Novel Corresponding-States Principle Approach for the Equation of State of Isotopologues: H$_2$^{18}O as an Example

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The corresponding-states principle (CSP) has been considered for the development of the equations of state (EOS) of minor isotopologues that are usually unknown. We demonstrate that, for isotopologues of a given molecular fluid, a general extended multi-parameter corresponding-states EOS can be reduced to the three-parameter EOS, utilizing the critical parameters (temperature and density) and Pitzer's acentric factor as correlation parameters. Appropriate general CSP mathematical formalism and equations for constructing the EOS of minor isotopologues are described in detail. The formalism and equations were applied to isotopologues of water and demonstrated that the isotopic effect on the critical parameters and the acentric factor of H$_2$^{18}O can be successfully calculated from the EOS of H$_2$O and experimental data on the isotope effects (liquid−vapor isotope fractionation factor and molar volume isotope effect). We have also shown that the experimental data on the vapor pressure isotope effect (VPIE) for ^{18}O-substituted water are inconsistent within the framework of thermodynamics with the liquid−vapor oxygen isotope fractionation factor. The novel approach of CSP to isotopologues developed in this study creates a new opportunity for constructing the EOS of minor isotopologues for many other molecular fluids.

1. Introduction

Isotope effects in molecular fluids are of great interest, because the sign and magnitude of changes in the thermodynamic properties of molecular fluids upon isotopic substitution are closely related to the nature of intermolecular forces and the motion of molecules in the vapor and condensed phases. Since the pioneering work on the quantum statistical mechanical foundation for isotope effects by Bigeleisen and Mayer[1] and Urey,[2] the reduced isotope partition function ratio (RIPFR) of molecular fluids, a primary physical quantity for isotopic species, has been calculated using the ideal-gas approximation (i.e., no intermolecular interactions). In the past several decades, numerous physicochemical isotope effects (e.g., vapor pressure, molar volume, viscosity, heat capacity) of molecular fluids have been the subject of numerous experimental studies.[3−5] Recently, advanced *ab initio* approaches, molecular dynamics simulation,[6,7] integral equation theory,[8] and quantum-mechanical density function theory[9] have been increasingly utilized for calculating the isotope effects in high-density molecular fluids, including the condensed phases. Despite these in-depth experimental, theoretical, and simulation studies on the isotope effects of molecular fluids at various conditions, a full and accurate description of thermodynamic properties (e.g., equation of state for pressure−temperature−volume relations) of minor isotopic molecules (isotopologues) is very limited.

We have recently suggested the use of multi-parameter equation of states (EOS) of major and minor isotopologues of a given molecular fluid for calculating the reduced isotope partition function ratio (RIPFR) of "real-gas" fluids over a wide range of temperatures and pressures.[10,11] If high-precision multi-parameter EOS's are available for both isotopologues in describing their PVT properties, this approach can provide high accuracy in the calculation of nonideal behavior for the isotopic properties of molecular fluids. Using the EOS's for H$_2$^{16}O and D$_2$O available from the literature, Polyakov et al.[11] calculated the effect of pressure (density) on the RIPFR of liquid, vapor, and supercritical waters to 800 K and 100 MPa. Their results showed a good agreement with experimental data.[12] However, EOS's with sufficiently high precision are usually not available for minor isotopologues for the majority of molecular fluids, limiting the application of the EOS-based method developed by Polyakov et al.[11]

In the present study, we investigated the use of the corresponding-states principle (CSP) for constructing the EOS's of minor isotopologues. The CSP approach, which is arguably the best suited for a set of isotopologues of a given molecule, will remove the restriction of our EOS-based method. We present the formalism and equations for isotopologues within the framework of CSP and apply them to ^{18}O-substituted water (H$_2$^{18}O) as an example.

2. Corresponding-States Principle

According to the original two-parameter formulation, the CSP can be expressed as

$$\frac{P}{\rho RT} = Z(\tau,\delta) \qquad (1)$$

where P is pressure, R is the universal gas constant, T is absolute temperature, and ρ is the molar density, defining the compressibility factor Z as a function of $\tau \equiv T_{cr}/T$ and $\delta \equiv \rho/\rho_{cr}$ where T_{cr} and ρ_{cr} are the critical temperature and critical molar density, respectively. The CSP claims that the dimensionless function Z in eq 1 is a universal function for all substances, as originally

proposed by van der Waals, who pointed out that, because this equation is written in the dimensionless form, it is the same for all fluids.

2.1. Extended Corresponding-States Principle. The simple two-parameter version of the corresponding states principle satisfied experimental observations only in the case of spherical and nearly spherical molecules such as heavy noble gases, methane, nitrogen, and oxygen. To extend the corresponding-states approach to a wider set of more complex fluids, additional parameters must be considered. Various modifications of these extended corresponding-states EOS were recently reviewed by Ely and Marrucho.[13] Here, we consider a corresponding-states EOS involving an additional characterization parameter, namely, Pitzer's acentric factor[14] (ω):

$$\frac{P}{\rho RT} = Z(\tau,\delta,\omega)_{\omega=0} + \left(\frac{\partial Z(\tau,\delta,\omega)}{\partial \omega}\right)_{\omega=0} \omega \qquad (2)$$

Equation 2 is a first-order Taylor expansion of the compressibility factor with respect to the acentric factor. The acentric factor characterizes the deviation of the molecule potential from a spherical shape, as suggested by Pitzer.[14] This parameter is found to be extremely useful in the corresponding-state-like correlation.[13,15] Pitzer[14] defined a ratio of the saturated pressure (P_s) at $T = 0.7T_{cr}$ to the critical pressure (P_{cr}) as a measure for the acentric factor:

$$\omega = -\log\left(\frac{P_s}{P_{cr}}\right)_{T=0.7T_{cr}} - 1 \qquad (3)$$

Equation 3 provides a possible rationale for experimental determination of the acentric factor. The corresponding-states approach, including the acentric factor and other correlation parameters, is usually referred to as the extended CSP.[13]

The main problem behind the three-parameter extended CSP is the determination of the $\partial Z/\partial \omega$ term in eq 2. A common technique to perform this calculation was suggested by Lee and Kessler[16] involving the equation

$$\frac{\partial Z}{\partial \omega} = \frac{Z - Z_0}{\omega} \qquad (4)$$

where Z and Z_0 are the compressibility factors of a reference fluid and a simple spherical molecule (e.g., noble gases), respectively, and ω is an acentric factor of a reference fluid.

