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Calculation of individual isotope equilibrium constants for geochemical reactions

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Abstract—Theory is derived from the work of Urey (Urey H. C. [1947] The thermodynamic properties of isotopic substances. *J. Chem. Soc.* 562–581) to calculate equilibrium constants commonly used in geochemical equilibrium and reaction-transport models for reactions of individual isotopic species. Urey showed that equilibrium constants of isotope exchange reactions for molecules that contain two or more atoms of the same element in equivalent positions are related to isotope fractionation factors by $\alpha = (K^{\text{ex}})^{1/n}$, where n is the number of atoms exchanged. This relation is extended to include species containing multiple isotopes, for example $^{13}\text{C}^{16}\text{O}^{18}\text{O}$ and $^1\text{H}^2\text{H}^{18}\text{O}$. The equilibrium constants of the isotope exchange reactions can be expressed as ratios of individual isotope equilibrium constants for geochemical reactions. Knowledge of the equilibrium constant for the dominant isotopic species can then be used to calculate the individual isotope equilibrium constants.

Individual isotope equilibrium constants are calculated for the reaction $\text{CO}_{2\text{g}} = \text{CO}_{2\text{aq}}$ for all species that can be formed from ^{12}C , ^{13}C , ^{16}O , and ^{18}O ; for the reaction between $^{12}\text{C}^{18}\text{O}_{2\text{aq}}$ and $^1\text{H}_2^{18}\text{O}_1$; and among the various ^1H , ^2H , ^{16}O , and ^{18}O species of H_2O . This is a subset of a larger number of equilibrium constants calculated elsewhere (Thorstenson D. C. and Parkhurst D. L. [2002] Calculation of individual isotope equilibrium constants for implementation in geochemical models. Water-Resources Investigation Report 02-4172. U.S. Geological Survey). Activity coefficients, activity-concentration conventions for the isotopic variants of H_2O in the solvent $^1\text{H}_2^{16}\text{O}$, and salt effects on isotope fractionation have been included in the derivations. The effects of nonideality are small because of the chemical similarity of different isotopic species of the same molecule or ion. The temperature dependence of the individual isotope equilibrium constants can be calculated from the temperature dependence of the fractionation factors.

The derivations can be extended to calculation of individual isotope equilibrium constants for ion pairs and equilibrium constants for isotopic species of other chemical elements. The individual isotope approach calculates the same phase isotopic compositions as existing methods, but also provides concentrations of individual species, which are needed in calculations of mass-dependent effects in transport processes. The equilibrium constants derived in this paper are used to calculate the example of gas-water equilibrium for CO_2 in an acidic aqueous solution. Copyright © 2004 Elsevier Ltd

1. INTRODUCTION

The theory relating isotope fractionation factors to the equilibrium constants of isotope exchange reactions was discussed by Harold C. Urey in his classic paper “The Thermodynamic Properties of Isotopic Substances” (Urey, 1947), referred to as “Urey” henceforth. Urey employed statistical mechanics and spectroscopic data to calculate the equilibrium constants for many isotope exchange reactions. Comparison of the calculated equilibrium constants with measured fractionation factors required derivation of the algebraic relation between the constants and fractionation factors. The result is Eqn. 1, which holds for most isotope exchange reactions under conditions that are closely approximated by many geochemical systems:

$$\alpha = (K^{\text{ex}})^{1/n}, \quad (1)$$

where α is the equilibrium isotope fractionation factor between reactant and product molecules, K^{ex} is the equilibrium constant for the isotope exchange reaction, and n is the number of atoms exchanged in the reaction. The derivation of Eqn. 1 assumes ideal gas behavior, although Urey applied similar calculations to liquids and solids. Urey discussed problems associated with

the application to condensed phases, but derived no formal activity-concentration relations.

This paper extends the algebraic derivation of Eqn. 1 to include mixed isotopic species such as $^{13}\text{C}^{16}\text{O}^{18}\text{O}_\text{g}$ and $^1\text{H}^2\text{H}^{18}\text{O}_\text{g}$, and also extends Urey’s work by showing that the equilibrium constants of isotope exchange reactions can be expressed as ratios of equilibrium constants for individual isotope reactions of types that are commonly used in geochemical equilibrium and reaction-transport models (dissociation, association, dissolution, precipitation, redox, etc.), thus allowing calculation of these equilibrium constants from fractionation factors. The individual isotope equilibrium constants can be calculated for all mixed isotopic species for which elemental fractionation data and equilibrium constants for intraspecies reactions (discussed below) are known or can be assumed. The temperature dependence of the equilibrium constants can be calculated from that of the fractionation factors. Rigorous activity-concentration relations are maintained throughout these calculations. The algebra is presented in considerable detail in the hope that others will be able to use this paper as a template for extension to other isotopes.

The values of the individual isotope equilibrium constants and their associated reactions can be used as input data in any geochemical model that treats the gas and solid phases as multicomponent solutions. This approach provides a method of geochemical modeling in which isotopic fractionation and chemical speciation are fully integrated, in contrast to the commonly used

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modeling approaches that perform chemical and isotopic calculations separately. The existing modeling approaches use fractionation factors explicitly in their calculations (see section 6, Comparison of Methods), and are thus implicitly based, via Eqn. 1, on equilibrium constants for isotope exchange reactions, generally between phases. Modeling based on the individual isotope equilibrium constants treats a given molecular isotopic species simply as another constituent in a conventional chemical speciation model, and is based on reactions between the given species and others in the same or different phases.

Existing methods are aimed primarily at calculating the isotopic content of gas, liquid, and mineral phases by using results of prior nonisotopic chemical speciation calculations. The individual isotope method provides as primary output the complete distribution of all molecular isotopic species for which equilibrium constants have been included in the model, from which the isotopic content of phases may be calculated as desired. If appropriate speciation equations were added to the existing methods, the two approaches must, if carried out with sufficient numerical precision, approach the same equilibrium distribution of species and phase isotopic characteristics.

In addition to providing an alternative modeling approach for calculation of isotope effects in reaction-transport modeling, the distribution of species provided by the individual isotope approach should prove useful in kinetic and mechanistic studies. Any calculation that depends on relative free energies of isotopic molecular species, or any calculation that deals with fractionation due to isotope mass effects in transport processes, requires the individual isotope approach. An example of the former, involving a thought experiment on carbonate precipitation kinetics, is discussed in section 6; an example of calculated mass effects in diffusive gas transport of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ is presented in Parkhurst et al. (2000). Finally, the information provided by isotopic speciation may prove useful in ways yet to be recognized.

These concepts are illustrated by calculation of the individual isotope equilibrium constants for reactions among $\text{CO}_{2\text{g}}$ and $\text{CO}_{2\text{aq}}$ species (including the isotopes ^{12}C , ^{13}C , ^{16}O , and ^{18}O), their temperature dependence, and the effects of nonideality. Reactions between $\text{CO}_{2\text{g}}$ and $\text{CO}_{2\text{aq}}$ are chosen for presentation here because the algebra required is straightforward and relatively concise; this is not the case for more complex molecular and ionic species. The text also discusses equilibrium constants for ion pairs, equilibrium constants for the dominant isotopic species, the asymmetric bicarbonate ion, application to other isotopes, and a comparison of this and other methods.

Thorstenson and Parkhurst (2002), referred to as T&P henceforth, use these concepts to construct a model in the reaction-transport code PHREEQC (Parkhurst and Appelo, 1999) that contains all isotopic species that can be formed from ^1H , ^2H , ^{12}C , ^{13}C , ^{16}O , and ^{18}O in the molecules/phases $\text{CO}_{2\text{g}}$, $\text{CO}_{2\text{aq}}$ (representing $\text{CO}_{2\text{aq}} + \text{H}_2\text{CO}_{3\text{aq}}$; see Garrels and Christ, 1965, p. 76), $\text{HCO}_{3\text{aq}}^-$, $\text{CO}_{3\text{aq}}^{2-}$, $\text{CaCO}_{3\text{s}}$, $\text{H}_2\text{O}_{\text{g}}$, $\text{H}_2\text{O}_{\text{l}}$, $\text{H}_3\text{O}_{\text{aq}}^+$, OH_{aq}^- , and the OH_{aq}^- , $\text{HCO}_{3\text{aq}}^-$, and $\text{CO}_{3\text{aq}}^{2-}$ ion pairs with the cations Na_{aq}^+ , K_{aq}^+ , $\text{Ca}_{\text{aq}}^{+2}$, and $\text{Mg}_{\text{aq}}^{+2}$. Equilibrium constants for selected species containing ^3H and ^{14}C are also calculated by T&P. Note that a complete treatment or model of the above elements would require inclusion of the various isotopes of Na_{aq}^+ , K_{aq}^+ , $\text{Ca}_{\text{aq}}^{+2}$, and $\text{Mg}_{\text{aq}}^{+2}$, as well as those discussed above. The methods outlined in this paper provide a template for doing this.

2. ISOTOPE RATIOS IN GASEOUS AND AQUEOUS CO_2

The Henry's Law equilibrium constants for the various isotopic species of CO_2 are used to illustrate the derivation of the intraspecies equilibrium constants, and the derivation of expressions for isotope ratios using the intraspecies constants. The subscript j denotes either gas or aqueous species.

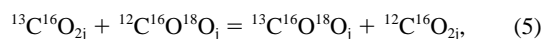
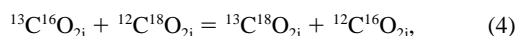
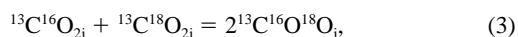
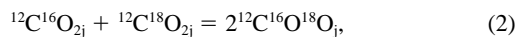
2.1. Species and Symmetry Numbers

Urey calculated equilibrium constants for isotope exchange reactions from ratios of partition functions of the molecular species in the reactions by assuming that temperature was sufficiently high that the ratios of partition functions—and thus equilibrium constants—could be calculated solely from spectroscopic data for the vibrational frequencies. A consequence of this assumption is that for reactions among different isotopic variants of a given chemical species, for example formation of $^{12}\text{C}^{16}\text{O}^{18}\text{O}_j$ from $^{12}\text{C}^{16}\text{O}_{2j}$ and $^{12}\text{C}^{18}\text{O}_{2j}$, the equilibrium constants can be calculated solely from the symmetry numbers of the molecular species (Urey, 1947; Bigeleisen, 1955). These reactions are referred to as intraspecies reactions.

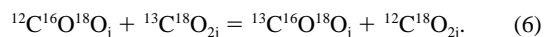
The symmetry number, σ , can be determined by counting the number of indistinguishable orientations of a molecule that can be reached by rotational symmetry operations; for example, $\sigma_{\text{O}_2} = 2$, $\sigma_{\text{CO}} = 1$, and $\sigma_{\text{CH}_4} = 12$ (Atkins, 1982, p. 721). For the isotopes ^{12}C , ^{13}C , ^{16}O , and ^{18}O , six CO_2 species exist in the gas and aqueous phases. They are $^{12}\text{C}^{16}\text{O}_{2j}$, $^{12}\text{C}^{16}\text{O}^{18}\text{O}_j$, $^{12}\text{C}^{18}\text{O}_{2j}$, $^{13}\text{C}^{16}\text{O}_{2j}$, $^{13}\text{C}^{16}\text{O}^{18}\text{O}_j$, and $^{13}\text{C}^{18}\text{O}_{2j}$. The CO_2 molecule is linear, and thus the symmetry numbers of the isotopic species are $\sigma = 2$, $\sigma = 1$, $\sigma = 2$, $\sigma = 2$, $\sigma = 1$, and $\sigma = 2$.

2.2. Equilibrium Constants for Intraspecies Reactions among the CO_2 Species

The equilibrium constants for intraspecies isotopic reactions among the CO_2 species (gaseous or aqueous) are assumed to be determined by their symmetry numbers alone. Reactions are presented for ^{12}C and ^{13}C . The possible reactions are



and



The equilibrium constants for reactions 2–6, calculated from symmetry numbers, are (Urey, 1947, pp. 563–565)

$$K_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_j} = \frac{n_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_j}^2}{n_{^{12}\text{C}^{16}\text{O}_{2j}} n_{^{12}\text{C}^{18}\text{O}_{2j}}} = \frac{Q_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_j}^2}{Q_{^{12}\text{C}^{16}\text{O}_{2j}} Q_{^{12}\text{C}^{18}\text{O}_{2j}}} = 4, \quad (7)$$

$$K_{^{13}\text{C}^{16}\text{O}^{18}\text{O}_j} = \frac{n_{^{13}\text{C}^{16}\text{O}^{18}\text{O}_j}^2}{n_{^{13}\text{C}^{16}\text{O}_{2j}} n_{^{13}\text{C}^{18}\text{O}_{2j}}} = \frac{Q_{^{13}\text{C}^{16}\text{O}^{18}\text{O}_j}^2}{Q_{^{13}\text{C}^{16}\text{O}_{2j}} Q_{^{13}\text{C}^{18}\text{O}_{2j}}} = 4, \quad (8)$$

$$K_{^{13}\text{C}^{18}\text{O}_{2j}} = \frac{n_{^{13}\text{C}^{18}\text{O}_{2j}} n_{^{12}\text{C}^{16}\text{O}_{2j}}}{n_{^{13}\text{C}^{16}\text{O}_{2j}} n_{^{12}\text{C}^{18}\text{O}_{2j}}} = \frac{Q_{^{13}\text{C}^{18}\text{O}_{2j}} Q_{^{12}\text{C}^{16}\text{O}_{2j}}}{Q_{^{13}\text{C}^{16}\text{O}_{2j}} Q_{^{12}\text{C}^{18}\text{O}_{2j}}} = 1, \quad (9)$$

$$K_{^{13}\text{C}^{16}\text{O}^{18}\text{O}_j} = \frac{n_{^{13}\text{C}^{16}\text{O}^{18}\text{O}_j} n_{^{12}\text{C}^{16}\text{O}_j}}{n_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_j} n_{^{13}\text{C}^{16}\text{O}_j}} = \frac{Q_{^{13}\text{C}^{16}\text{O}^{18}\text{O}_j} Q_{^{12}\text{C}^{16}\text{O}_j}}{Q_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_j} Q_{^{13}\text{C}^{16}\text{O}_j}} = 1, \quad (10)$$

and

$$K_{^{13}\text{C}^{16}\text{O}^{18}\text{O}_j} = \frac{n_{^{13}\text{C}^{16}\text{O}^{18}\text{O}_j} n_{^{12}\text{C}^{18}\text{O}_j}}{n_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_j} n_{^{13}\text{C}^{18}\text{O}_j}} = \frac{Q_{^{13}\text{C}^{16}\text{O}^{18}\text{O}_j} Q_{^{12}\text{C}^{18}\text{O}_j}}{Q_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_j} Q_{^{13}\text{C}^{18}\text{O}_j}} = 1, \quad (11)$$

where n_j = number of molecules and Q_j is the partition function. In Eqns. 7–11, $Q_j = 1/\sigma_j$ where σ_j is the symmetry number for species j .

