Simonson's results[14] and our calculations from eq 12 (Table 2) shows that our approach provides adequate description for experimental data on the enthalpy of reaction 7. From eq 11, and coefficients in Tables 1 and 3, we can obtain the third-order polynomial for the $K_{L-V(HDO)}$

$$10^3 \ln K_{L-V(HDO)} = -10.0572 + 52.1716(1 - T/T_{cr}) - 103.0257(1 - T/T_{cr})^2 + 293.3924(1 - T/T_{cr})^3 \quad (14)$$

4. Results and Discussion

A comparison among different formalisms for representing the deviation from the rule of the geometric mean in the coordinate system of $2K_{L-V(HDO)} - K_{L-V(D_2O)}$ versus temperature is given in Figure 2. For the value of $K_{L-V(HDO)}$, four equations are compared: (a) the third-order polynomial based on the mass spectrometric data (Table 1), (b) the best-fit empirical equation of Horita and Wesolowski[1] based on the mass spectrometric data, (c) the third-order polynomial (eq 11) based on calorimetric measurements of enthalpy by Simonson,[14] and (d) Van Hook's[12,13] formalism, $\ln K_{L-V(HDO)} = \ln K_{L-V(D_2O)}/1.91$(eq 10). In all cases, $\ln K_{L-V(D_2O)}$ from eq 5 and Table 1 was used, which was in turn calculated from EOS of Kestin et al.[5,6] and eq 3. As shown in Figure 2, overall agreements among the four equations are excellent. The results that were obtained from mass spectrometric data for the vapor−liquid system show complex behaviors with maxima and minima, suggesting that the value of $\Delta H_v - \Delta H_l$ in eq 12 changes its sign. On the other hand, the curve (eq 11), which is based on eq 5 and the enthalpy measurements of Simonson,[14] shows a smooth temperature dependence (positive values of $\Delta H_v - \Delta H_l$ and $\ln K_{D(v)} - \ln K_{D(l)}$), approaching a zero value at the critical temperature of H_2O. The equation of Van Hook's[12,13] formalism agrees quantitatively with that based on the calorimetric measurements within errors. Thus, this new equation appears to best describe the temperature dependency of the deviation from the rule of the geometric mean ($\ln K_{D(v)} - \ln K_{D(l)}$) from the triple to critical point of H_2O.

A comparison is also made for the value of $\ln K_{L-V(HDO)}$ in Figure 3. The equation based on the rule of the geometric mean ($\ln K_{L-V(D_2O)}/2$) always underestimates that of our approach for $\ln K_{L-V(HDO)}$ (eq 14). The best-fit empirical equation based on mass spectrometric data[1] starts to deviate significantly from eq 14 above 580 K, because of the limited data with large errors in this temperature range. Van Hook's approach ($\ln K_{L-V(HDO)} = \ln K_{L-V(D_2O)}/1.91$) agrees well with Horita and Wesolowski's

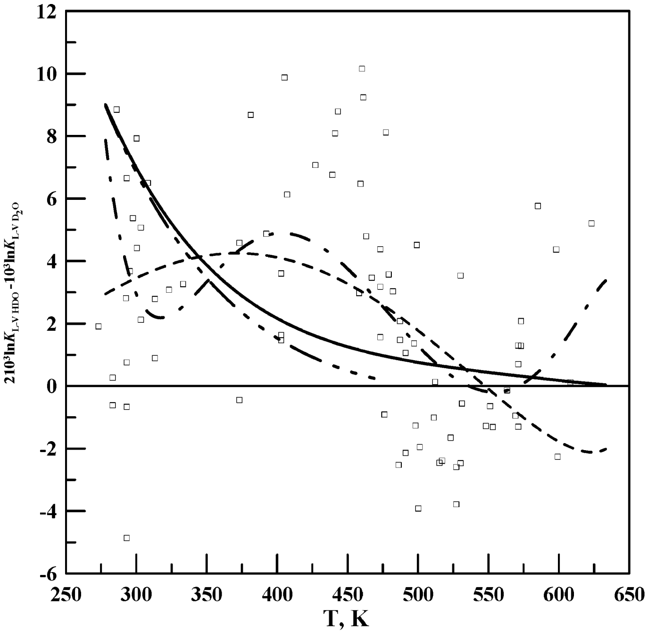

Figure 2. Comparison of different approaches to evaluate the deviation from the rule of the geometric mean. Open squares are obtained from $\ln K_{L-V(D_2O)}$ based on the EOS[5,6] and from $\ln K_{L-V(HDO)}$ of mass spectrometric data.[1,10] (- - -) Polynomial equation of the classical near-critical expansion based on mass spectrometric experiments. (- • -) Horita and Wesolowski[1] best-fit curve. (—) Polynomial equation of the classical near-critical expansion based on Simonson's[14] calorimetric data. (− ···) Van Hook's[12,13] formalism.