2.2. Applications to Isotopologues. The CSP can be best applied to a set of isotopologues of a given molecular fluid (e.g., H_2O, D_2O, and $H_2^{18}O$ of water), because of the very similar thermodynamic properties of the isotope species, which is one of the conditions for successful applications of the CSP.[13] There have been a few attempts to apply the corresponding-states correlation to isotope substitution phenomena. De Boer[17] was the first to successfully predict the VPIE effect of noble gases. However, subsequent attempts to predict the VPIE of more complex substances failed.[7] Xiang[18] applied the extended CSP to calculating the vapor pressure and critical point of tritium oxide. Recently, Van Hook[19,20] et al. applied the CSP (cubic-order or "almost cubic-order" EOS) to a set of substances with experimentally determined critical parameters ($^3He/^4He$, H_2/D_2, CH_4/CD_4, H_2O/D_2O, etc.). These studies demonstrated that satisfactory agreement with the experimental data on VPIE and molar volume isotope effects (MVIE) can be obtained only within the framework of the extended three-parameter CSP and that the isotope effect on the acentric factor has to be taken into account.

One could argue that more sophisticated CSP correlations (e.g., four-parameter equation) might be required for isotopologues of water, because water is the prototypical polar substance. In fact, four-parameter CSP has been successfully applied not only to substances consisting of weakly non-spherical and nonpolar molecules but also to polar substances consisting of highly non-spherical molecules.[21–25] Here, we demonstrate that the extended three-parameter CSP discussed above can be applied to a set of isotopologues of molecular fluids, including non-spherical and polar ones, provided that some modifications are introduced.

According to Xiang's formulations,[25] the compressibility factor for a strongly non-spherical polar fluid can be written as a four-parameter equation:

$$Z(\tau,\delta) = Z^{(0)}(\tau,\delta) + Z^{(1)}(\tau,\delta)\omega + Z^{(2)}(\tau,\delta)\theta \qquad (5)$$

where $Z^{(0)}(\tau,\delta)$ is the compressibility factor of spherical fluids whose acentric (ω) and aspherical (θ) factors are 0 (e.g., noble gases). $Z^{(1)}(\tau,\delta)$ is a function describing the deviation from a spherical-fluid EOS (cf. eq 2). $Z^{(2)}(\tau,\delta)$ is a function used to describe the behavior of polar, highly non-spherical fluids. The aspherical factor is defined in the Xiang CSP formulation as[25]

$$\theta \equiv (Z_{cr} - 0.29)^2 \qquad (6)$$

Considering that 0.29 is a critical compressibility factor for spherically symmetric fluids (argon, krypton, etc.), and that the acentric factor is a linear function of the term ($Z_{cr} - 0.29$) for weakly non-spherical and nonpolar fluids,[14] the correspondence-states EOS (5) can be expressed as an expansion of the compressibility factor in a ($Z_{cr} - 0.29$) power series.

Writing eq 5 for an isotopologue, we get

$$Z^*(\tau,\delta) = Z^{(0)}(\tau,\delta) + Z^{(1)}(\tau,\delta)\omega^* + Z^{(2)}(\tau,\delta)\theta^* \qquad (7)$$

Hereafter, the asterisk denotes quantities referring to an isotopologue containing rare isotopes (e.g., D_2O, $H_2^{18}O$, etc.). Subtracting eq 5 from eq 7, and then substituting the aspherical factor according to eq 6, one can get, after neglecting quadratic terms of ($Z^*_{cr} - Z_{cr}$),

$$Z^*(\tau,\delta) - Z(\tau,\delta) = Z^{(1)}(\tau,\delta)(\omega^* - \omega) + 2Z^{(2)}(\tau,\delta)(Z_{cr} - 0.29)(Z^*_{cr} - Z_{cr}) \qquad (8)$$

From eq 8, it follows that

$$Z^*_{cr} - Z_{cr} = \frac{Z^{(1)}(1,1)}{1 - 2Z^{(2)}(1,1)(Z_{cr} - 0.29)}(\omega^* - \omega) \qquad (9)$$

Substituting eq 9 into eq 8, one can derive

$$Z^*(\tau,\delta) - Z(\tau,\delta) = \left[Z^{(1)}(\tau,\delta) + \frac{2Z^{(2)}(\tau,\delta)(Z_{cr} - 0.29)}{1 - 2Z^{(2)}(1,1)(Z_{cr} - 0.29)}Z^{(1)}(1,1)\right](\omega^* - \omega) \qquad (10)$$

Equations 5 and 10 can be generalized by expanding the compressibility factor into even higher ($Z_{cr} - 0.29$) terms:

$$Z(\tau,\delta) = Z^{(0)}(\tau,\delta) + Z^{(1)}(\tau,\delta)\omega + \sum_{i=2}^{n} Z^{(i)}(\tau,\delta)(Z_{cr} - 0.29)^i \qquad (11)$$

$$Z^*(\tau,\delta) - Z(\tau,\delta) =$$
$$\left[Z^{(1)}(\tau,\delta) + \frac{\sum_{i=2}^{n} iZ^{(i)}(\tau,\delta)(Z_{cr} - 0.29)^{i-1}}{1 - \sum_{i=2}^{n} iZ^{(i)}(1,1)(Z_{cr} - 0.29)^{i-1}} Z^{(1)}(1,1) \right](\omega^* - \omega)$$
$$(12)$$

In eqs 11 and 12, second and higher terms of $(Z_{cr}^* - Z_{cr})$ were neglected due to small differences in the properties of isotopologues. Notice that the terms in the square brackets of eqs 10 and 12 depend only on the compressibility factors and functions of the main isotopologue. Thus, the four-parameter or higher-term EOS for a set of isotopologues can be reduced to eq 10 or 12, respectively, which are in turn equivalent to the three-parameter CSP (eqs 2 and 4). The significant difference between the three-parameter CSP (eq 2) and eqs 10 and 12 lies in the fact that the derivative of the compressibility factor with respect to the acentric factor $(\partial Z/\partial \omega)$ is a universal function for all substances within the framework of the three-parameter CSP, whereas the functions in the square brackets in eqs 10 and 12 are the same only for isotopologues of a given substance.

Summarizing, one can write the extended three-parameter CSP relevant to a set of isotopologues of a given substance as follows:

$$Z(\tau,\delta,\omega^*) = Z(\tau,\delta,\omega) + \tilde{Z}^{(1)}(\tau,\delta,\omega)(\omega^* - \omega) \quad (13)$$

where $\tilde{Z}^{(1)}$ is defined according to eq 12 by the following expression:

$$\tilde{Z}^{(1)}(\tau,\delta,\omega) = \frac{\partial Z(\tau,\delta,\omega)}{\partial \omega} =$$
$$Z^{(1)}(\tau,\delta) + \frac{\sum_{i=2}^{n} iZ^{(i)}(\tau,\delta)(Z_{cr} - 0.29)^{i-1}}{1 - \sum_{i=2}^{n} iZ^{(i)}(1,1)(Z_{cr} - 0.29)^{i-1}} Z^{(1)}(1,1) \quad (14)$$

We should emphasize that these equations are valid for a set of isotopologues of a molecular fluid, even if a four- or higher-term EOS is required to represent the PVT properties of a major isotopologue of the fluid.