Equations 7–11 provide the following relations:

$$\frac{n_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_j}^2}{n_{^{12}\text{C}^{16}\text{O}_j} n_{^{12}\text{C}^{18}\text{O}_j}} = 4, \quad (12)$$

$$\frac{n_{^{13}\text{C}^{16}\text{O}^{18}\text{O}_j}^2}{n_{^{13}\text{C}^{16}\text{O}_j} n_{^{13}\text{C}^{18}\text{O}_j}} = 4, \quad (13)$$

$$\frac{n_{^{13}\text{C}^{18}\text{O}_j}}{n_{^{13}\text{C}^{16}\text{O}_j}} = \frac{n_{^{12}\text{C}^{18}\text{O}_j}}{n_{^{12}\text{C}^{16}\text{O}_j}}, \quad (14)$$

$$\frac{n_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_j}}{n_{^{13}\text{C}^{16}\text{O}_j}} = \frac{n_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_j}}{n_{^{12}\text{C}^{16}\text{O}_j}}, \quad (15)$$

and

$$\frac{n_{^{13}\text{C}^{16}\text{O}^{18}\text{O}_j}}{n_{^{13}\text{C}^{18}\text{O}_j}} = \frac{n_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_j}}{n_{^{12}\text{C}^{18}\text{O}_j}}. \quad (16)$$

Equations 12–16 allow calculation of isotope ratios for the CO_2 species.

2.3. Isotope Ratios

Isotope ratios, R , are based on the total number of molecules of each isotope. The $^{13}\text{C}/^{12}\text{C}$ ratio in CO_2 is given by

$$R_{\text{CO}_2}^{^{13}\text{C}} = \frac{n_{^{13}\text{C}^{16}\text{O}_j} + n_{^{13}\text{C}^{16}\text{O}^{18}\text{O}_j} + n_{^{13}\text{C}^{18}\text{O}_j}}{n_{^{12}\text{C}^{16}\text{O}_j} + n_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_j} + n_{^{12}\text{C}^{18}\text{O}_j}}, \quad (17)$$

or

$$R_{\text{CO}_2}^{^{13}\text{C}} = \frac{n_{^{13}\text{C}^{16}\text{O}_j} \left(1 + \frac{n_{^{13}\text{C}^{16}\text{O}^{18}\text{O}_j}}{n_{^{13}\text{C}^{16}\text{O}_j}} + \frac{n_{^{13}\text{C}^{18}\text{O}_j}}{n_{^{13}\text{C}^{16}\text{O}_j}} \right)}{n_{^{12}\text{C}^{16}\text{O}_j} \left(1 + \frac{n_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_j}}{n_{^{12}\text{C}^{16}\text{O}_j}} + \frac{n_{^{12}\text{C}^{18}\text{O}_j}}{n_{^{12}\text{C}^{16}\text{O}_j}} \right)} = \frac{n_{^{13}\text{C}^{16}\text{O}_j}}{n_{^{12}\text{C}^{16}\text{O}_j}}. \quad (18)$$

The terms in parentheses are equal because of Eqns. 14–16, which also allow equation 18 to be written as

$$R_{\text{CO}_2}^{^{13}\text{C}} = \frac{n_{^{13}\text{C}^{16}\text{O}_j}}{n_{^{12}\text{C}^{16}\text{O}_j}} = \frac{n_{^{13}\text{C}^{16}\text{O}^{18}\text{O}_j}}{n_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_j}} = \frac{n_{^{13}\text{C}^{18}\text{O}_j}}{n_{^{12}\text{C}^{18}\text{O}_j}}. \quad (19)$$

The $^{18}\text{O}/^{16}\text{O}$ ratio in CO_2 is

$$R_{\text{CO}_2}^{^{18}\text{O}} = \frac{2n_{^{12}\text{C}^{18}\text{O}_j} + n_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_j} + 2n_{^{13}\text{C}^{18}\text{O}_j} + n_{^{13}\text{C}^{16}\text{O}^{18}\text{O}_j}}{2n_{^{12}\text{C}^{16}\text{O}_j} + n_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_j} + 2n_{^{13}\text{C}^{16}\text{O}_j} + n_{^{13}\text{C}^{16}\text{O}^{18}\text{O}_j}}. \quad (20)$$

An expression for $R_{\text{CO}_2}^{^{18}\text{O}}$ can be derived in terms of $^{12}\text{C}^{18}\text{O}_j$ and $^{12}\text{C}^{16}\text{O}_j$, as shown by Urey. Using equations 12 and

13 to substitute for $n_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_j}$ and $n_{^{13}\text{C}^{16}\text{O}^{18}\text{O}_j}$ in Eqn. 20 yields

$$R_{\text{CO}_2}^{^{18}\text{O}} = \frac{2n_{^{12}\text{C}^{18}\text{O}_j} + 2n_{^{12}\text{C}^{16}\text{O}_j}^{1/2} n_{^{12}\text{C}^{18}\text{O}_j}^{1/2} + 2n_{^{13}\text{C}^{18}\text{O}_j} + 2n_{^{13}\text{C}^{16}\text{O}_j}^{1/2} n_{^{13}\text{C}^{18}\text{O}_j}^{1/2}}{2n_{^{12}\text{C}^{16}\text{O}_j} + 2n_{^{12}\text{C}^{16}\text{O}_j}^{1/2} n_{^{12}\text{C}^{18}\text{O}_j}^{1/2} + 2n_{^{13}\text{C}^{16}\text{O}_j} + 2n_{^{13}\text{C}^{16}\text{O}_j}^{1/2} n_{^{13}\text{C}^{18}\text{O}_j}^{1/2}}. \quad (21)$$

Equations 14–16 are used as needed in the following equations.

From Eqn. 21

$$\begin{aligned} R_{\text{CO}_2}^{^{18}\text{O}} &= \frac{2n_{^{12}\text{C}^{18}\text{O}_j} \left(1 + \frac{n_{^{12}\text{C}^{16}\text{O}_j}^{1/2}}{n_{^{12}\text{C}^{18}\text{O}_j}^{1/2}} \right) + 2n_{^{13}\text{C}^{18}\text{O}_j} \left(1 + \frac{n_{^{13}\text{C}^{16}\text{O}_j}^{1/2}}{n_{^{13}\text{C}^{18}\text{O}_j}^{1/2}} \right)}{2n_{^{12}\text{C}^{16}\text{O}_j} \left(1 + \frac{n_{^{12}\text{C}^{18}\text{O}_j}^{1/2}}{n_{^{12}\text{C}^{16}\text{O}_j}^{1/2}} \right) + 2n_{^{13}\text{C}^{16}\text{O}_j} \left(1 + \frac{n_{^{13}\text{C}^{18}\text{O}_j}^{1/2}}{n_{^{13}\text{C}^{16}\text{O}_j}^{1/2}} \right)} \\ &= \frac{(n_{^{12}\text{C}^{18}\text{O}_j} + n_{^{13}\text{C}^{18}\text{O}_j}) \left(1 + \frac{n_{^{12}\text{C}^{16}\text{O}_j}^{1/2}}{n_{^{12}\text{C}^{18}\text{O}_j}^{1/2}} \right)}{(n_{^{12}\text{C}^{16}\text{O}_j} + n_{^{13}\text{C}^{16}\text{O}_j}) \left(1 + \frac{n_{^{13}\text{C}^{18}\text{O}_j}^{1/2}}{n_{^{12}\text{C}^{16}\text{O}_j}^{1/2}} \right)} \\ &= \frac{n_{^{12}\text{C}^{18}\text{O}_j} \left(1 + \frac{n_{^{13}\text{C}^{18}\text{O}_j}}{n_{^{12}\text{C}^{18}\text{O}_j}} \right) \left(\frac{n_{^{12}\text{C}^{18}\text{O}_j}^{1/2} + n_{^{12}\text{C}^{16}\text{O}_j}^{1/2}}{n_{^{12}\text{C}^{18}\text{O}_j}^{1/2}} \right)}{n_{^{12}\text{C}^{16}\text{O}_j} \left(1 + \frac{n_{^{13}\text{C}^{16}\text{O}_j}}{n_{^{12}\text{C}^{16}\text{O}_j}} \right) \left(\frac{n_{^{12}\text{C}^{16}\text{O}_j}^{1/2} + n_{^{12}\text{C}^{18}\text{O}_j}^{1/2}}{n_{^{12}\text{C}^{16}\text{O}_j}^{1/2}} \right)} \\ &= \frac{n_{^{12}\text{C}^{18}\text{O}_j}}{n_{^{12}\text{C}^{16}\text{O}_j}} \left(\frac{n_{^{12}\text{C}^{16}\text{O}_j}^{1/2}}{n_{^{12}\text{C}^{18}\text{O}_j}^{1/2}} \right) = \frac{n_{^{12}\text{C}^{18}\text{O}_j}}{n_{^{12}\text{C}^{16}\text{O}_j}}. \quad (22) \end{aligned}$$

In addition to Urey's derivation of Eqn. 22, $R_{\text{CO}_2}^{^{18}\text{O}}$ can be expressed in terms of $^{12}\text{C}^{16}\text{O}^{18}\text{O}_j$ by using Eqns. 12 and 13 in the numerator of Eqn. 20 to give

$$\begin{aligned} R_{\text{CO}_2}^{^{18}\text{O}} &= \frac{n_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_j} + 2 \left(\frac{n_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_j}^2}{4n_{^{12}\text{C}^{16}\text{O}_j}} \right) + n_{^{13}\text{C}^{16}\text{O}^{18}\text{O}_j} + 2 \left(\frac{n_{^{13}\text{C}^{16}\text{O}^{18}\text{O}_j}^2}{4n_{^{13}\text{C}^{16}\text{O}_j}} \right)}{2n_{^{12}\text{C}^{16}\text{O}_j} \left(1 + \frac{n_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_j}}{2n_{^{12}\text{C}^{16}\text{O}_j}} \right) + 2n_{^{13}\text{C}^{16}\text{O}_j} \left(1 + \frac{n_{^{13}\text{C}^{16}\text{O}^{18}\text{O}_j}}{2n_{^{13}\text{C}^{16}\text{O}_j}} \right)} \\ &= \frac{(n_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_j} + n_{^{13}\text{C}^{16}\text{O}^{18}\text{O}_j}) \left\{ 1 + \frac{n_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_j}}{2n_{^{12}\text{C}^{16}\text{O}_j}} \right\}}{2(n_{^{12}\text{C}^{16}\text{O}_j} + n_{^{13}\text{C}^{16}\text{O}_j}) \left\{ 1 + \frac{n_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_j}}{2n_{^{12}\text{C}^{16}\text{O}_j}} \right\}} \\ &= \frac{n_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_j} \left(1 + \frac{n_{^{13}\text{C}^{16}\text{O}^{18}\text{O}_j}}{n_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_j}} \right) \left\{ 1 + \frac{n_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_j}}{2n_{^{12}\text{C}^{16}\text{O}_j}} \right\}}{2n_{^{12}\text{C}^{16}\text{O}_j} \left(1 + \frac{n_{^{13}\text{C}^{16}\text{O}_j}}{n_{^{12}\text{C}^{16}\text{O}_j}} \right) \left\{ 1 + \frac{n_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_j}}{2n_{^{12}\text{C}^{16}\text{O}_j}} \right\}} \\ &= \frac{n_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_j}}{2n_{^{12}\text{C}^{16}\text{O}_j}}, \quad (23) \end{aligned}$$

where the equality of the bracketed terms in the numerator and denominator of Eqn. 23 is defined by equations 14–16. Using Eqns. 14–16 in Eqns. 22 and 23 gives

$$R_{\text{CO}_2}^{^{18}\text{O}} = \frac{n_{^{12}\text{C}^{18}\text{O}_j}^{1/2}}{n_{^{12}\text{C}^{16}\text{O}_j}^{1/2}} = \frac{n_{^{13}\text{C}^{18}\text{O}_j}^{1/2}}{n_{^{13}\text{C}^{16}\text{O}_j}^{1/2}} = \frac{n_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_j}}{2n_{^{12}\text{C}^{16}\text{O}_j}} = \frac{n_{^{13}\text{C}^{16}\text{O}^{18}\text{O}_j}}{2n_{^{13}\text{C}^{16}\text{O}_j}}. \quad (24)$$

Equations 19 and 24 define the $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ ratios, respectively, for CO_2 . The isotope ^{17}O has not been included

here because of time and space considerations, and because of redundancy with ^{18}O for mass dependent fractionation processes.