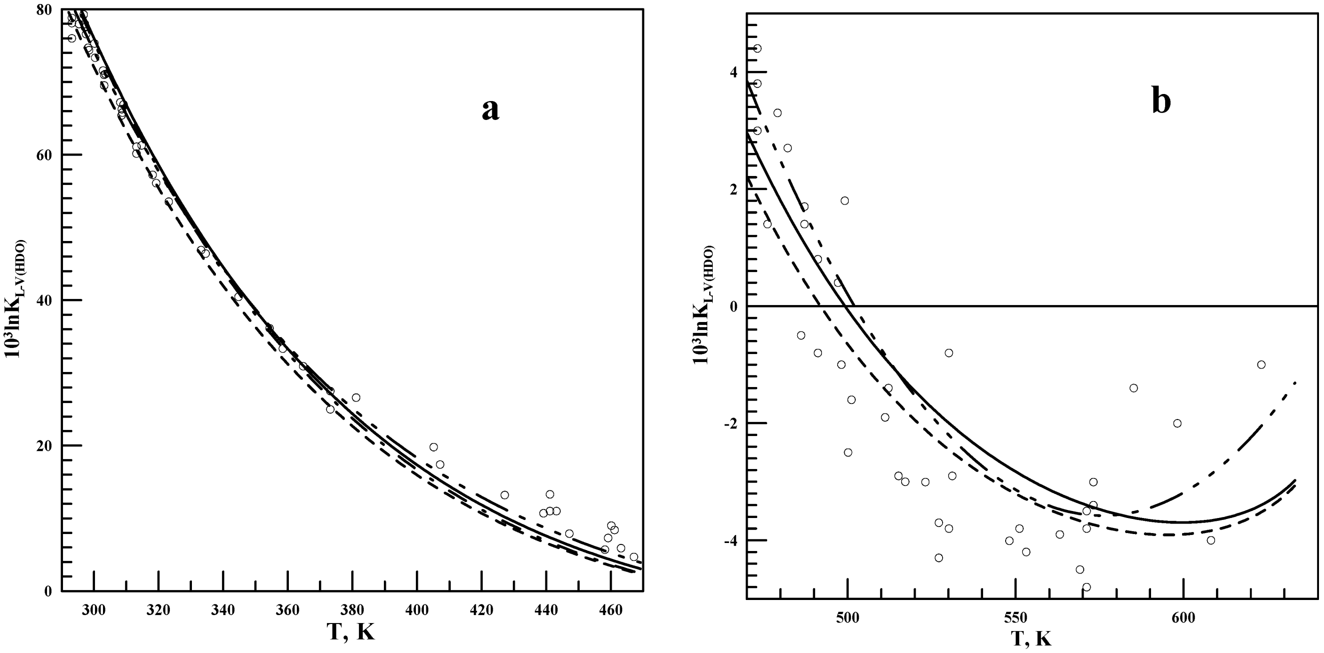

Figure 3. Comparisons of different formalisms for representing the value of ln $K_{L-V(HDO)}$: (a) below 473 K and (b) from 473 K to critical temperature. (—) This study, classical near-critical expansion based on calorimetric data (Simonson, ref 14). (- - -) The rule of the geometric mean. (- • -) Van Hook's formalism.[12,13] (— •••) Best-fit curve of mass spectrometric data.[1] () Experimental mass spectrometric measurements (Horita and Wesolowski[1] and Majoube[10]).

experimental results[1] and our new formalism (eq 14) at temperatures up to 370 K (Figure 3a). With increasing temperature to 473 K, the Van Hook formalism approached the equation based on the rule of the geometric mean.

VPIE data of D_2O and H_2O obtained from the EOS[5,6] give a crossover (ln $K_{L-V(D_2O)} = 0$) temperature of about 494 K (221 °C), in excellent agreement with direct measurements.[17] For the HDO−H_2O fractionation factor (ln $K_{L-V(HDO)}$), Horita and Wesolowski[1] obtained a crossover temperature of 502 ± 13 K (229 ± 13 °C). Our new formalism (eq 14) gives a crossover temperature of 500 K (227 °C), which is in an agreement with the experimental data of ln $K_{L-V(HDO)}$. The small difference (6−8 K) in the crossover temperature between the two values of ln $K_{L-V(D_2O)}$ and ln $K_{L-V(HDO)}$ is derived from the term ln ($K_{D(v)}/K_{D(l)}$)in eq 9.

In conclusion, we have developed a third-order polynomial equation, which provides correct near-critical asymptotic behavior, for representing the deviation from the rule of the geometric mean, ln ($K_{D(v)}/K_{D(l)}$) (eq 11), and the liquid−vapor isotope fractionation ln $K_{L-V(HDO)}$ (eq 14) over the entire range of the liquid−vapor boundary. Experimental data of the enthalpy of H_2O−D_2O mixing[14] were used instead of mass spectrometric data of ln $K_{L-V(HDO)}$, along with the EOS of H_2O and D_2O[5,6] and the calculated reduced partition function ratio for gaseous isotopic waters.[15] Our new equations for ln($K_{D(v)}/K_{D(l)}$) and ln $K_{L-V(HDO)}$ can accurately represent the temperature dependencies of these values over the entire liquid−vapor boundary of water.

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