3. Corresponding-States Principle and Thermodynamic Properties of Isotopologues

Thus far, we discussed the specificity of the general CSP approach relevant to isotopologues and mathematical representation of EOS's for isotopologues in the three-parameter extended CSP formalism. In this section, we present the mathematical technique for constructing the EOS's for isotopologues and calculating the RIPFR based on the developed isotope version of the three-parameter extended CSP (eq 13).

Polyakov et al.[10,11] presented the EOS-based technique for calculating the nonideal-gas RIPFR. The RIPFR is a main physical quantity that determines equilibrium stable isotope fractionation:[1,2]

$$\ln\left(\frac{s^*}{s}f\right) \equiv \frac{A(T,\rho) - A^*(T,\rho)}{RT} - 1.5n \ln(m^*/m) \quad (15)$$

where $s^*/s f$ is the RIPFR, A is the Helmholtz free energy, m is the mass of the major isotope undergoing isotopic substitution, m^* is the mass of the rare isotope (e.g., masses of ^{16}O and ^{18}O, respectively, in the case of $^{16}O \rightarrow {}^{18}O$ substitution), and n is the multiplicity of the isotopic substitution (number of isotopically substituted atoms in the chemical formula unit, e.g., unity in the case of H_2O and two in the case of D_2O). The second term in the right-hand side of eq 15 represents the high-temperature (classical physics) limit for the difference of isotopic free energies divided by RT. The factor 1.5 in eq 15 results from a power exponential in the mass dependence of the partition function in the classical limit. An experimentally measurable stable isotope equilibrium fractionation factor is expressed in terms of the RIPFR as

$$\ln \alpha_{A-B}^e = \ln\left(\frac{s^*}{s}f\right)_A - \ln\left(\frac{s^*}{s}f\right)_B \quad (16)$$

where α_{A-B}^e is the equilibrium stable isotope fractionation factor between substances A and B.[26]

The RIPFR can be expressed as a sum of two parts, namely (i) the ideal-gas RIPFR and (ii) the term describing the deviation of the RIPFR from the ideal-gas value by the following equation:[11]

$$\ln\left(\frac{s^*}{s}f\right) = \ln\left(\frac{s^*}{s}f(T)\right)_{id} +$$
$$\left\{\frac{A(T,\rho) - A(T,0)}{RT} - \frac{A^*(T,\rho) - A^*(T,0)}{RT}\right\} \quad (17)$$

In eq 17, $((s^*/s)f(T))_{id}$ is the ideal-gas RIPFR, and the second term denotes the deviation from the ideal gas counterpart. The latter term is responsible for the density (pressure) effect on the RIPFR. At a given temperature, one can write a common thermodynamic equation:

$$A(T,\rho) - A(T,0) = \int_0^\rho P/\rho^2 \, d\rho \quad (18)$$

Application of eq 18 to both isotopologues in eq 17 allows calculation of the nonideal-gas part of RIPFR in eq 17, provided that the PVT properties of two isotopologues of interest are known from respective EOS's. Accurate multi-parameter EOS's for both $H_2^{16}O$ and D_2O isotopologues are available and were used previously to calculate the effect of density (pressure) on the RIPFR for hydrogen.[11] However, the EOS is usually known only for the most abundant isotopologue.

At a given T and ρ, the dimensionless values of τ and δ change because of the changes in critical temperature and density caused by isotope substitution:

$$\tau^* - \tau \equiv \Delta\tau = \frac{Z_{cr}^*}{T} - \frac{T_{cr}}{T} = \tau\left(\frac{\Delta T_{cr}}{T_{cr}}\right) \quad (19)$$

$$\delta^* - \delta \equiv \Delta\delta = \frac{\rho}{\rho_{cr}^*} - \frac{\rho}{\rho_{cr}} \approx -\delta\left(\frac{\Delta\rho_{cr}}{\rho_{cr}}\right) \quad (20)$$

where we neglected the term $\sim(\Delta\rho_{cr}/\rho)^2$ in eq 20.

Taking into account small differences in the critical parameters of isotope species and holding terms linear with respect to these differences, one can write eq 13 according to the extended CSP at a given T and ρ:

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$$Z(\tau^*,\delta^*,\omega^*) = Z(\tau,\delta,\omega) + \tau \frac{\partial Z(\tau,\delta,\omega)}{\partial \tau}\left(\frac{\Delta T_{cr}}{T_{cr}}\right) -$$
$$\delta \frac{\partial Z(\tau,\delta,\omega)}{\partial \delta}\left(\frac{\Delta \rho_{cr}}{\rho_{cr}}\right) + \omega \frac{\partial Z(\tau,\delta,\omega)}{\partial \omega}\left(\frac{\Delta \omega}{\omega}\right) \quad (21)$$

where $\Delta\omega = \omega^* - \omega$. Equation 21 expresses the compressibility factor of the isotopologue of interest (e.g., $H_2^{18}O$) in terms of the compressibility factor and its derivatives of the most abundant isotopologue for which the EOS is known (e.g., $H_2^{16}O$).

Modern, fundamental multi-parameter EOS's of many fluids are expressed explicitly in the dimensionless Helmholtz free energy as a function of the dimensionless temperature and density:

$$\frac{A(T,\rho)}{RT} = \phi^0(\tau,\delta) + \phi^r(\tau,\delta) \quad (22)$$

The functions $\phi^0(\tau,\delta)$ and $\phi^r(\tau,\delta)$ represent the ideal gas and the residual contributions to the dimensionless Helmholtz free energy, respectively. The fundamental EOS can then be converted to the equation for the compressibility factor by the following thermodynamic relation:

$$\frac{P(\tau,\delta)}{\rho RT} = Z(\tau,\delta) = 1 + \delta \frac{\partial \phi^r(\tau,\delta)}{\partial \delta} \quad (23)$$

The fundamental EOS (22), referring to one isotopologue, represents the Helmholtz free energy at a given value of the acentric factor. From the point of view of the extended CSP, isotopic substitution at a given temperature and density results in changes not only of the critical parameters, but also of the corresponding acentric factor. Thus, the residual part of the Helmholtz free energy in eq 22 can now be written as

$$\phi^r(\tau^*,\delta^*,\omega^*) = \phi^r(\tau,\delta,\omega) + \tau \frac{\partial \phi^r(\tau,\delta,\omega)}{\partial \tau}\left(\frac{\Delta T_{cr}}{T_{cr}}\right) -$$
$$\delta \frac{\partial \phi^r(\tau,\delta,\omega)}{\partial \delta}\left(\frac{\Delta \rho_{cr}}{\rho_{cr}}\right) + \omega \frac{\partial \phi^r(\tau,\delta,\omega)}{\partial \omega}\left(\frac{\Delta \omega}{\omega}\right) \quad (24)$$

which is equivalent to eq 21, according to eqs 22 and 23. Moreover, the ideal-gas part of the fundamental EOS can be expressed in terms of the ideal-gas RIPFR; i.e., from eqs 15 and 22, one can write

$$\frac{A_{id}^*}{RT} = \frac{A_{id}}{RT} + \left(\frac{A_{id}^*}{RT} - \frac{A_{id}}{RT}\right) = \frac{A_{id}}{RT} - \ln\left(\frac{s^*}{s}f\right)_{id} + 1.5n\ln(m^*/m) \quad (25)$$

where A_{id} is the ideal-gas part of the Helmholtz free energy.