The algebraic simplification of the isotope ratios that leads to Eqns. 19 and 24 occurs if two or more atoms of the same element occupy equivalent positions in the molecule, and the equilibrium constants for the intraspecies reactions (Eqns. 2 and 3) are determined solely by symmetry numbers (Urey, 1947). When these two conditions hold, the symmetry number of the molecule is an integer multiple of the number of atoms in the molecule, n ; that is, $\sigma_{\text{CO}_2} = 2$, $\sigma_{\text{CO}_3^{2-}} = 6$, and so on. The intraspecies equilibrium constants are then equal to n^n . Urey points out that these two conditions do not hold for the hydrogen isotopes because of the large isotope effect on vibration frequencies, and do not hold for asymmetrical molecules such as NNO. The bicarbonate ion is also asymmetric and requires a different algebraic treatment than the CO_2 species, which is discussed later.

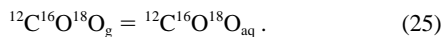
3. CALCULATION OF INDIVIDUAL ISOTOPE EQUILIBRIUM CONSTANTS

3.1. Equilibrium Constants for the Reaction $\text{CO}_{2\text{gas}}\text{-CO}_{2\text{aqueous}}$

The isotope ratios given in Eqns. 19 and 24 from the basis for the algebraic expression of the fractionation factors for $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ between $\text{CO}_{2\text{g}}$ and $\text{CO}_{2\text{aq}}$, thus permitting calculation of the individual isotope Henry's Law constants for the six isotopic species of CO_2 .

3.1.1. $^{12}\text{C}^{16}\text{O}^{18}\text{O}$

For $^{12}\text{C}^{16}\text{O}^{18}\text{O}$, the reaction used in PHREEQC is



The first step is to express the fractionation factor in terms of the reactant and product species, choosing the appropriate ratios from Eqn. 24. For Eqn. 25, the appropriate expression of the fractionation factor is

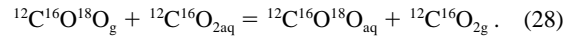
$$\alpha_{\text{CO}_{2\text{aq}}\text{-CO}_{2\text{g}}}^{18\text{O}} = \frac{R_{\text{CO}_{2\text{aq}}}^{18\text{O}}}{R_{\text{CO}_{2\text{g}}}^{18\text{O}}} = \frac{\left(\frac{n_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_{\text{aq}}}}{2n_{^{12}\text{C}^{16}\text{O}_{2\text{aq}}}}\right)}{\left(\frac{n_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_{\text{g}}}}{2n_{^{12}\text{C}^{16}\text{O}_{2\text{g}}}}\right)}. \quad (26)$$

The next step is to convert the fractionation factor to common concentration units. In this case, dividing numerator and denominator of Eqn. 26 by 1 kg water and by total moles of gas gives

$$\alpha_{\text{CO}_{2\text{aq}}\text{-CO}_{2\text{g}}}^{18\text{O}} = \frac{n_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_{\text{aq}}} n_{^{12}\text{C}^{16}\text{O}_{2\text{g}}}}{n_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_{\text{g}}} n_{^{12}\text{C}^{16}\text{O}_{2\text{aq}}}} = \frac{m_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_{\text{aq}}} X_{^{12}\text{C}^{16}\text{O}_{2\text{g}}}}{X_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_{\text{g}}} m_{^{12}\text{C}^{16}\text{O}_{2\text{aq}}}}, \quad (27)$$

where m_i is molality and X_i is mole fraction, respectively, of species i .

The terms in Eqn. 27 have the form of a concentration-based equilibrium constant for an isotope exchange reaction. The exchange reaction for Eqn. 27 is



The next step is to write the equilibrium constant, $K_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_{\text{aq}}}^{\text{ex}}$, for this reaction in terms of activities, then activity coefficients and concentrations (activity-concentration relations used here are from Garrels and Christ, 1965, pp. 20–73; conventions for gases are found on pp. 21–33). Garrels and Christ (1965) point out that mixtures of real gases are generally treated as ideal solutions of real gases, for which

$$a_j = \chi_j P_{\text{tot}} X_j = \frac{f_j}{f_j^{\circ}}, \quad (29)$$

where P_{tot} is total gas pressure, a_j is the activity, χ_j is the activity coefficient, X_j is the mole fraction, f_j is the fugacity, and f_j° is the fugacity in the standard state of gas j . The equilibrium constant for Eqn. 28 is thus

$$\begin{aligned} K_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_{\text{aq}}}^{\text{ex}} &= \frac{a_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_{\text{aq}}}}{a_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_{\text{g}}}} \frac{a_{^{12}\text{C}^{16}\text{O}_{2\text{g}}}}{a_{^{12}\text{C}^{16}\text{O}_{2\text{aq}}}} \\ &= \frac{\gamma_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_{\text{aq}}} (\chi_{^{12}\text{C}^{16}\text{O}_{2\text{g}}} P_{\text{tot}}) m_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_{\text{aq}}} X_{^{12}\text{C}^{16}\text{O}_{2\text{g}}}}{(\chi_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_{\text{g}}} P_{\text{tot}}) \gamma_{^{12}\text{C}^{16}\text{O}_{2\text{aq}}} X_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_{\text{g}}} m_{^{12}\text{C}^{16}\text{O}_{2\text{aq}}}}, \end{aligned} \quad (30)$$

where γ_j is the activity coefficient for aqueous species j . From Eqns. 27 and 30

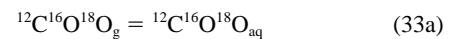
$$K_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_{\text{aq}}}^{\text{ex}} = \left(\frac{\gamma_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_{\text{aq}}} \chi_{^{12}\text{C}^{16}\text{O}_{2\text{g}}}}{\gamma_{^{12}\text{C}^{16}\text{O}_{2\text{aq}}} \chi_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_{\text{g}}}} \right) (\alpha_{\text{CO}_{2\text{aq}}\text{-CO}_{2\text{g}}}^{18\text{O}})_{\text{exp}}, \quad (31)$$

where the subscript exp indicates that the true value of $K_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_{\text{aq}}}^{\text{ex}}$ can only be evaluated exactly if the parameters in the subscripted parentheses are known for the experiments in which $\alpha_{\text{CO}_{2\text{aq}}\text{-CO}_{2\text{g}}}^{18\text{O}}$ was measured.

The equilibrium constant for the isotope exchange reaction can always be expressed as a ratio of equilibrium constants for other individual isotope reactions. Expressing this ratio with the Henry's Law equilibrium constants:

$$K_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_{\text{aq}}}^{\text{ex}} = \frac{a_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_{\text{aq}}}}{a_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_{\text{g}}}} \frac{a_{^{12}\text{C}^{16}\text{O}_{2\text{g}}}}{a_{^{12}\text{C}^{16}\text{O}_{2\text{aq}}}} = \frac{K_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_{\text{aq}}}^{\text{H}}}{K_{^{12}\text{C}^{16}\text{O}_{2\text{aq}}}^{\text{H}}}, \quad (32)$$

where $K_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_{\text{aq}}}^{\text{H}}$ and $K_{^{12}\text{C}^{16}\text{O}_{2\text{aq}}}^{\text{H}}$ are the equilibrium constants for the reactions



and



The value of $K_{^{12}\text{C}^{16}\text{O}_{2\text{aq}}}^{\text{H}}$ is assumed for the moment to equal the standard thermochemical constant; this assumption is discussed in more detail later. From Eqns. 31 and 32,

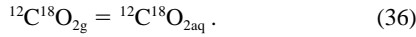
$$\begin{aligned} K_{12C^{16}O^{18}O_{aq}}^H &= K_{12C^{16}O_{2aq}}^H K_{12C^{16}O^{18}O_{aq}}^{ex} \\ &= K_{12C^{16}O_{2aq}}^H \left(\frac{\gamma_{12C^{16}O^{18}O_{aq}}}{\gamma_{12C^{16}O_{2aq}}} \frac{\chi_{12C^{16}O_{2g}}}{\chi_{12C^{16}O^{18}O_g}} \right)_{exp} (\alpha_{CO_{2aq}-CO_{2g}}^{18O}). \end{aligned} \quad (34)$$

With known values of $K_{12C^{16}O_{2aq}}^H$ and the activity coefficients, $K_{12C^{16}O^{18}O_{aq}}^H$ can be calculated from the measured value of $\alpha_{CO_{2aq}-CO_{2g}}^{18O}$. In PHREEQC the equilibrium constants are used in logarithmic form; rewriting Eqn. 34,

$$\begin{aligned} \log K_{12C^{16}O^{18}O_{aq}}^H &= \log K_{12C^{16}O_{2aq}}^H + \log(\alpha_{CO_{2aq}-CO_{2g}}^{18O}) \\ &+ \log \left(\frac{\gamma_{12C^{16}O^{18}O_{aq}}}{\gamma_{12C^{16}O_{2aq}}} \frac{\chi_{12C^{16}O_{2g}}}{\chi_{12C^{16}O^{18}O_g}} \right)_{exp}. \end{aligned} \quad (35)$$

3.1.2. $^{12}C^{18}O_2$

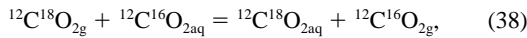
For $^{12}C^{18}O_2$, the reaction is



For reaction 36, the appropriate expression of the fractionation factor is (from Eqn. 24)

$$\begin{aligned} (\alpha_{CO_{2aq}-CO_{2g}}^{18O})^2 &= \left(\frac{R_{CO_{2aq}}^{18O}}{R_{CO_{2g}}^{18O}} \right)^2 = \frac{\left(\frac{n_{12C^{18}O_{2aq}}}{n_{12C^{16}O_{2aq}}} \right)}{\left(\frac{n_{12C^{18}O_{2g}}}{n_{12C^{16}O_{2g}}} \right)} \\ &= \frac{n_{12C^{18}O_{2aq}}}{n_{12C^{18}O_{2g}}} \frac{n_{12C^{16}O_{2g}}}{n_{12C^{16}O_{2aq}}} = \frac{m_{12C^{18}O_{2aq}}}{X_{12C^{18}O_{2g}}} \frac{X_{12C^{16}O_{2g}}}{m_{12C^{16}O_{2aq}}}. \end{aligned} \quad (37)$$

The isotope exchange reaction for equation 37 is



and the equilibrium constant is

$$\begin{aligned} K_{12C^{18}O_{2aq}}^{ex} &= \frac{a_{12C^{18}O_{2aq}} a_{12C^{16}O_{2g}}}{a_{12C^{18}O_{2g}} a_{12C^{16}O_{2aq}}} \\ &= \frac{\gamma_{12C^{18}O_{2aq}}}{(\chi_{12C^{18}O_{2g}} P_{tot})} \frac{(\chi_{12C^{16}O_{2g}} P_{tot})}{\gamma_{12C^{16}O_{2aq}}} \frac{m_{12C^{18}O_{2aq}}}{X_{12C^{18}O_{2g}}} \frac{X_{12C^{16}O_{2g}}}{m_{12C^{16}O_{2aq}}}. \end{aligned} \quad (39)$$

Following Eqns. 30–35 yields

$$\begin{aligned} \log K_{12C^{18}O_{2aq}}^H &= \log K_{12C^{16}O_{2aq}}^H + 2\log(\alpha_{CO_{2aq}-CO_{2g}}^{18O}) \\ &+ \log \left(\frac{\gamma_{12C^{18}O_{2aq}}}{\gamma_{12C^{16}O_{2aq}}} \frac{\chi_{12C^{16}O_{2g}}}{\chi_{12C^{18}O_{2g}}} \right)_{exp}. \end{aligned} \quad (40)$$

3.1.3. $^{13}C^{16}O_2$

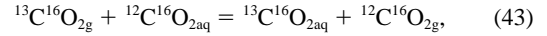
For $^{13}C^{16}O_2$, the reaction is



For reaction 41, the appropriate expression of the fractionation factor is (from Eqn. 19)

$$\begin{aligned} \alpha_{CO_{2aq}-CO_{2g}}^{13C} &= \frac{R_{CO_{2aq}}^{13C}}{R_{CO_{2g}}^{13C}} = \frac{\left(\frac{n_{13C^{16}O_{2aq}}}{n_{12C^{16}O_{2aq}}} \right)}{\left(\frac{n_{13C^{16}O_{2g}}}{n_{12C^{16}O_{2g}}} \right)} \\ &= \frac{n_{13C^{16}O_{2aq}}}{n_{13C^{16}O_{2g}}} \frac{n_{12C^{16}O_{2g}}}{n_{12C^{16}O_{2aq}}} = \frac{m_{13C^{16}O_{2aq}}}{X_{13C^{16}O_{2g}}} \frac{X_{12C^{16}O_{2g}}}{m_{12C^{16}O_{2aq}}}. \end{aligned} \quad (42)$$