Combining eqs 22, 24, and 25, one can obtain a general expression for the extended corresponding-states EOS for isotopic species:

$$\frac{A^*(T,\rho)}{RT} = \phi^0(\tau,\delta) + \phi^r(\tau,\delta,\omega) - \ln\left(\frac{s^*}{s}f\right)_{id} +$$
$$1.5n\ln(m^*/m) + \tau \frac{\partial \phi^r(\tau,\delta,\omega)}{\partial \tau}\left(\frac{\Delta T_{cr}}{T_{cr}}\right) - \delta \frac{\partial \phi^r(\tau,\delta,\omega)}{\partial \delta}\left(\frac{\Delta \rho_{cr}}{\rho_{cr}}\right) +$$
$$\omega \frac{\partial \phi^r(\tau,\delta,\omega)}{\partial \omega}\left(\frac{\Delta \omega}{\omega}\right) \quad (26)$$

Thus, the equation for the RIPFR can be written as

$$\ln\left(\frac{s^*}{s}f\right) = \ln\left(\frac{s^*}{s}f\right)_{id} - \tau \frac{\partial \phi^r(\tau,\delta,\omega)}{\partial \tau}\left(\frac{\Delta T_{cr}}{T_{cr}}\right) +$$
$$\delta \frac{\partial \phi^r(\tau,\delta,\omega)}{\partial \delta}\left(\frac{\Delta \rho_{cr}}{\rho_{cr}}\right) - \omega \frac{\partial \phi^r(\tau,\delta,\omega)}{\partial \omega}\left(\frac{\Delta \omega}{\omega}\right) \quad (27)$$

In summary, we have shown that the thermodynamic properties of minor isotopologues can be calculated over a wide range of temperatures and pressures from the knowledge of (a) the ideal-gas RIPFR, (b) the EOS of a major isotopologue, (c) the derivatives of the residual function of the dimensionless Helmholtz free energy with respect to the dimensionless variables of temperature and density and the acentric factor, and (d) the isotopic effects on the critical parameters and the acentric factor. Several properties (ideal-gas RIPFR, EOS of a major isotopologue, derivatives of the EOS with respect to the dimensionless variables) are usually available from the literature. However, the remaining properties in eq 27 (i.e., the isotopic effects on the critical parameters and the acentric factor as well as the derivative of EOS with respect to the acentric factor) are usually unknown. For this reason, below, we have developed a new strategy to obtain these unknown properties for minor isotopologues using available experimental data, which includes the isotopic fractionation factor, the molar volume isotope effect (MVIE), and the vapor pressure isotope effect. We tested our new method for ^{18}O-substituted water ($H_2^{18}O$).

4. Application of Corresponding-States Principle to $H_2^{18}O$

4.1. Available Data of Water Isotopologues. The most advanced EOS for normal water ($H_2^{16}O$) was developed by Wagner and Pruβ.[27] This equation refers to the fundamental EOS and is written in a dimensionless form (eq 22). The critical parameters of the $H_2^{16}O$ isotopologue are very well-known: $T_{cr} = 647.096 \pm 0.01$ K and $\rho_{cr} = 322 \pm 3$ kg/m^3. The ideal-gas function $\phi^0(\tau,\delta)$ is expressed by 8 fitted parameters, and the residual (nonideal-gas) function $\phi^r(\tau,\delta)$ contains 234 fitted parameters. The derivative of $\phi^r(\tau,\delta)$ with respect to τ and δ is also known. This equation is the official International Association for the Properties of Water and Steam formulation 1995 (IAPWS-95) for the thermodynamic properties of the $H_2^{16}O$ water isotopologue. The EOS is valid at temperatures from the melting temperature to 1273 K and at pressures up to 1000 MPa. The authors claim that it can be extrapolated to pressures up to 100 GPa and temperatures up to 5000 K in the stable fluid region.[27]

Kestin et al.[28] developed an EOS for heavy water (D_2O). This equation also presents the dimensionless fundamental EOS but in somewhat different form:

$$\bar{A}(1/\tau,\delta) = \bar{A}_0(1/\tau,\delta) + \bar{A}_1(1/\tau,\delta) \quad (28)$$

where $\bar{A}$, $\bar{A}_0$, and $\bar{A}_1$ are the complete, ideal-gas, and residual (nonideal-gas) dimensionless Helmholtz free energy functions, respectively. To convert the Helmholtz free energy to the dimensionless form, Kestin et al.[28] divided it by (P_{cr}/ρ_{cr}). $\bar{A}$ relates to (A/RT) as

$$\frac{A}{RT} = D\tau\bar{A} \quad (29)$$

where $D = P_{cr}/\rho_{cr}RT_{cr} \approx 0.226454$ is the critical compressibility factor for D_2O. (Here, we used the value of the critical parameters of D_2O from Kestin et al.[28]) The same relations hold for $\bar{A}_0$ and $\bar{A}_1$. The relation that is analogous to eq 23 is given as

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$$Z_D(1/\tau,\delta) = 1 + D\tau\delta\left(\frac{\partial \bar{A}_1(1/\tau,\delta)}{\partial \delta}\right) \quad (30)$$

where Z_D is the compressibility factor of D_2O. The EOS for D_2O is valid at temperatures from the melting point to 800 K and at pressures up to 100 MPa.[28]

The ideal-gas RIPFR for oxygen ($H_2^{18}O-H_2^{16}O$) was calculated by Bron et al.[29] and Richet et al.[30] The oxygen isotope fractionation factor between liquid water and water vapor is accurately determined along the entire liquid−vapor boundary.[31,32] Molar volume (density) isotope effects between $H_2^{16}O$ and ^{18}O-substitued liquid water are also known at 100 kPa (1 bar) and at 273−343 K.[33] These experimentally determined isotope effects can be used to construct an EOS of $H_2^{18}O$ based on the extended CSP, as demonstrated below.

4.2. Extended Three-Parameter Corresponding-States EOS. A liquid−vapor isotope fractionation factor can be expressed as differences in RIPFR's between the liquid water and saturated water vapor:

$$\ln \alpha_{L-V} = \ln \frac{s^*}{s} f(T,\rho_L) - \ln \frac{s^*}{s} f(T,\rho_V) \quad (31)$$

where α_{L-V} is the liquid−vapor fractionation factor and the subscripts L and V denote liquid and vapor phases, respectively.

Substituting eq 27 into 31, one obtains

$$\ln \alpha_{L-V} = \tau\left(\frac{\partial \phi^r(\tau,\delta_V,\omega)}{\partial \tau} - \frac{\partial \phi^r(\tau,\delta_L,\omega)}{\partial \tau}\right)\left(\frac{\Delta T_{cr}}{T_{cr}}\right) + \left(\delta_L\frac{\partial \phi^r(\tau,\delta_L,\omega)}{\partial \delta} - \delta_V\frac{\partial \phi^r(\tau,\delta_V,\omega)}{\partial \delta}\right)\left(\frac{\Delta \rho_{cr}}{\rho_{cr}}\right) + \omega\left(\frac{\partial \phi^r(\tau,\delta_V,\omega)}{\partial \omega} - \frac{\partial \phi^r(\tau,\delta_L,\omega)}{\partial \omega}\right)\left(\frac{\Delta \omega}{\omega}\right) \quad (32)$$

An appropriate expression for the MVIE (or more precisely the molar density isotope effect (MρIE)) can be derived from the EOS of eq 23 taking into account that the MρIE is defined at a given pressure and temperature. In this case, the change in δ under the isotope substitution results from both changes in density and the critical density:

$$\Delta\delta \equiv \delta^* - \delta = \delta\left(\frac{\Delta \rho}{\rho} - \frac{\Delta \rho_{cr}}{\rho_{cr}}\right) \quad (33)$$

It follows from eq 23 at a given pressure and temperature for both isotopologues:

$$\rho^* Z^* - \rho Z = 0 \quad (34)$$

Retaining first-order terms with respect to isotopic substitution, one can write

$$Z(\Delta\rho/\rho) + \Delta Z = 0 \quad (35a)$$

$$Z\frac{\Delta\rho}{\rho} + \frac{\partial Z}{\partial \tau}\Delta\tau + \frac{\partial Z}{\partial \delta}\Delta\delta + \frac{\partial Z}{\partial \omega}\Delta\omega = 0 \quad (35b)$$

Substituting eqs 33 and 19 for $\Delta\delta$ and $\Delta\tau$, respectively, into eq 35b, the following expression for the MρIE is obtained after some algebraic manipulation:

$$\frac{\Delta\rho}{\rho} = \frac{\delta\frac{\partial Z}{\partial \delta}}{Z + \delta\frac{\partial Z}{\partial \delta}}\left(\frac{\Delta\rho_{cr}}{\rho_{cr}}\right) - \frac{\tau\frac{\partial Z}{\partial \tau}}{Z + \delta\frac{\partial Z}{\partial \delta}}\left(\frac{\Delta T_{cr}}{T_{cr}}\right) - \frac{\omega\frac{\partial Z}{\partial \omega}}{Z + \delta\frac{\partial Z}{\partial \delta}}\left(\frac{\Delta\omega}{\omega}\right) \quad (36)$$

The two equations, 32 and 36, obtained within the framework of the extended three-parameter correspondence-states EOS, have three unknowns, the isotopic effects on the critical parameters (density and temperature) and the acentric factor, ($\Delta\rho_{cr}/\rho_{cr}$, $\Delta T_{cr}/T_{cr}$, and $\Delta\omega/\omega$). In addition to these three unknown values, the derivative terms with respect to the acentric factor ($\partial\phi^r/\partial\omega$ and $\partial Z/\partial\omega$) in eqs 32 and 36 are also unknown. However, the accurate EOS for other isotopologues of water (D_2O)[28] allows us to calculate these two derivative terms within the framework of the CSP for isotopologues. The acentric factor derivative of the compressibility factor can be derived from

$$\frac{\partial Z(\tau,\delta,\omega)}{\partial \omega} \approx \frac{Z_D(\tau,\delta) - Z(\tau,\delta)}{\omega_D - \omega} \quad (37)$$

where the subscript D denotes the compressibility factor and the acentric factor for D_2O, which can be calculated using the EOS for D_2O.[28] Then, the substitution of eqs 28−30 in eq 37 gives

$$\frac{\partial Z(\tau,\delta,\omega)}{\partial \omega} \approx \frac{D\tau\delta\left(\frac{\partial \bar{A}_1(1/\tau,\delta)}{\partial \delta}\right) - \delta\frac{\partial \phi^r(\tau,\delta)}{\partial \delta}}{\omega_D - \omega} \quad (38)$$

The acentric factors for normal and heavy water computed from the EOS for $H_2^{16}O$[27] and D_2O[28] are $\omega = 0.344\,290$ and $\omega_D = 0.364\,438$, respectively.

The equation for the acentric factor derivative of the residual part of the Helmholtz free energy ϕ^r can be written as

$$\frac{\partial \phi^r(\tau,\delta,\omega)}{\partial \omega} \approx \frac{D\tau\bar{A}_1(1/\tau,\delta) - \phi^r(\tau,\delta)}{\omega_D - \omega} \quad (39)$$

The substitution of eqs 38 and 39 into eqs 32 and 36 yields the two equations with the three unknowns ($\Delta T_{cr}/T_{cr}$, $\Delta\rho_{cr}/\rho_{cr}$, and $\Delta\omega/\omega$), expressing isotopic effects on the critical parameters and the acentric factor. The values of these three unknowns can be obtained by solving the two equations by means of a linear least-square fitting procedure, involving two sets of experimental data from the literature: α_{L-V}, the liquid−vapor isotope fractionation factor,[31,32] and the molar density isotope effect, MρIE:[33]