The isotope exchange reaction is



and the equilibrium constant is

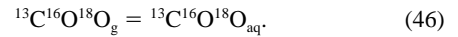
$$\begin{aligned} K_{13C^{16}O_{2aq}}^{ex} &= \frac{a_{13C^{16}O_{2aq}} a_{12C^{16}O_{2g}}}{a_{13C^{16}O_{2g}} a_{12C^{16}O_{2aq}}} \\ &= \frac{\gamma_{13C^{16}O_{2aq}}}{(\chi_{13C^{16}O_{2g}} P_{tot})} \frac{(\chi_{12C^{16}O_{2g}} P_{tot})}{\gamma_{12C^{16}O_{2aq}}} \frac{m_{13C^{16}O_{2aq}}}{X_{13C^{16}O_{2g}}} \frac{X_{12C^{16}O_{2g}}}{m_{12C^{16}O_{2aq}}}. \end{aligned} \quad (44)$$

Again following Eqns. 30–35,

$$\begin{aligned} \log K_{13C^{16}O_{2aq}}^H &= \log K_{12C^{16}O_{2aq}}^H + \log(\alpha_{CO_{2aq}-CO_{2g}}^{13C}) \\ &+ \log \left(\frac{\gamma_{13C^{16}O_{2aq}}}{\gamma_{12C^{16}O_{2aq}}} \frac{\chi_{12C^{16}O_{2g}}}{\chi_{13C^{16}O_{2g}}} \right)_{exp}. \end{aligned} \quad (45)$$

3.1.4. $^{13}C^{16}O^{18}O$

For $^{13}C^{16}O^{18}O$, the reaction is



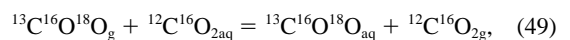
In this case a product of fractionation factors is required to provide appropriate species; the algebra remains unchanged. Choosing appropriate ratios from Eqns. 19 and 24 to define the fractionation factors gives

$$\begin{aligned} (\alpha_{CO_{2aq}-CO_{2g}}^{13C})(\alpha_{CO_{2aq}-CO_{2g}}^{18O}) &= \left(\frac{R_{CO_{2aq}}^{13C}}{R_{CO_{2g}}^{13C}} \right) \left(\frac{R_{CO_{2aq}}^{18O}}{R_{CO_{2g}}^{18O}} \right) \\ &= \frac{\left(\frac{n_{13C^{16}O^{18}O_{aq}}}{n_{12C^{16}O^{18}O_{aq}}} \right) \left(\frac{n_{12C^{16}O^{18}O_{aq}}}{2n_{12C^{16}O_{2aq}}} \right)}{\left(\frac{n_{13C^{16}O^{18}O_g}}{n_{12C^{16}O^{18}O_g}} \right) \left(\frac{n_{12C^{16}O^{18}O_g}}{2n_{12C^{16}O_{2g}}} \right)}. \end{aligned} \quad (47)$$

Converting to concentration units yields

$$\begin{aligned} (\alpha_{CO_{2aq}-CO_{2g}}^{13C})(\alpha_{CO_{2aq}-CO_{2g}}^{18O}) &= \frac{n_{13C^{16}O^{18}O_{aq}}}{n_{13C^{16}O^{18}O_g}} \frac{n_{12C^{16}O_{2g}}}{n_{12C^{16}O_{2aq}}} \\ &= \frac{m_{13C^{16}O^{18}O_{aq}}}{X_{13C^{16}O^{18}O_g}} \frac{X_{12C^{16}O_{2g}}}{m_{12C^{16}O_{2aq}}}. \end{aligned} \quad (48)$$

The isotope exchange reaction for Eqn. 48 is



and the equilibrium constant is

$$\begin{aligned} K_{^{13}\text{C}^{16}\text{O}^{18}\text{O}_{\text{aq}}}^{\text{ex}} &= \frac{a_{^{13}\text{C}^{16}\text{O}^{18}\text{O}_{\text{aq}}}}{a_{^{13}\text{C}^{16}\text{O}^{18}\text{O}_{\text{g}}}} \frac{a_{^{12}\text{C}^{16}\text{O}_{2\text{g}}}}{a_{^{12}\text{C}^{16}\text{O}_{2\text{aq}}}} \\ &= \frac{\gamma_{^{13}\text{C}^{16}\text{O}^{18}\text{O}_{\text{aq}}}}{(\chi_{^{13}\text{C}^{16}\text{O}^{18}\text{O}_{\text{g}}})} \frac{(\chi_{^{12}\text{C}^{16}\text{O}_{2\text{g}}} P_{\text{tot}})}{\gamma_{^{12}\text{C}^{16}\text{O}_{2\text{aq}}}} \frac{m_{^{13}\text{C}^{16}\text{O}^{18}\text{O}_{\text{aq}}}}{X_{^{13}\text{C}^{16}\text{O}^{18}\text{O}_{\text{g}}}} \frac{X_{^{12}\text{C}^{16}\text{O}_{2\text{g}}}}{m_{^{12}\text{C}^{16}\text{O}_{2\text{aq}}}}. \end{aligned} \quad (50)$$

Again following the sequence of Eqns. 30–35,

$$\begin{aligned} \log K_{^{13}\text{C}^{16}\text{O}^{18}\text{O}_{\text{aq}}}^{\text{H}} &= \log K_{^{12}\text{C}^{16}\text{O}_{2\text{aq}}}^{\text{H}} + \log(\alpha_{\text{CO}_{2\text{aq}}-\text{CO}_{2\text{g}}}^{^{13}\text{C}}) \\ &+ \log(\alpha_{\text{CO}_{2\text{aq}}-\text{CO}_{2\text{g}}}^{^{18}\text{O}}) + \log\left(\frac{\gamma_{^{13}\text{C}^{16}\text{O}^{18}\text{O}_{\text{aq}}}}{\gamma_{^{12}\text{C}^{16}\text{O}_{2\text{aq}}}} \frac{\chi_{^{12}\text{C}^{16}\text{O}_{2\text{g}}}}{\chi_{^{13}\text{C}^{16}\text{O}^{18}\text{O}_{\text{g}}}}\right)_{\text{exp}}. \end{aligned} \quad (51)$$

3.1.5. $^{13}\text{C}^{18}\text{O}_2$

The equations for $^{13}\text{C}^{18}\text{O}_{2\text{aq}}$ are analogous to those for $^{13}\text{C}^{16}\text{O}^{18}\text{O}_{\text{aq}}$. The isotope ratios are

$$\begin{aligned} (\alpha_{\text{CO}_{2\text{aq}}-\text{CO}_{2\text{g}}}^{^{13}\text{C}})(\alpha_{\text{CO}_{2\text{aq}}-\text{CO}_{2\text{g}}}^{^{18}\text{O}})^2 &= \left(\frac{R_{\text{CO}_{2\text{aq}}}^{^{13}\text{C}}}{R_{\text{CO}_{2\text{g}}}^{^{13}\text{C}}}\right) \left(\frac{R_{\text{CO}_{2\text{aq}}}^{^{18}\text{O}}}{R_{\text{CO}_{2\text{g}}}^{^{18}\text{O}}}\right)^2 \\ &= \frac{\left(\frac{n_{^{13}\text{C}^{18}\text{O}_{2\text{aq}}}}{n_{^{12}\text{C}^{18}\text{O}_{2\text{aq}}}}\right) \left(\frac{n_{^{12}\text{C}^{18}\text{O}_{2\text{aq}}}}{n_{^{12}\text{C}^{16}\text{O}_{2\text{aq}}}}\right)}{\left(\frac{n_{^{13}\text{C}^{18}\text{O}_{2\text{g}}}}{n_{^{12}\text{C}^{18}\text{O}_{2\text{g}}}}\right) \left(\frac{n_{^{12}\text{C}^{18}\text{O}_{2\text{g}}}}{n_{^{12}\text{C}^{16}\text{O}_{2\text{g}}}}\right)}, \end{aligned} \quad (52)$$

or

$$(\alpha_{\text{CO}_{2\text{aq}}-\text{CO}_{2\text{g}}}^{^{13}\text{C}})(\alpha_{\text{CO}_{2\text{aq}}-\text{CO}_{2\text{g}}}^{^{18}\text{O}})^2 = \frac{n_{^{13}\text{C}^{18}\text{O}_{2\text{aq}}}}{n_{^{13}\text{C}^{18}\text{O}_{2\text{g}}}} \frac{n_{n_{^{12}\text{C}^{18}\text{O}_{2\text{aq}}}}}{n_{^{12}\text{C}^{16}\text{O}_{2\text{aq}}}} = \frac{m_{^{13}\text{C}^{18}\text{O}_{2\text{aq}}}}{X_{^{13}\text{C}^{18}\text{O}_{2\text{g}}}} \frac{X_{^{12}\text{C}^{16}\text{O}_{2\text{g}}}}{m_{^{12}\text{C}^{16}\text{O}_{2\text{aq}}}}. \quad (53)$$

Familiar algebra leads to

$$\begin{aligned} \log K_{^{13}\text{C}^{18}\text{O}_{2\text{aq}}}^{\text{H}} &= \log K_{^{12}\text{C}^{16}\text{O}_{2\text{aq}}}^{\text{H}} + \log(\alpha_{\text{CO}_{2\text{aq}}-\text{CO}_{2\text{g}}}^{^{13}\text{C}}) \\ &+ 2\log(\alpha_{\text{CO}_{2\text{aq}}-\text{CO}_{2\text{g}}}^{^{18}\text{O}}) + \log\left(\frac{\gamma_{^{13}\text{C}^{18}\text{O}_{2\text{aq}}}}{\gamma_{^{12}\text{C}^{16}\text{O}_{2\text{aq}}}} \frac{\chi_{^{12}\text{C}^{16}\text{O}_{2\text{g}}}}{\chi_{^{13}\text{C}^{18}\text{O}_{2\text{g}}}}\right)_{\text{exp}}. \end{aligned} \quad (54)$$

The five individual isotope equilibrium Henry's Law constants for CO_2 can now be calculated given a value of the equilibrium constant for the dominant isotopic species, $K_{^{12}\text{C}^{16}\text{O}_{2\text{aq}}}^{\text{H}}$, and experimental or assumed fractionation factors.

3.2. Equilibrium Constants for Reactions Involving Liquid Water

The example that follows in section 7 involves equilibrium among $\text{CO}_{2\text{aq}}$, H_2O , $\text{CO}_{2\text{g}}$, and $\text{H}_2\text{O}_{\text{g}}$. The calculation thus requires equilibrium constants for various liquid and gas species. Two of these are derived below as illustrations; the remainder are presented in T&P. The equation formulation in PHREEQC permits only one solvent, $^1\text{H}_2\ ^{16}\text{O}_1$. The isotopic variants of liquid water other than $^1\text{H}_2\ ^{16}\text{O}_1$ are treated mathematically as electrically neutral solutes denoted by the subscript aq, while recognizing that they are physically molecules of solvent. These waterlike species thus require activity-concentration conventions that render their chemical behavior similar

to liquid water, rather than the conventions used for normal aqueous solutes. These relations are derived in section 3.6 and used as required without derivation in section 3.2.1 that follows. The derivation sequence follows that described above.

3.2.1. $^{12}\text{C}^{18}\text{O}_{2\text{aq}}-^1\text{H}_2\ ^{18}\text{O}_1$

This is the reaction that relates the ^{18}O content of liquid water to the ^{18}O content of the isotopic variants of $\text{CO}_{2\text{aq}}$ and $\text{CO}_{2\text{gas}}$. The fractionation factor is

$$\alpha_{\text{CO}_{2\text{aq}}-\text{H}_2\text{O}}^{^{18}\text{O}} = \frac{R_{\text{CO}_{2\text{aq}}}^{^{18}\text{O}}}{R_{\text{H}_2\text{O}_1}^{^{18}\text{O}}}, \quad (55)$$

where the numerator is a ratio selected from $R_{\text{CO}_{2\text{aq}}}^{^{18}\text{O}} = \frac{n_{^{12}\text{C}^{18}\text{O}_{2\text{aq}}}}{n_{^{12}\text{C}^{16}\text{O}_{2\text{aq}}}}$

$$= \frac{n_{^{13}\text{C}^{18}\text{O}_{2\text{aq}}}}{n_{^{13}\text{C}^{16}\text{O}_{2\text{aq}}}} = \frac{n_{^{12}\text{C}^{16}\text{O}^{18}\text{O}_{\text{aq}}}}{2n_{^{12}\text{C}^{16}\text{O}_{2\text{aq}}}} = \frac{n_{^{13}\text{C}^{16}\text{O}^{18}\text{O}_{\text{aq}}}}{2n_{^{13}\text{C}^{16}\text{O}_{2\text{aq}}}} \quad (\text{Eqn. 24 rewritten}), \text{ and}$$

the denominator is selected from $R_{\text{H}_2\text{O}_1}^{^{18}\text{O}} = \frac{n_{^1\text{H}_2\ ^{18}\text{O}_1}}{n_{^1\text{H}_2\ ^{16}\text{O}_1}} = \frac{n_{^1\text{H}_2\ ^{18}\text{O}_1}}{n_{^1\text{H}_2\ ^{16}\text{O}_1}}$