$$(\Delta T_{cr}/T_{cr}) = (0.3207 \pm 0.0041) \times 10^{-3}$$

$$(\Delta\rho_{cr}/\rho_{cr}) = (1.471 \pm 0.016) \times 10^{-3}$$

$$(\Delta\omega/\omega) = (1.363 \pm 0.015) \times 10^{-3} \quad (40)$$

Figure 1 shows that fitting results from the extended three-parameter approach agree very well with the experimental data on the fractionation factor and MρIE. Finally, the Helmholtz free energy of $H_2^{18}O$ can be calculated from eq 26 using the values of ($\Delta T_{cr}/T_{cr}$), ($\Delta\rho_{cr}/\rho_{cr}$), and ($\Delta\omega/\omega$) from eq 40 and the acentric factor derivative from eq 39. The ideal-gas RIPFR for
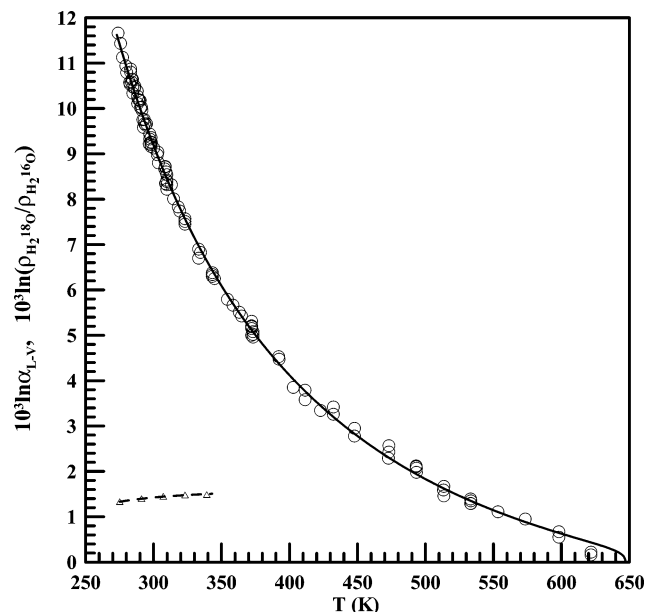
Figure 1. Fitting result of the experimental MρIE (open triangles) and the liquid−vapor isotope fractionation factor (open circle) by the three-parameter corresponding-states EOS. The extended three-parameter corresponding-states EOS can satisfactorily describe the temperature behavior of both the liquid−vapor fractionation factor and MρIE. Liquid−vapor isotope fractionation factors from Horita and Wesolowski[31] and Majoube[32] and MρIE values from the compilation of Kell.[33]

Figure 2. A comparison of $H_2^{16}O/H_2^{18}O$ VPIE data between experimental studies by Jakli and Staschewski[34] (open diamond) and Szapiro and Steckel[35] (open triangle) and our calculations based on the corresponding-states EOS (solid line), along with the liquid−vapor isotope fractionation factor (dashed line). According to the thermodynamic equation, eq 42, the value of the VPIE must be larger than the value of the liquid−vapor fractionation factor. The experimental VPIE data are inconsistent with this relationship. The difference between calculated VPIE (solid line) and the liquid−vapor fractionation curve (dashed line) increases with temperature. At the critical temperature of about 647.09 K, the difference exceeds 1‰, reflecting the difference in the critical pressure of the $H_2^{16}O$ and $H_2^{18}O$ isotopologues.

oxygen ($H_2^{18}O−H_2^{16}O$) can be taken from Bron et al.[29] or Richet et al.[30] The RIPRF of the "real-gas" water can also be calculated from eq 27. In the case of water isotopologues, in addition to the EOS of a major isotopologue (H_2O), another EOS for D_2O was available, which was used to calculate the derivatives with respect the acentric factor ($\partial\phi^r/\partial\omega$ and $\partial Z/\partial\omega$) as described above. In general, for applications of the extended three-parameter formalism of eqs 32 and 36 to isotopologues of other molecular fluids (e.g., CO_2, CH_4), the derivative terms can be derived from eqs 13 and 14, where only the compressibility factors of a main isotopologue are needed for the calculation.

It is interesting to compare isotopic effects on the critical parameters for $H_2^{18}O$ and D_2O: the values for the latter are experimentally well determined.[28] D_2O has a value of ($\Delta T_{cr}/T_{cr}$) $\approx$ −0.0050 ($\Delta T_{cr} \approx$ −3.2 K), which is not only more than 10 times larger than that for $H_2^{18}O$ ($\Delta T_{cr} \approx$ 0.2 K), but also opposite in sign. The isotopic effect on the critical density of D_2O is also much larger and opposite in sign compared to that of $H_2^{18}O$. The lower critical parameters (temperature and density) of D_2O relative to $H_2^{16}O$ are consistent with the fact that there is a crossover point at 221 °C, above which the vapor pressure isotope effect, $P(H_2O)/P(D_2O)$, is smaller than unity.[11,31] This crossover point is not observed for the liquid−vapor $H_2^{16}O−H_2^{18}O$ isotope fractionation curve (Figure 1). The calculated isotope effects on the critical parameters for $H_2^{18}O$ (ΔT_{cr} = 0.2 K and $\Delta\rho_{cr} \approx$ 0.45 kg/m³) are probably too small to be accurately measured by experiments. This is the case for the majority of isotopologues of other molecular fluids. For this reason, the novel CSP approach developed here would be the only method currently available for determining the isotope effects on the critical parameters.

4.3. Isotope Fractionation Factor and Vapor Pressure Isotope Effects. In our application of the extended, three-parameter CSP to the isotopologues of water, the experimental data of the liquid−vapor isotope fractionation factor (α_{L-V}) and molar density isotope effects ($\Delta\rho/\rho$) were used to obtain the isotope effects on the critical parameters and the acentric factor
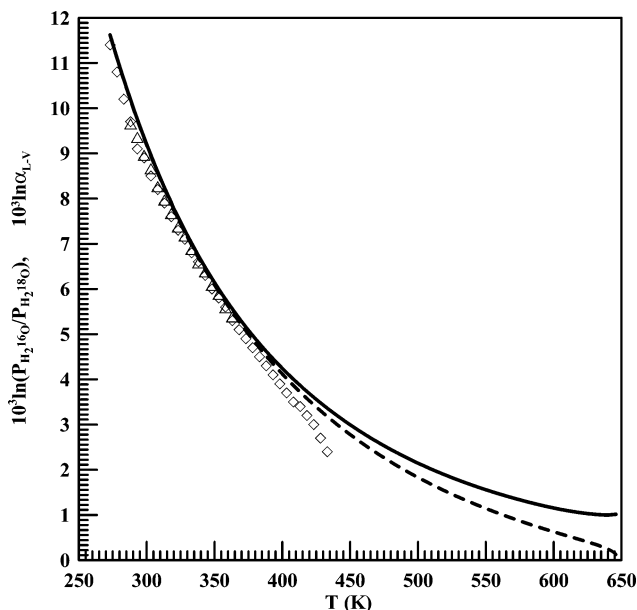
(eqs 32 and 36). A third experimental data set available for $H_2^{18}O$, which can also be used for the construction of the EOS, is the vapor pressure isotope effect, VPIE = $P(H_2^{16}O)/P(H_2^{18}O)$. However, the experimental data of VPIE for $H_2^{18}O$ are in apparent disagreement with those of the liquid−vapor isotope fractionation factor within the framework of thermodynamics as discussed below.

The saturation pressures for $H_2^{16}O$ and ^{18}O-substituted water can be calculated from the EOS (eq 23):

$$\frac{P_s}{RT} = \rho_V Z(\tau, \delta_V, \omega) \tag{41a}$$

$$\frac{P_s^*}{RT} = \rho_V^*\left[Z(\tau^*, \delta_V^*, \omega) + \omega\,\frac{\partial Z(\tau^*, \delta_V^*)}{\partial\omega}\left(\frac{\Delta\omega}{\omega}\right)\right] \tag{41b}$$

where P_s is the saturation pressure. In order to calculate the saturation pressures of isotopologues, the saturation vapor densities along the liquid−vapor boundary should be calculated from the fundamental EOS (eq 22) using the conditions of equal pressure and Gibbs free energy for the coexisting liquid and vapor phases. For H_2O, we reproduced the results of Wagner and Pruβ.[27] For ^{18}O-substituted water, the CSP-derived fundamental EOS (eq 26) was used for the calculations; mathematical details of these calculations are given in the Appendix I.