$= \frac{n_{^1\text{H}_2\ ^{18}\text{O}_1}}{n_{^1\text{H}_2\ ^{16}\text{O}_1}}$ (Eqn. 19 rewritten for H_2O_1). The ^{18}O fractionation factor can thus be written

$$\alpha_{\text{CO}_{2\text{aq}}-\text{H}_2\text{O}_1}^{^{18}\text{O}} = \frac{R_{\text{CO}_{2\text{aq}}}^{^{18}\text{O}}}{R_{\text{H}_2\text{O}_1}^{^{18}\text{O}}} = \frac{\left(\frac{n_{^{12}\text{C}^{18}\text{O}_{2\text{aq}}}}{n_{^{12}\text{C}^{16}\text{O}_{2\text{aq}}}}\right)}{\left(\frac{n_{^1\text{H}_2\ ^{18}\text{O}_1}}{n_{^1\text{H}_2\ ^{16}\text{O}_1}}\right)}, \quad (56a)$$

or

$$(\alpha_{\text{CO}_{2\text{aq}}-\text{H}_2\text{O}_1}^{^{18}\text{O}})^2 = \frac{\left(\frac{n_{^{12}\text{C}^{18}\text{O}_{2\text{aq}}}}{n_{^{12}\text{C}^{16}\text{O}_{2\text{aq}}}}\right)}{\left(\frac{n_{^1\text{H}_2\ ^{18}\text{O}_1}}{n_{^1\text{H}_2\ ^{16}\text{O}_1}}\right)}. \quad (56b)$$

The relation between mole ratio and molality for each of the waterlike isotopic variants i other than $^1\text{H}_2\ ^{16}\text{O}_1$ is given by

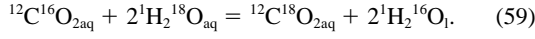
$$\frac{n_i}{n_{^1\text{H}_2\ ^{16}\text{O}_1}} = \frac{m_i}{55.56}, \quad (57)$$

where $55.56 = 1000/\text{gfw}(^1\text{H}_2\ ^{16}\text{O}_1)$. Using Eqn. 57 in Eqn. 56b for $(\alpha_{\text{CO}_{2\text{aq}}-\text{H}_2\text{O}_1}^{^{18}\text{O}})^2$ gives

$$\begin{aligned} (\alpha_{\text{CO}_{2\text{aq}}-\text{H}_2\text{O}_1}^{^{18}\text{O}})^2 &= \frac{\left(\frac{n_{^{12}\text{C}^{18}\text{O}_{2\text{aq}}}}{n_{^{12}\text{C}^{16}\text{O}_{2\text{aq}}}}\right)}{\left(\frac{n_{^1\text{H}_2\ ^{18}\text{O}_{\text{aq}}}}{n_{^1\text{H}_2\ ^{16}\text{O}_1}}\right)^2} = \frac{m_{^{12}\text{C}^{18}\text{O}_{2\text{aq}}}}{m_{^{12}\text{C}^{16}\text{O}_{2\text{aq}}}} \frac{1}{\left(\frac{m_{^1\text{H}_2\ ^{18}\text{O}_{\text{aq}}}}{55.56}\right)^2} \\ &= \frac{m_{^{12}\text{C}^{18}\text{O}_{2\text{aq}}}}{\left(\frac{1}{55.56}\right)^2 m_{^{12}\text{C}^{16}\text{O}_{2\text{aq}}} m_{^1\text{H}_2\ ^{18}\text{O}_{\text{aq}}}^2}. \end{aligned} \quad (58)$$

The exchange of ^{18}O between CO_2 and H_2O cannot be written explicitly as an isotope exchange reaction because $^1\text{H}_2\ ^{18}\text{O}_{\text{aq}}$ is treated as a solute and $^1\text{H}_2\ ^{16}\text{O}_1$ is treated as the solvent. The

correct reaction, which in this case is also the PHREEQC reaction, is



Defining the activity coefficients of the isotopic variants of $\text{H}_2\text{O}_{\text{aq}}$ by $\gamma_{\text{iaq}} \equiv \frac{a_{^1\text{H}_2^{16}\text{O}_l}}{55.56}$ (see section 3.6) the equilibrium constant for reaction 59 is written

$$\begin{aligned} K_{^{12}\text{C}^{18}\text{O}_{2\text{aq}}}^{\text{rxn}} &= \frac{a_{^{12}\text{C}^{18}\text{O}_{2\text{aq}}} a_{^1\text{H}_2^{16}\text{O}_l}^2}{a_{^{12}\text{C}^{16}\text{O}_{2\text{aq}}} a_{^1\text{H}_2^{18}\text{O}_{\text{aq}}}^2} \\ &= \frac{\gamma_{^{12}\text{C}^{18}\text{O}_{2\text{aq}}} m_{^{12}\text{C}^{18}\text{O}_{2\text{aq}}} a_{^1\text{H}_2^{16}\text{O}_l}^2}{\gamma_{^{12}\text{C}^{16}\text{O}_{2\text{aq}}} m_{^{12}\text{C}^{16}\text{O}_{2\text{aq}}} \gamma_{^1\text{H}_2^{18}\text{O}_{\text{aq}}}^2 m_{^1\text{H}_2^{18}\text{O}_{\text{aq}}}^2} \\ &= \frac{\gamma_{^{12}\text{C}^{18}\text{O}_{2\text{aq}}} a_{^1\text{H}_2^{16}\text{O}_l}^2 m_{^{12}\text{C}^{18}\text{O}_{2\text{aq}}}}{\gamma_{^{12}\text{C}^{16}\text{O}_{2\text{aq}}} \left(\frac{a_{^1\text{H}_2^{16}\text{O}_l}}{55.56} \right)^2 m_{^{12}\text{C}^{16}\text{O}_{2\text{aq}}} m_{^1\text{H}_2^{18}\text{O}_{\text{aq}}}^2} \\ &= \frac{m_{^{12}\text{C}^{18}\text{O}_{2\text{aq}}} \gamma_{^{12}\text{C}^{18}\text{O}_{2\text{aq}}}}{\left(\frac{1}{55.56} \right)^2 m_{^{12}\text{C}^{16}\text{O}_{2\text{aq}}} m_{^1\text{H}_2^{18}\text{O}_{\text{aq}}}^2 \gamma_{^{12}\text{C}^{16}\text{O}_{2\text{aq}}}}. \quad (60) \end{aligned}$$

From Eqns. 58 and 60,

$$K_{^{12}\text{C}^{18}\text{O}_{2\text{aq}}}^{\text{rxn}} = (\alpha_{\text{CO}_{2\text{aq}}-^1\text{H}_2\text{O}_l}^{18\text{O}})^2 \left(\frac{\gamma_{^{12}\text{C}^{18}\text{O}_{2\text{aq}}}}{\gamma_{^{12}\text{C}^{16}\text{O}_{2\text{aq}}}} \right)_{\text{exp}}, \quad (61)$$

and

$$\log K_{^{12}\text{C}^{18}\text{O}_{2\text{aq}}}^{\text{rxn}} = 2 \log (\alpha_{\text{CO}_{2\text{aq}}-^1\text{H}_2\text{O}_l}^{18\text{O}}) + \log \left(\frac{\gamma_{^{12}\text{C}^{18}\text{O}_{2\text{aq}}}}{\gamma_{^{12}\text{C}^{16}\text{O}_{2\text{aq}}}} \right)_{\text{exp}}. \quad (62)$$

3.2.2. $^1\text{H}^2\text{H}^{18}\text{O}_{\text{gas}}-^1\text{H}^2\text{H}^{18}\text{O}_l$

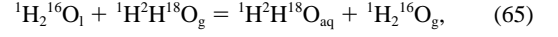
The $^2\text{H}/^1\text{H}$ isotope ratio for H_2O is (Eqn. 24 rewritten for H_2O)

$$R_{\text{H}_2\text{O}}^{2\text{H}} = \left(\frac{n_{^1\text{H}_2^{16}\text{O}_l}}{n_{^1\text{H}_2^{18}\text{O}_l}} \right)^{1/2} = \left(\frac{n_{^1\text{H}_2^{18}\text{O}_l}}{n_{^1\text{H}_2^{16}\text{O}_l}} \right)^{1/2} = \frac{n_{^1\text{H}^2\text{H}^{16}\text{O}_l}}{2n_{^1\text{H}_2^{16}\text{O}_l}} = \frac{n_{^1\text{H}^2\text{H}^{18}\text{O}_l}}{2n_{^1\text{H}_2^{18}\text{O}_l}}. \quad (63)$$

Using the appropriate product of fractionation factors yields

$$\begin{aligned} &(\alpha_{\text{H}_2\text{O}_l-^1\text{H}_2\text{O}_g}^{18\text{O}})(\alpha_{\text{H}_2\text{O}_l-^1\text{H}_2\text{O}_g}^{2\text{H}}) \\ &= \frac{R_{\text{H}_2\text{O}_l}^{18\text{O}} R_{\text{H}_2\text{O}_l}^{2\text{H}}}{R_{\text{H}_2\text{O}_g}^{18\text{O}} R_{\text{H}_2\text{O}_g}^{2\text{H}}} = \frac{\left(\frac{n_{^1\text{H}^2\text{H}^{18}\text{O}_{\text{aq}}}}{n_{^1\text{H}^2\text{H}^{16}\text{O}_{\text{aq}}}} \right) \left(\frac{n_{^1\text{H}^2\text{H}^{16}\text{O}_l}}{2n_{^1\text{H}_2^{16}\text{O}_l}} \right)}{\left(\frac{n_{^1\text{H}^2\text{H}^{18}\text{O}_g}}{n_{^1\text{H}^2\text{H}^{16}\text{O}_g}} \right) \left(\frac{n_{^1\text{H}_2^{16}\text{O}_g}}{2n_{^1\text{H}_2^{16}\text{O}_g}} \right)} \\ &= \frac{\left(\frac{n_{^1\text{H}^2\text{H}^{18}\text{O}_{\text{aq}}}}{n_{^1\text{H}_2^{16}\text{O}_l}} \right)}{\left(\frac{n_{^1\text{H}^2\text{H}^{18}\text{O}_g}}{n_{^1\text{H}_2^{16}\text{O}_g}} \right)} = m_{^1\text{H}^2\text{H}^{18}\text{O}_{\text{aq}}} \left(\frac{1}{55.56} \right) \left(\frac{X_{^1\text{H}_2^{16}\text{O}_g}}{X_{^1\text{H}^2\text{H}^{18}\text{O}_g}} \right). \quad (64) \end{aligned}$$

Again recognizing that an isotope exchange reaction cannot be written because of solute-solvent conventions, the necessary reaction is



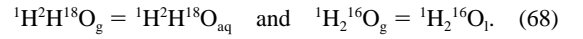
and the equilibrium constant is

$$\begin{aligned} K_{^1\text{H}^2\text{H}^{18}\text{O}_{\text{aq}}}^{\text{rxn}} &= \frac{a_{^1\text{H}^2\text{H}^{18}\text{O}_{\text{aq}}} a_{^1\text{H}_2^{16}\text{O}_g}}{a_{^1\text{H}^2\text{H}^{18}\text{O}_g} a_{^1\text{H}_2^{16}\text{O}_l}} \\ &= \frac{a_{^1\text{H}_2^{16}\text{O}_l} \left(\frac{1}{55.56} \right) m_{^1\text{H}^2\text{H}^{18}\text{O}_{\text{aq}}} \chi_{^1\text{H}_2^{16}\text{O}_g} X_{^1\text{H}_2^{16}\text{O}_g} P_{\text{tot}}}{\chi_{^1\text{H}^2\text{H}^{18}\text{O}_g} X_{^1\text{H}^2\text{H}^{18}\text{O}_g} P_{\text{tot}} a_{^1\text{H}_2^{16}\text{O}_l}} \\ &= \left(\frac{\chi_{^1\text{H}_2^{16}\text{O}_g}}{\chi_{^1\text{H}^2\text{H}^{18}\text{O}_g}} \right)_{\text{exp}} m_{^1\text{H}^2\text{H}^{18}\text{O}_{\text{aq}}} \left(\frac{1}{55.56} \right) \left(\frac{X_{^1\text{H}_2^{16}\text{O}_g}}{X_{^1\text{H}^2\text{H}^{18}\text{O}_g}} \right). \quad (66) \end{aligned}$$

From Eqns. 64 and 66

$$K_{^1\text{H}^2\text{H}^{18}\text{O}_{\text{aq}}}^{\text{ex}} = \left(\frac{\chi_{^1\text{H}_2^{16}\text{O}_g}}{\chi_{^1\text{H}^2\text{H}^{18}\text{O}_g}} \right)_{\text{exp}} (\alpha_{\text{H}_2\text{O}_l-^1\text{H}_2\text{O}_g}^{18\text{O}}) (\alpha_{\text{H}_2\text{O}_l-^1\text{H}_2\text{O}_g}^{2\text{H}}). \quad (67)$$

The PHREEQC reactions are



Thus

$$K_{^1\text{H}^2\text{H}^{18}\text{O}_{\text{aq}}}^{\text{rxn}} = \frac{a_{^1\text{H}^2\text{H}^{18}\text{O}_{\text{aq}}} a_{^1\text{H}_2^{16}\text{O}_g}}{a_{^1\text{H}^2\text{H}^{18}\text{O}_g} a_{^1\text{H}_2^{16}\text{O}_l}} = \frac{K_{^1\text{H}^2\text{H}^{18}\text{O}_{\text{aq}}}^{\text{H}}}{K_{^1\text{H}_2^{16}\text{O}_l}^{\text{H}}}, \quad (69)$$

$$\begin{aligned} K_{^1\text{H}^2\text{H}^{18}\text{O}_{\text{aq}}}^{\text{H}} &= K_{^1\text{H}_2^{16}\text{O}_l}^{\text{H}} K_{^1\text{H}^2\text{H}^{18}\text{O}_{\text{aq}}}^{\text{rxn}} \\ &= K_{^1\text{H}_2^{16}\text{O}_l}^{\text{H}} (\alpha_{\text{H}_2\text{O}_l-^1\text{H}_2\text{O}_g}^{18\text{O}}) (\alpha_{\text{H}_2\text{O}_l-^1\text{H}_2\text{O}_g}^{2\text{H}}) \left(\frac{\chi_{^1\text{H}_2^{16}\text{O}_g}}{\chi_{^1\text{H}^2\text{H}^{18}\text{O}_g}} \right)_{\text{exp}}, \quad (70) \end{aligned}$$

and

$$\begin{aligned} \log K_{^1\text{H}^2\text{H}^{18}\text{O}_{\text{aq}}}^{\text{H}} &= \log K_{^1\text{H}_2^{16}\text{O}_l}^{\text{H}} + \log (\alpha_{\text{H}_2\text{O}_l-^1\text{H}_2\text{O}_g}^{18\text{O}}) \\ &\quad + \log (\alpha_{\text{H}_2\text{O}_l-^1\text{H}_2\text{O}_g}^{2\text{H}}) + \log \left(\frac{\chi_{^1\text{H}_2^{16}\text{O}_g}}{\chi_{^1\text{H}^2\text{H}^{18}\text{O}_g}} \right)_{\text{exp}}. \quad (71) \end{aligned}$$

3.3. Individual Isotope Equilibrium Constants for the Dominant Isotopic Species

Henry's Law and CO_2 are again used for illustration. The Henry's Law equilibrium constant for a gas consisting of a mixture of inseparable component gases is based on measurement of the total concentration of the mixture, the definition of a single activity coefficient for the mixture, and measurement of the partial pressure of the mixture. The Henry's Law constant for total carbon dioxide, $\text{CO}_{2j,\text{tot}}$, where $\text{CO}_{2j,\text{tot}}$ is defined by Eqn. 72,

$$\begin{aligned} \text{CO}_{2j,\text{tot}} &\equiv ^{12}\text{C}^{16}\text{O}_{2j} + ^{12}\text{C}^{16}\text{O}^{18}\text{O}_j + ^{12}\text{C}^{18}\text{O}_{2j} \\ &\quad + ^{13}\text{C}^{16}\text{O}_{2j} + ^{13}\text{C}^{16}\text{O}^{18}\text{O}_j + ^{13}\text{C}^{18}\text{O}_{2j}, \quad (72) \end{aligned}$$

is defined by Eqn. 73:

$$K_{\text{CO}_{2\text{aq,tot}}}^{\text{H}} \equiv \frac{\gamma_{\text{CO}_{2\text{aq,tot}}} (m_{12\text{C}^{16}\text{O}_{2\text{aq}}} + m_{12\text{C}^{16}\text{O}^{18}\text{O}_{\text{aq}}} + m_{12\text{C}^{18}\text{O}_{2\text{aq}}} + m_{13\text{C}^{16}\text{O}_{2\text{aq}}} + m_{13\text{C}^{16}\text{O}^{18}\text{O}_{\text{aq}}} + m_{13\text{C}^{18}\text{O}_{2\text{aq}}})}{\chi_{\text{CO}_{2\text{g,tot}}} (P_{12\text{C}^{16}\text{O}_{2\text{g}}} + P_{12\text{C}^{16}\text{O}^{18}\text{O}_{\text{g}}} + P_{12\text{C}^{18}\text{O}_{2\text{g}}} + P_{13\text{C}^{16}\text{O}_{2\text{g}}} + P_{13\text{C}^{16}\text{O}^{18}\text{O}_{\text{g}}} + P_{13\text{C}^{18}\text{O}_{2\text{g}}})}. \quad (73)$$

The expression can be rewritten as follows:

$$K_{\text{CO}_{2\text{aq,tot}}}^{\text{H}} \equiv \frac{\gamma_{\text{CO}_{2\text{aq,tot}}} m_{12\text{C}^{16}\text{O}_{2\text{aq}}}}{\chi_{\text{CO}_{2\text{g,tot}}} P_{12\text{C}^{16}\text{O}_{2\text{g}}}} \left(1 + \frac{m_{12\text{C}^{16}\text{O}^{18}\text{O}_{\text{aq}}}}{m_{12\text{C}^{16}\text{O}_{2\text{aq}}}} + \frac{m_{12\text{C}^{18}\text{O}_{2\text{aq}}}}{m_{12\text{C}^{16}\text{O}_{2\text{aq}}}} + \frac{m_{13\text{C}^{16}\text{O}_{2\text{aq}}}}{m_{12\text{C}^{16}\text{O}_{2\text{aq}}}} + \frac{m_{13\text{C}^{16}\text{O}^{18}\text{O}_{\text{aq}}}}{m_{12\text{C}^{16}\text{O}_{2\text{aq}}}} + \frac{m_{13\text{C}^{18}\text{O}_{2\text{aq}}}}{m_{12\text{C}^{16}\text{O}_{2\text{aq}}}} \right) \times \frac{1}{\left(1 + \frac{P_{12\text{C}^{16}\text{O}^{18}\text{O}_{\text{g}}}}{P_{12\text{C}^{16}\text{O}_{2\text{g}}}} + \frac{P_{12\text{C}^{18}\text{O}_{2\text{g}}}}{P_{12\text{C}^{16}\text{O}_{2\text{g}}}} + \frac{P_{13\text{C}^{16}\text{O}_{2\text{g}}}}{P_{12\text{C}^{16}\text{O}_{2\text{g}}}} + \frac{P_{13\text{C}^{16}\text{O}^{18}\text{O}_{\text{g}}}}{P_{12\text{C}^{16}\text{O}_{2\text{g}}}} + \frac{P_{13\text{C}^{18}\text{O}_{2\text{g}}}}{P_{12\text{C}^{16}\text{O}_{2\text{g}}}} \right)}, \quad (74)$$

$$K_{\text{CO}_{2\text{aq,tot}}}^{\text{H}} = \frac{\gamma_{\text{CO}_{2\text{aq,tot}}} \chi_{12\text{C}^{16}\text{O}_{2\text{g}}} \gamma_{12\text{C}^{16}\text{O}_{2\text{aq}}} m_{12\text{C}^{16}\text{O}_{2\text{aq}}}}{\chi_{\text{CO}_{2\text{g,tot}}} \gamma_{12\text{C}^{16}\text{O}_{2\text{aq}}} \chi_{12\text{C}^{16}\text{O}_{2\text{g}}} P_{12\text{C}^{16}\text{O}_{2\text{g}}}} \left\{ \frac{1 + 2R_{\text{CO}_{2\text{aq}}}^{18\text{O}} + (R_{\text{CO}_{2\text{aq}}}^{18\text{O}})^2 + R_{\text{CO}_{2\text{aq}}}^{13\text{C}}}{[1 + 2R_{\text{CO}_{2\text{aq}}}^{18\text{O}} + (R_{\text{CO}_{2\text{aq}}}^{18\text{O}})^2]} \right\} \times \frac{1}{\left\{ \frac{(1 + 2R_{\text{CO}_{2\text{g}}}^{18\text{O}} + (R_{\text{CO}_{2\text{g}}}^{18\text{O}})^2 + R_{\text{CO}_{2\text{g}}}^{13\text{C}})}{[1 + 2R_{\text{CO}_{2\text{g}}}^{18\text{O}} + (R_{\text{CO}_{2\text{g}}}^{18\text{O}})^2]} \right\}}, \quad \text{or} \quad (75)$$

$$K_{\text{CO}_{2\text{aq,tot}}}^{\text{H}} \equiv \frac{\gamma_{\text{CO}_{2\text{aq,tot}}} \chi_{12\text{C}^{16}\text{O}_{2\text{g}}}}{\gamma_{12\text{C}^{16}\text{O}_{2\text{aq}}} \chi_{\text{CO}_{2\text{g,tot}}}} \times K_{12\text{C}^{16}\text{O}_{2\text{aq}}}^{\text{H}} \frac{(1 + R_{\text{CO}_{2\text{aq}}}^{13\text{C}})(1 + R_{\text{CO}_{2\text{aq}}}^{18\text{O}})^2}{(1 + R_{\text{CO}_{2\text{g}}}^{13\text{C}})(1 + R_{\text{CO}_{2\text{g}}}^{18\text{O}})^2}. \quad (76)$$

Using the definition of the fractionation factor gives

$$K_{\text{CO}_{2\text{aq,tot}}}^{\text{H}} \equiv \frac{\gamma_{\text{CO}_{2\text{aq,tot}}} \chi_{12\text{C}^{16}\text{O}_{2\text{g}}}}{\gamma_{12\text{C}^{16}\text{O}_{2\text{aq}}} \chi_{\text{CO}_{2\text{g,tot}}}} K_{12\text{C}^{16}\text{O}_{2\text{aq}}}^{\text{H}} \times \frac{(1 + [\alpha_{\text{CO}_{2\text{aq}}-\text{CO}_{2\text{g}}}^{13\text{C}}] R_{\text{CO}_{2\text{g}}}^{13\text{C}})(1 + [\alpha_{\text{CO}_{2\text{aq}}-\text{CO}_{2\text{g}}}^{18\text{O}}] R_{\text{CO}_{2\text{g}}}^{18\text{O}})^2}{(1 + R_{\text{CO}_{2\text{g}}}^{13\text{C}})(1 + R_{\text{CO}_{2\text{g}}}^{18\text{O}})^2}, \quad (77)$$

and thus solving for the individual isotope equilibrium constant for the dominant species, $K_{12\text{C}^{16}\text{O}_{2\text{aq}}}^{\text{H}}$, gives

$$K_{12\text{C}^{16}\text{O}_{2\text{aq}}}^{\text{H}} = K_{\text{CO}_{2\text{aq,tot}}}^{\text{H}} \left(\frac{\gamma_{12\text{C}^{16}\text{O}_{2\text{aq}}} \chi_{\text{CO}_{2\text{g,tot}}}}{\gamma_{\text{CO}_{2\text{aq,tot}}} \chi_{12\text{C}^{16}\text{O}_{2\text{g}}}} \right) \times \frac{(1 + R_{\text{CO}_{2\text{g}}}^{13\text{C}})(1 + R_{\text{CO}_{2\text{g}}}^{18\text{O}})^2}{(1 + [\alpha_{\text{CO}_{2\text{aq}}-\text{CO}_{2\text{g}}}^{13\text{C}}] R_{\text{CO}_{2\text{g}}}^{13\text{C}})(1 + [\alpha_{\text{CO}_{2\text{aq}}-\text{CO}_{2\text{g}}}^{18\text{O}}] R_{\text{CO}_{2\text{g}}}^{18\text{O}})^2}. \quad (78)$$

If the parameters $P_{\text{CO}_{2\text{g,tot}}}$, $m_{\text{CO}_{2\text{aq,tot}}}$, $R_{\text{CO}_{2\text{g}}}^{13\text{C}}$, $R_{\text{CO}_{2\text{aq}}}^{13\text{C}}$, $R_{\text{CO}_{2\text{g}}}^{18\text{O}}$ and $R_{\text{CO}_{2\text{aq}}}^{18\text{O}}$ are all measured precisely in the same experiment, or extrapolated precisely to infinite dilution, then all of the parameters defined in Eqns. 76–78 can be calculated exactly, provided the ratio of activity coefficients is known. $K_{12\text{C}^{16}\text{O}_{2\text{aq}}}^{\text{H}}$

could then be calculated from the standard thermochemical value of $K_{\text{CO}_{2\text{aq,tot}}}^{\text{H}}$. However, experimental isotope studies determine the ratios R_{aq} and R_{g} (and thus α) precisely, with less emphasis on absolute solubilities, whereas the experimental solubility studies, from which the standard thermochemical properties of substances are calculated, measure $K_{\text{CO}_{2\text{aq,tot}}}^{\text{H}}$ precisely, but generally do not take account of the fact that the substances are mixtures of isotopes. In many cases the problem, as Urey pointed out, is that effects related to the minor isotopes are too small to be measured. Regardless, isotope studies leading to an evaluation of α are usually not the same studies that define the values of $K_{\text{CO}_{2\text{aq,tot}}}^{\text{H}}$.

3.4. Symmetry Assumptions in the Isotope Ratios

The equilibrium constants for the reactions $^{12}\text{C}^{18}\text{O}_{2\text{g}} = ^{12}\text{C}^{18}\text{O}_{2\text{aq}}$ are derived earlier by using the isotope ratios in Eqns. 19 and 24. The Urey relationship of Eqn. 1, $\alpha = (K^{\text{ex}})^{1/n}$ where K^{ex} is the equilibrium constant of the isotope exchange reaction, holds if these equations and their analogs for other species are valid. Urey points out that the algebraic simplification that leads to Eqns. 19 and 24 and their analogs does not occur for asymmetric molecules but does not derive equations for this case.

Urey also points out that, although the effects are small, the symmetry-derived intraspecies constants are not exact for reactions involving hydrogen isotopes because of the mass effect on vibration frequencies. For example, calculated values (Urey, table IV) of the equilibrium constants for the reactions $^1\text{H}_2^{16}\text{O} + ^2\text{H}_2^{16}\text{O} = 2^1\text{H}^2\text{H}^{16}\text{O}$ and $^1\text{H}_2^{16}\text{O} + ^3\text{H}_2^{16}\text{O} = 2^1\text{H}^3\text{H}^{16}\text{O}$ are $K = 3.96$ and $K = 3.42$ at 298.1 K, instead of the statistical value of 4 derived solely from symmetry considerations. Calculations of individual isotope equilibrium constants based on these values could be made, in concept, by extending the numerical methods discussed subsequently for the asymmetric bicarbonate ion.