Results of the calculation are plotted in Figure 2 and compared with those from the most complete experimental VPIE data sets.[34,35] There is an obvious disagreement between the experimental data from the literature and our calculations for the VPIE. Our EOS-based calculations show that the VPIE is greater than the experimental liquid−vapor fractionation factor, but the experimental VPIE data by Jakli and Staschewski[34] and

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Szapiro and Steckel[35] are smaller than the fractionation factor. These experimental VPIE data are at odds with the thermodynamic relation between the VPIE and the liquid−vapor fractionation factor:

$$\ln \alpha_{L-V} = \left(\frac{PV_V}{RT} - \frac{PV_L}{RT}\right) \ln \frac{P}{P^*} \qquad (42)$$

The derivation of this simple, yet general equation is purely based on the thermodynamics, involving no assumptions (see Appendix II for the derivation). Similar equations were obtained by Bigeleisen[36] and by Japas et al.[37] The compressibility factor ($Z = PV/RT$) of real fluids is smaller than unity (unity for an ideal gas). The compressibility factor for liquid is smaller than that of the coexisting vapor. Therefore, the term in the parentheses in eq 42 is always smaller than unity, approaching zero at the critical point. This behavior indicates that the VPIE, i.e., $\ln(P/P^*)$, is always larger in magnitude than the liquid−vapor fractionation factor, $\ln \alpha_{L-V}$. Thus, the sets of experimental data for the liquid−vapor fractionation factor and the VPIE are inconsistent with each other. A critical evaluation of many sets of experimental data of $\ln \alpha_{L-V}$ by Horita and Wesolowski[31] strongly suggest that these data are of high quality. For this reason, we have chosen to use the fractionation factor, rather than the VPIE data, as input data to our corresponding-states principle approach as shown above. The quality of experimental data of VPIE is called into question, and further experimental studies are welcome to resolve this inconsistency.

The difference between the calculated VPIE from the EOS and the liquid−vapor fractionation factor increases with increasing temperature. This behavior seems to be reasonable, because the thermodynamic properties of saturated vapor deviate from those of an ideal-gas with increasing temperature and density. Our calculations of the VPIE near the critical temperature should be viewed with caution because the EOS for D_2O[28] is not valid in this region. The difference between the VPIE and the liquid−vapor isotope fractionation factor at room temperature does not exceed 0.03‰ according to eq 42. The previous estimate (0.5‰) by Jakli and Van Hook[38] seriously overestimated this difference because they did not take into account the contribution from the potential part of the free energy in their calculation for the term $\int_V^{V^*} P \, dV$ at room temperature.

5. Conclusion

We have developed a novel approach for calculating the EOS and the reduced partition function ratio of minor isotopologues of molecular fluids within the framework of the corresponding-states principle (CSP). The CSP approach would be particularly useful for representing the thermodynamic properties of isotopologues of a given molecule due to their very similar values. The relevant CSP mathematical formalism has been developed, and the main equations for the CSP application to isotopologues have been derived. The Xiang formulation for multi-parameter CSP[25] has been used to show that the extended three-parameter CSP is sufficient in principle for calculating the EOS of an isotopologue of a molecule, because of small differences in their thermodynamic properties. The equations obtained here open the possibility for calculating the EOS of minor isotopologues from a set of experimental data on the isotopic effects (e.g., liquid−vapor fractionation factor and molar volume isotope effects), if the correspondent-states EOS is known for a major isotopologue in the Xiang formulation.[25]

The CSP approach developed in this study was applied to an ^{18}O-substituted isotopologue ($H_2^{18}O$) of water. The extended three-parameter CSP, including the Pitzer acentric factor, provided satisfactory agreement with the experimental data. From the isotopic effects on the critical parameters and the Pitzer acentric factor obtained from the least-square fitting procedure, the fundamental EOS for oxygen substituted water ($H_2^{18}O$) has been described using the CSP. The EOS is valid in the range from the triple point to 800 K and pressures up to 100 MPa.

The VPIE on $^{16}O \rightarrow {}^{18}O$ substitution of water that was calculated from the newly developed $H_2^{18}O$ EOS disagrees with the experimental data from the literature. A simple, yet well-established thermodynamic relationship also revealed the inconsistency in experimental data between the VPIE and liquid−vapor fractionation factor. This contradiction appears to be due to problems associated with the experimental VPIE data. The difference between the VPIE and the liquid−vapor isotope fractionation factor is small at low temperature but increases with increasing temperature. The previous calculation overestimated this difference at room temperature.

Appendix

I. Calculations of the VPIE for $^{16}O \rightarrow {}^{18}O$ Substitution in Water. Equations 41a and b were used as the starting point for calculating VPIE:

$$\frac{P_s}{RT} = \rho_V Z(\tau, \delta_V, \omega) \qquad (41a)$$

$$\frac{P_s^*}{RT} = \rho_V^* \left[Z(\tau^*, \delta_V^*, \omega) + \omega \frac{\partial Z(\tau^*, \delta_V^*)}{\partial \omega} \left(\frac{\Delta\omega}{\omega}\right) \right] \qquad (41b)$$

Subtracting eq 41a from eq 41b, dividing the result by P_s, keeping terms, which are the first-order in isotope substitution, and remembering eq 23, one can get

$$\frac{P_s^*}{P_s} - 1 = \frac{\Delta\rho_V}{\rho_V} + \tau \frac{\partial Z(\tau, \delta_V, \omega)}{\partial \tau} \left(\frac{\Delta T_{cr}}{T_{cr}}\right) +$$
$$\delta_v \frac{\partial Z(\tau, \delta_V, \omega)}{\partial \delta} \left(\frac{\Delta\rho_V}{\rho_V} - \frac{\Delta\rho_{cr}}{\rho_{cr}}\right) + \omega \frac{\partial Z(\tau, \delta_V, \omega)}{\partial \omega} \left(\frac{\Delta\omega}{\omega}\right) \quad (AI.1)$$

All values needed for computing the VPIE in eq AI.1 are known, except for the $\Delta\rho_V/\rho_V$ that is the relative change in saturation density resulting from the isotope substitution of $^{16}O \rightarrow {}^{18}O$. $\Delta\rho_V/\rho_V$ can be found from the equilibrium conditions on the liquid−vapor boundary for both isotopologues. The first condition of equal pressures of the coexisting liquid and vapor phases results in

$$\rho_L Z_L = \rho_V Z_V \qquad (AI.2)$$

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$$\rho_L^* Z_L^* = \rho_V^* Z_V^* \qquad (AI.3)$$

Subtracting eq AI.2 from AI.3 and treating the obtained equation similar to the derivation of eq 36, one can obtain

$$\left[\delta_L Z_L + \delta_L^2 \frac{\partial Z_L}{\partial \delta_L}\right]\left(\frac{\Delta \rho_L}{\rho_L}\right) - \left[\delta_V Z_V + \delta_L^2 \frac{\partial Z_V}{\partial \delta_V}\right]\left(\frac{\Delta \rho_V}{\rho_V}\right) =$$
$$\tau\left(\delta_V \frac{\partial Z_V}{\partial \tau} - \delta_L \frac{\partial Z_L}{\partial \tau}\right)\left(\frac{\Delta T_{cr}}{T_{cr}}\right) - \left(\delta_V^2 \frac{\partial Z_V}{\partial \delta_V} - \delta_L^2 \frac{\partial Z_L}{\partial \delta_L}\right)\left(\frac{\Delta \rho_{cr}}{\rho_{cr}}\right) +$$
$$\omega\left(\delta_V \frac{\partial Z_V}{\partial \omega} - \delta_L \frac{\partial Z_L}{\partial \omega}\right)\left(\frac{\Delta \omega}{\omega}\right) \quad (AI.4)$$

The second condition, the equality of the Gibbs free energy between coexisting liquid and vapor phases (Maxwell criterion), can be written in a dimensionless form as

$$\frac{A_V}{RT} + Z_V = \frac{A_L}{RT} + Z_L \qquad (AI.5)$$

$$\frac{A_V^*}{RT} + Z_V^* = \frac{A_L^*}{RT} + Z_L^* \qquad (AI.6)$$

Subtracting eq AI.5 from AI.6 and keeping the first-order term in isotope substitution, one can get

$$\left(\delta_L \frac{\partial \phi_L^r}{\partial \delta_L} + \delta_L \frac{\partial Z_L}{\partial \delta_L} + 1\right)\left(\frac{\Delta \rho_L}{\rho_L}\right) -$$
$$\left(\delta_V \frac{\partial \phi_V^r}{\partial \delta_V} + \delta_V \frac{\partial Z_V}{\partial \delta_V} + 1\right)\left(\frac{\Delta \rho_V}{\rho_V}\right) =$$
$$\tau\left(\frac{\partial(\phi_V^r - \phi_L^r + Z_V - Z_L)}{\partial \tau}\right)\left(\frac{\Delta T_{cr}}{T_{cr}}\right) - \left(\delta_V \frac{\partial(\phi_V^r + Z_V)}{\partial \delta} -\right.$$
$$\left.\delta_L \frac{\partial(\phi_L^r + Z_L)}{\partial \delta}\right)\left(\frac{\Delta \rho_{cr}}{\rho_{cr}}\right) + \omega\left(\frac{\partial(\phi_V^r - \phi_V^r + Z_V - Z_L)}{\partial \omega}\right)\left(\frac{\Delta \omega}{\omega}\right)$$
$$(AI.7)$$

Equations AI.4 and AI.7 represent the system of the algebraic linear equations with respect to the unknowns $\Delta\rho_V/\rho_V$ and $\Delta\rho_L/\rho_L$.

The algorithm for the calculations at a given temperature consists of (i) calculating the densities of saturated vapor and liquid for $H_2^{16}O$ by the Wagner and Pruβ (2002) algorithm; (ii) calculating τ, δ_V, δ_L, and all terms, except for the unknowns in $\Delta\rho_V/\rho_V$ and $\Delta\rho_L/\rho_L$; (iii) solving the system of eqs AI.4 and AI.7; (iv) substituting $\Delta\rho_V/\rho_V$ into eq AI.4 and finally calculating the VPIE.

II. Relation between the VPIE and Liquid−Vapor Isotope Fractionation Factor. Because the relation (eq 42) between the VPIE and the liquid−vapor isotope fractionation factor is very important for our consideration, we present a simple, yet general derivation of this relation, allowing the reader to understand properly all assumptions under which the relation is valid.

For the liquid−vapor equilibrium of isotopologues at given temperature, one can write

$$G_V(T,P) = G_L(T,P)$$

$$G_V^*(T,P^*) = G_L^*(T,P^*) \qquad (AII.1)$$

where G is the Gibbs free energy.

Subtracting the second equation of eq AII.1 from the first one and dividing both parts of the obtained equation by RT, one gets

$$\frac{G_V(T,P) - G_V^*(T,P^*)}{RT} = \frac{G_V(T,P) - G_V^*(T,P^*)}{RT} \qquad (AII.2)$$

Extracting the RIPFR according to its definition $((s^*/s)f) \equiv (G(T,P) - G^*(T,P)/RT) - 1.5\ln(m/m^*)$ and taking into account the relationship $\Delta G = \int V\, dP$ in isothermal processes, one can obtain

$$\ln\left(\frac{s^*}{s}f\right)_V - \int_P^{P^*} \frac{V_V}{RT}\, dP = \ln\left(\frac{s^*}{s}f\right)_L - \int_P^{P^*} \frac{V_L}{RT}\, dP \qquad (AII.3)$$

The integrals in eq AII.3 can be evaluated by the following way using the Lagrange theorem

$$\int_P^{P^*} \frac{V^*}{RT}\, dP = \frac{V^* + \epsilon \Delta V^*}{RT}\Delta P \approx \frac{V^*}{RT}\Delta P = \frac{P^* V^*}{RT}\left(\frac{P^* - P}{P^*}\right) =$$
$$Z^*\left(1 - \frac{P}{P^*}\right) \approx -Z^* \ln\frac{P}{P^*} \quad (AII.4)$$

where ϵ is a factor of < 1, ΔV^* is the change in the volume of the isotopologue caused by pressure change from P to P^*, and $Z = (PV/RT)$ is the compressibility factor. The first equation in AII.4 is the subject of the Lagrange theorem. We have also neglected the term proportional to $\Delta V^* \Delta P$ because it is quadratic with respect to isotope substitution.

The application of eq AII.4 to AII.3 yields

$$\ln\left(\frac{P}{P^*}\right)(Z_V^* - Z_L^*) = \ln \alpha_{L-V} \qquad (AII.5)$$

where we used eq 31 for α_{L-V}. Note that $Z^* \cong Z$ because of the second power with respect to isotope substitution gives

$$\ln\left(\frac{P}{P^*}\right)(Z_V - Z_L) = \ln \alpha_{L-V} \qquad (42)$$

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(26) The isotope composition of substance A (R_A) is expressed as a ratio of concentrations of isotopes of interest. For example, $R_A = [^{18}O]/[^{16}O]$ for oxygen isotopes. The stable isotope fractionation factor (α_{A-B}) between two substances A and B is defined as the ratio $\alpha_{A-B} = R_A/R_B$. The equilibrium isotope fractionation factor (α_{A-B}^e) can be expressed in terms of the RIPFR as shown in eq 16 (see refs 1 and 2).

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