In judging the importance of errors such as the mass effect for hydrogen for modeling applications, a fundamental difference between the work of Urey and this report must be recognized. Urey *calculated* fractionation effects in isotope exchange reactions; thus, errors in spectroscopic data and/or approximations in the calculations contribute to the predicted distribution of isotopes *between* reactants and products. In this paper, *measured* fractionation factors are used to calculate the individual equilibrium constants for reactions between reactants and products. The symmetry-based intraspecies equilibrium constants are used to calculate the distribution of species *within* reactant or products. Thus, correct isotope effects will be preserved *between* reactants and products, even if small errors are introduced in the distribution of isotopic species *within* reactants or products as a result of the symmetry approximations or the assumption that activity coefficient ratios for isotopic species (discussed shortly) are equal to one.

3.5. Temperature Dependence

PHREEQC uses a five-term analytical expression for the temperature dependence of $\log_{10} K$:

$$\log_{10} K = A_1 + A_2 T + \frac{A_3}{T} + A_4 \log_{10} T + \frac{A_5}{T^2}, \quad (79)$$

where the A_i are empirical constants and T is temperature in °K. Fractionation factors are generally reported in equations of

the form $10^3 \ln \alpha = [a(10^6/T^2) + b(10^3/T) + c]$, which will be written here as

$$10^3 \ln \alpha = A_1^\alpha + \frac{A_3^\alpha}{T} + \frac{A_5^\alpha}{T^2}. \quad (80)$$

Equation 80 is the form in which the fractionation factors are presented in Table 3, which can be rewritten as Eqn. 81

$$\log_{10} \alpha = \frac{A_1^\alpha}{10^3 \ln 10} + \frac{A_3^\alpha}{[10^3 \ln 10]T} + \frac{A_5^\alpha}{[10^3 \ln 10]T^2}. \quad (81)$$

The temperature dependence of the individual isotope equilibrium constant is illustrated by example. Restating Eqn. 35

$$\begin{aligned} \log K_{12C^{16}O^{18}O_{aq}}^H &= \log K_{12C^{16}O_{2aq}}^H + \log (\alpha_{CO_{2aq}-CO_{2g}}^{18O}) \\ &+ \log \left(\frac{\gamma_{12C^{16}O^{18}O_{aq}} \chi_{12C^{16}O_{2g}}}{\gamma_{12C^{16}O_{2aq}} \chi_{12C^{16}O^{18}O_g}} \right)_{\text{exp}}. \end{aligned} \quad (82)$$

The fractionation factor temperature dependence is

$$10^3 \ln (\alpha_{CO_{2aq}-CO_{2g}}^{18O}) = A_1^\alpha + \frac{A_3^\alpha}{T} + \frac{A_5^\alpha}{T^2}, \text{ or} \quad (83)$$

$$\begin{aligned} \log (\alpha_{CO_{2aq}-CO_{2g}}^{18O}) &= \frac{A_1^\alpha}{10^3 \ln 10} \\ &+ \frac{A_3^\alpha}{[10^3 \ln 10]T} + \frac{A_5^\alpha}{[10^3 \ln 10]T^2}. \end{aligned} \quad (84)$$

Assuming the activity coefficient term is unity, Eqns. 79 (written for $\log K_{12C^{16}O^{18}O_{aq}}^H$), 82, and 84 give

$$\begin{aligned} \log K_{12C^{16}O^{18}O_{aq}}^H &= \left(A_1 + \frac{A_1^\alpha}{10^3 \ln 10} \right) \\ &+ A_2 T + \left(A_3 + \frac{A_3^\alpha}{10^3 \ln 10} \right) \left(\frac{1}{T} \right) \\ &+ A_4 \log_{10} T + \left(A_5 + \frac{A_5^\alpha}{10^3 \ln 10} \right) \left(\frac{1}{T^2} \right). \end{aligned} \quad (85)$$

The temperature dependence of $\log K_{12C^{16}O^{18}O_{aq}}^H$ is now expressed as a five-term analytical expression that can be directly input to the PHREEQC database. For simplicity, PHREEQC allows definition of separate temperature dependence expressions for the reference equilibrium constant and each fractionation factor. The coefficients are combined to produce the proper temperature dependence of the equilibrium constant for the isotopic species.

3.6. Nonideality

3.6.1. Activity of Water and Isotopic Waterlike Species

For any reaction involving liquid water, for example $2H_2O_l = H_3O_{aq}^+ + OH_{aq}^-$, the various isotopes of H and O are distributed among the molecules of the solvent water, as well as the various aqueous solutes. The equation structure in PHREEQC permits the presence of only one solvent, ${}^1H_2{}^{16}O_l$. Other isotopic waterlike species, denoted by the subscript aq, such as ${}^1H^2H{}^{16}O_{aq}$, ${}^2H_2{}^{16}O_{aq}$, ${}^1H_2{}^{18}O_{aq}$, ${}^1H^2H{}^{18}O_{aq}$, and ${}^2H_2{}^{18}O_{aq}$, are treated mathematically as electrically neutral solutes in

PHREEQC. The following discussion is limited to these five most abundant species, but will hold for all other waterlike species. The concentration scale and the activity-concentration conventions differ for solute and solvent. Following Garrels and Christ (1965, pp. 65–66) the activity of liquid water is defined in PHREEQC by

$$a_{{}^1H_2{}^{16}O_l} = 1 - 0.017 \sum_i^{N_{aq}} \frac{n_i}{W_{aq}}, \quad (86)$$

where N_{aq} is the number of aqueous species (including the water-like isotopic variants of ${}^1H_2{}^{16}O_l$) other than water, n_i is the number of moles of these species, and W_{aq} is the mass of solvent water. The reference state for the solvent is pure water and the concentration scale is mole fraction. The activity of neutral solutes, other than isotopic variants of water, is defined by $a_i = \gamma_i m_i$, where $\log \gamma_i = b_i \mu$, b_i is an empirical constant, and μ is the ionic strength. Therefore, for these neutral solutes

$$a_i = (10^{b_i \mu}) m_i. \quad (87)$$

The reference state is infinite dilution, and the concentration scale is molal. These conventions lead to unrealistic results when applied to the isotopic waterlike species. The activity of pure ${}^1H^2H{}^{16}O_l$, for example, would be ~ 53 , whereas that of pure ${}^1H_2{}^{16}O_l$ is 1.0. In addition, as electrolyte concentrations increase, $a_{{}^1H_2{}^{16}O_l}$ would decrease according to Eqn. 86, whereas $a_{{}^1H^2H{}^{16}O_l} / m_{{}^1H^2H{}^{16}O_l}$ would increase according to Eqn. 87.

To make the concentration scales and the activity-concentration relations consistent for ${}^1H_2{}^{16}O_l$ and for ${}^1H^2H{}^{16}O_{aq}$, ${}^2H_2{}^{16}O_{aq}$, ${}^1H_2{}^{18}O_{aq}$, and ${}^2H_2{}^{18}O_{aq}$, the activities and activity coefficients for the latter are defined as

$$a_i \equiv \gamma_i m_i \quad (88a)$$

and

$$\begin{aligned} \gamma_i &\equiv a_{{}^1H_2{}^{16}O_l} \left(\frac{1}{[1000/18.0]} \right) = a_{{}^1H_2{}^{16}O_l} \left(\frac{1}{55.5555\dots} \right) \\ &\equiv a_{{}^1H_2{}^{16}O_l} \left(\frac{1}{55.56} \right), \end{aligned} \quad (88b)$$

where i refers to the five isotopic water-like species. The gram-formula-weight of ${}^1H_2{}^{16}O_l$ is 18.0. The assumptions underlying these conventions are based on the fact that equation 86 closely approximates the relation $a_{{}^1H_2{}^{16}O_l} = X_{{}^1H_2{}^{16}O_l}$, and using Eqn. 57 in Eqn. 88 closely approximates the relation $a_i = X_i$ where i represents ${}^1H^2H{}^{16}O_{aq}$, ${}^2H_2{}^{16}O_{aq}$, ${}^1H_2{}^{18}O_{aq}$, ${}^1H^2H{}^{18}O_{aq}$, or ${}^2H_2{}^{18}O_{aq}$. Equation 88 stipulates that the activities of the waterlike species will vary directly with their own concentrations, and will be affected by solutes other than themselves in the same manner as the solvent ${}^1H_2{}^{16}O_l$, that is, according to Eqn. 86.

Equation 88 requires that the activities of the water like species decrease with increasing solute concentration at the same rate as the activity of ${}^1H_2{}^{16}O_l$. However, in reality, the activities of the waterlike species do not decrease identically. Horita et al. (1993a,b; 1995) summarize earlier work and present much original data demonstrating the salt effect on deuterium and oxygen-18 activities in electrolyte solutions. Horita et al. (1993a) treat the isotope salt effect,

using deuterium as an example, in terms of the defined parameter

$$\Gamma \equiv \frac{a(\text{HDO})/a(\text{H}_2\text{O})}{X(\text{HDO})/X(\text{H}_2\text{O})}, \quad (89)$$

where a is activity and X is mole fraction. Note that $X(\text{HDO})/X(\text{H}_2\text{O}) = n(\text{HDO})/n(\text{H}_2\text{O})$, where n is number of moles, thus allowing Eqn. 89 to be written, in our notation,

$$\Gamma \equiv \frac{a_{\text{H}^2\text{H}^{16}\text{O}_{\text{aq}}}/a_{\text{H}_2^{16}\text{O}_1}}{X_{\text{H}^2\text{H}^{16}\text{O}_{\text{aq}}}/X_{\text{H}_2^{16}\text{O}_1}} = \frac{a_{\text{H}^2\text{H}^{16}\text{O}_{\text{aq}}}/a_{\text{H}_2^{16}\text{O}_1}}{n_{\text{H}^2\text{H}^{16}\text{O}_{\text{aq}}}/n_{\text{H}_2^{16}\text{O}_1}}, \text{ or} \quad (90)$$

$$\begin{aligned} a_{\text{H}^2\text{H}^{16}\text{O}_{\text{aq}}} &= a_{\text{H}_2^{16}\text{O}_1} \left(\frac{n_{\text{H}^2\text{H}^{16}\text{O}_{\text{aq}}}}{n_{\text{H}_2^{16}\text{O}_1}} \right) \Gamma = a_{\text{H}_2^{16}\text{O}_1} \left(\frac{m_{\text{H}^2\text{H}^{16}\text{O}_{\text{aq}}}}{55.56} \right) \Gamma \\ &= \left(a_{\text{H}_2^{16}\text{O}_1} \left(\frac{1}{55.56} \right) \Gamma \right) m_{\text{H}^2\text{H}^{16}\text{O}_{\text{aq}}}. \end{aligned} \quad (91)$$

Comparing Eqns. 91 and 88 shows that if the isotope salt effects are included, the activity coefficients for the waterlike species are

$$\gamma_i = a_{\text{H}_2^{16}\text{O}_1} \left(\frac{1}{55.56} \right) \Gamma. \quad (92)$$

Implementing Eqn. 92 in PHREEQC poses problems. Values of Γ are known for single salts (NaCl , MgCl_2 , Na_2SO_4 , etc.) or pairs of single salts as functions of concentration and temperature (Horita et al., 1993a,b; 1995). A general formulation in terms of activities of individual ions and ion pairs, as needed for PHREEQC, is unavailable. Values of Γ range from 1.0 for pure water to ~ 1.012 for $^1\text{H}^2\text{H}^{16}\text{O}_{\text{aq}}$ and ~ 0.998 for $^1\text{H}_2^{18}\text{O}_{\text{aq}}$ in solutions with ionic strengths up to 9.

3.6.2. Activity Coefficient Ratios

Ratios of activity coefficients appear in all of the equations used to calculate the individual isotope equilibrium constants. For example, in the equations (T&P, their table 2) for $\log K_{\text{H}^2\text{H}_2^{16}\text{O}_{\text{aq}}^+}$, $\log K_{\text{H}_2^{16}\text{O}_{\text{aq}}}$, and $\log K_{\text{Ca}^{12}\text{C}^{16}\text{O}_1^{18}\text{O}_{2\text{s}}}$ are found the terms $\log(\gamma_{\text{H}^2\text{H}_2^{16}\text{O}_{\text{aq}}^+}/\gamma_{\text{H}_2^{16}\text{O}_{\text{aq}}})_{\text{exp}}$, $\log(\gamma_{\text{H}_2^{16}\text{O}_{\text{aq}}}^4/\gamma_{\text{H}_2^{16}\text{O}_{\text{aq}}}^4)$, and $\log(\lambda_{\text{Ca}^{12}\text{C}^{16}\text{O}_1^{18}\text{O}_{2\text{s}}}/\lambda_{\text{Ca}^{12}\text{C}^{16}\text{O}_1^{18}\text{O}_{2\text{s}}})_{\text{exp}}$, respectively. In all cases, the ratios are of activity coefficients for different isotopic species of the same molecule in the same phase. The differences in molecular energies between different molecules are provided by the measured fractionation factors. The interaction of each isotopic species of a particular molecule with its chemical environment is expressed by the activity coefficient, which is assumed to be independent of the mass of the species. The PHREEQC aqueous model is an ion-association model in which the activity coefficients of aqueous species are based on the electrostatic-interaction extended Debye-Hückel equation

$$-\log \gamma_i = \frac{Az_i^2 \mu^{1/2}}{1 + a_i B \mu^{1/2}}, \quad (93)$$

where A and B are constants at a given temperature, z_i is the charge of species i , a_i is an ion-size parameter for species i , and μ is the ionic strength. There is no explicit mass dependence in the derivation of this equation or in the constants (Lewis and

Randall, 1961, pp. 332–343). PHREEQC also permits use of the WATEQ Debye-Hückel equation (Truesdell and Jones, 1974) and the Davies equation (Davies, 1962), which are empirical variations of Eqn. 93, and also contain no explicit mass dependence. Thus to the degree that this model represents the important physical processes, there is no mass dependence in the activity coefficients of the solutes. The absence of mass dependence for the activity coefficients of gases and solids is an arbitrary assumption.

The activity-coefficient terms in Eqns. 35, 40, 45, 51, 54, 62, and 71 (and in all equilibrium constants in T&P, their table 2) are thus assumed at present to be unity, their logarithms are zero, and the activity coefficient ratios are, in the absence of conflicting information, independent of concentration. Within the framework of this assumption isotope effects should not be a function solely of ionic strength, although there might be a slight interdependence through the fact that the distribution of isotopic species, some of which are ionic, can have an effect on the ionic strength. There is a potential concentration dependence in the isotope salt effect, but at present Γ can only be calculated for a total salt concentrations, or perhaps estimated as a function of ionic strength. In either case it will cancel in the activity coefficient ratios. Although the activity-coefficient terms are not implemented in the calculation of the individual isotope equilibrium constants, the terms have been included in the derivations for completeness in the event that further analysis or information allows calculation of the activity-coefficient ratios.

It should also be noted that the formalism of activity-concentration relations was not included in the definitions of the intraspecies equilibrium constants (Eqns. 2–16) because its inclusion would not permit the algebraic simplification leading to Eqns. 19 and 24. The requirements that this places on the activity coefficients is that ratios of activity coefficients of isotopic variants of the same molecule in the same phase must be equal. To be exact, Eqn. 14 in the aqueous phase, for example, requires that

$$\frac{\gamma_{\text{H}_2^{16}\text{O}_{\text{aq}}}}{\gamma_{\text{H}_2^{18}\text{O}_{\text{aq}}}} = \frac{\gamma_{\text{H}_2^{16}\text{O}_{\text{aq}}}}{\gamma_{\text{H}_2^{18}\text{O}_{\text{aq}}}} \quad (94a)$$

and

$$\frac{\gamma_{\text{H}_2^{16}\text{O}_{\text{aq}}}}{\gamma_{\text{H}_2^{18}\text{O}_{\text{aq}}}} = \frac{\gamma_{\text{H}_2^{16}\text{O}_{\text{aq}}}}{\gamma_{\text{H}_2^{18}\text{O}_{\text{aq}}}} \quad (94b)$$

The activity coefficients and their ratios do not need to be unity. Note that Eqn. 94 is satisfied, for example, by $\gamma_{\text{H}_2^{18}\text{O}_{\text{aq}}} = 0.5$, $\gamma_{\text{H}_2^{16}\text{O}_{\text{aq}}} = 1.0$, $\gamma_{\text{H}_2^{18}\text{O}_{\text{aq}}} = 2.0$, and $\gamma_{\text{H}_2^{16}\text{O}_{\text{aq}}} = 4.0$.

4. INDIVIDUAL ISOTOPE EQUILIBRIUM CONSTANTS FOR OTHER REACTIONS

4.1. Individual Isotope Equilibrium Constants for Ion Pairs

The method for calculating individual isotope equilibrium constants for ion pairs is presented for completeness, recognizing that isotope fractionation data do not exist at present for this application. Reactions are written from the free ion to the corresponding ion pair (rather than from $\text{CO}_{2\text{aq}}$, for example) because the algebra is greatly simplified. The assumption is

made throughout that the symmetry numbers for the ions in ion pairs are the same as those for the free ions, based largely on the fact that Bottinga (1968) used this assumption successfully in calculating partition functions for solid calcite. The $\text{Ca}^{13}\text{C}^{18}\text{O}_{3\text{aq}}^0$ ion pair is used for the following example.

The isotope ratios for the ion pairs are equivalent to those of the free ions, given the assumption of equal symmetry numbers. The isotope ratios of the species appropriate to this calculation are (from T&P, their table 1):

$$R_{\text{CO}_{3\text{aq}}^{-2}}^{18\text{O}} = \left(\frac{n_{12}\text{C}^{18}\text{O}_{3\text{aq}}^{-2}}{n_{12}\text{C}^{16}\text{O}_{3\text{aq}}^{-2}} \right)^{1/3} = \left(\frac{n_{13}\text{C}^{18}\text{O}_{3\text{aq}}^{-2}}{n_{13}\text{C}^{16}\text{O}_{3\text{aq}}^{-2}} \right)^{1/3} \quad (95)$$

and

$$R_{\text{CO}_{3\text{aq}}^{-2}}^{13\text{C}} = \frac{n_{13}\text{C}^{16}\text{O}_{3\text{aq}}^{-2}}{n_{12}\text{C}^{16}\text{O}_{3\text{aq}}^{-2}},$$

and

$$R_{\text{CaCO}_{3\text{aq}}^0}^{18\text{O}} = \left(\frac{n_{\text{Ca}^{12}\text{C}^{18}\text{O}_{3\text{aq}}^0}}{n_{\text{Ca}^{12}\text{C}^{16}\text{O}_{3\text{aq}}^0}} \right)^{1/3} = \left(\frac{n_{\text{Ca}^{13}\text{C}^{18}\text{O}_{3\text{aq}}^0}}{n_{\text{Ca}^{13}\text{C}^{16}\text{O}_{3\text{aq}}^0}} \right)^{1/3}$$

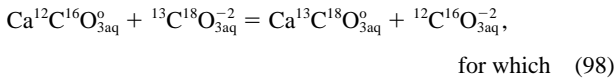
and

$$R_{\text{CaCO}_{3\text{aq}}^0}^{13\text{C}} = \frac{n_{\text{Ca}^{13}\text{C}^{16}\text{O}_{3\text{aq}}^0}}{n_{\text{Ca}^{12}\text{C}^{16}\text{O}_{3\text{aq}}^0}}. \quad (96)$$

The calculations follow the same sequence as presented earlier for the various CO_2 species:

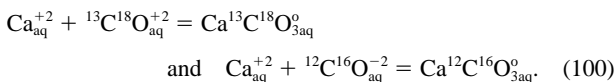
$$\begin{aligned} (\alpha_{\text{CaCO}_{3\text{aq}}^0}^{18\text{O}} - \text{CO}_{3\text{aq}}^{-2})^3 (\alpha_{\text{CaCO}_{3\text{aq}}^0}^{13\text{C}} - \text{CO}_{3\text{aq}}^{-2}) &= \frac{\left(\frac{n_{\text{Ca}^{13}\text{C}^{18}\text{O}_{3\text{aq}}^0}}{n_{\text{Ca}^{13}\text{C}^{16}\text{O}_{3\text{aq}}^0}} \right) \left(\frac{n_{\text{Ca}^{13}\text{C}^{16}\text{O}_{3\text{aq}}^0}}{n_{\text{Ca}^{12}\text{C}^{16}\text{O}_{3\text{aq}}^0}} \right)}{\left(\frac{n_{13}\text{C}^{18}\text{O}_{3\text{aq}}^{-2}}{n_{13}\text{C}^{16}\text{O}_{3\text{aq}}^{-2}} \right) \left(\frac{n_{13}\text{C}^{16}\text{O}_{3\text{aq}}^{-2}}{n_{12}\text{C}^{16}\text{O}_{3\text{aq}}^{-2}} \right)} \\ &= \frac{m_{\text{Ca}^{13}\text{C}^{18}\text{O}_{3\text{aq}}^0} m_{12}\text{C}^{16}\text{O}_{3\text{aq}}^{-2}}{m_{\text{Ca}^{12}\text{C}^{16}\text{O}_{3\text{aq}}^0} m_{13}\text{C}^{18}\text{O}_{3\text{aq}}^{-2}} \quad (97) \end{aligned}$$

The isotope exchange reaction corresponding to Eqn. 97 is



$$\begin{aligned} K_{\text{Ca}^{13}\text{C}^{18}\text{O}_{3\text{aq}}^0}^{\text{ex}} &= \frac{a_{\text{Ca}^{13}\text{C}^{18}\text{O}_{3\text{aq}}^0} a_{12}\text{C}^{16}\text{O}_{3\text{aq}}^{-2}}{a_{\text{Ca}^{12}\text{C}^{16}\text{O}_{3\text{aq}}^0} a_{13}\text{C}^{18}\text{O}_{3\text{aq}}^{-2}} \\ &= \frac{m_{\text{Ca}^{13}\text{C}^{18}\text{O}_{3\text{aq}}^0} m_{12}\text{C}^{16}\text{O}_{3\text{aq}}^{-2} \gamma_{\text{Ca}^{13}\text{C}^{18}\text{O}_{3\text{aq}}^0} \gamma_{12}\text{C}^{16}\text{O}_{3\text{aq}}^{-2}}{m_{\text{Ca}^{12}\text{C}^{16}\text{O}_{3\text{aq}}^0} m_{13}\text{C}^{18}\text{O}_{3\text{aq}}^{-2} \gamma_{\text{Ca}^{12}\text{C}^{16}\text{O}_{3\text{aq}}^0} \gamma_{13}\text{C}^{18}\text{O}_{3\text{aq}}^{-2}}, \text{ or} \\ &= (\alpha_{\text{CaCO}_{3\text{aq}}^0}^{18\text{O}} - \text{CO}_{3\text{aq}}^{-2})^3 (\alpha_{\text{CaCO}_{3\text{aq}}^0}^{13\text{C}} - \text{CO}_{3\text{aq}}^{-2}) \\ &\quad \times \left(\frac{\gamma_{\text{Ca}^{13}\text{C}^{18}\text{O}_{3\text{aq}}^0} \gamma_{12}\text{C}^{16}\text{O}_{3\text{aq}}^{-2}}{\gamma_{\text{Ca}^{12}\text{C}^{16}\text{O}_{3\text{aq}}^0} \gamma_{13}\text{C}^{18}\text{O}_{3\text{aq}}^{-2}} \right)_{\text{exp}}. \quad (99) \end{aligned}$$

The reactions used in PHREEQC are



$$\begin{aligned} K_{\text{Ca}^{13}\text{C}^{18}\text{O}_{3\text{aq}}^0}^{\text{ex}} &= \frac{a_{\text{Ca}^{13}\text{C}^{18}\text{O}_{3\text{aq}}^0} a_{12}\text{C}^{16}\text{O}_{3\text{aq}}^{-2}}{a_{\text{Ca}^{12}\text{C}^{16}\text{O}_{3\text{aq}}^0} a_{13}\text{C}^{18}\text{O}_{3\text{aq}}^{-2}} \\ &= \frac{a_{\text{Ca}^{13}\text{C}^{18}\text{O}_{3\text{aq}}^0} a_{\text{Ca}^{+2}\text{a}_{12}\text{C}^{16}\text{O}_{3\text{aq}}^{-2}}}{a_{\text{Ca}^{+2}\text{a}_{13}\text{C}^{18}\text{O}_{3\text{aq}}^{-2}} a_{\text{Ca}^{12}\text{C}^{16}\text{O}_{3\text{aq}}^0}} \\ &= \frac{K_{\text{Ca}^{13}\text{C}^{18}\text{O}_{3\text{aq}}^0}}{K_{\text{Ca}^{12}\text{C}^{16}\text{O}_{3\text{aq}}^0}}, \quad (101) \end{aligned}$$

$$\begin{aligned} K_{\text{Ca}^{13}\text{C}^{18}\text{O}_{3\text{aq}}^0} &= K_{\text{Ca}^{12}\text{C}^{16}\text{O}_{3\text{aq}}^0} (\alpha_{\text{CaCO}_{3\text{aq}}^0}^{18\text{O}} - \text{CO}_{3\text{aq}}^{-2})^3 (\alpha_{\text{CaCO}_{3\text{aq}}^0}^{13\text{C}} - \text{CO}_{3\text{aq}}^{-2}) \\ &\quad \times \left(\frac{\gamma_{\text{Ca}^{13}\text{C}^{18}\text{O}_{3\text{aq}}^0} \gamma_{12}\text{C}^{16}\text{O}_{3\text{aq}}^{-2}}{\gamma_{\text{Ca}^{12}\text{C}^{16}\text{O}_{3\text{aq}}^0} \gamma_{13}\text{C}^{18}\text{O}_{3\text{aq}}^{-2}} \right)_{\text{exp}}, \quad (102) \end{aligned}$$

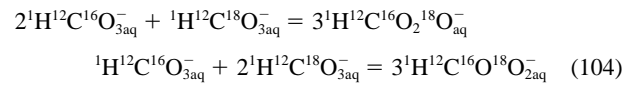
$$\begin{aligned} \log K_{\text{Ca}^{13}\text{C}^{18}\text{O}_{3\text{aq}}^0} &= \log K_{\text{Ca}^{12}\text{C}^{16}\text{O}_{3\text{aq}}^0} + 3 \log (\alpha_{\text{CaCO}_{3\text{aq}}^0}^{18\text{O}} - \text{CO}_{3\text{aq}}^{-2}) \\ &\quad + \log (\alpha_{\text{CaCO}_{3\text{aq}}^0}^{13\text{C}} - \text{CO}_{3\text{aq}}^{-2}) + \log \left(\frac{\gamma_{\text{Ca}^{13}\text{C}^{18}\text{O}_{3\text{aq}}^0} \gamma_{12}\text{C}^{16}\text{O}_{3\text{aq}}^{-2}}{\gamma_{\text{Ca}^{12}\text{C}^{16}\text{O}_{3\text{aq}}^0} \gamma_{13}\text{C}^{18}\text{O}_{3\text{aq}}^{-2}} \right)_{\text{exp}}. \quad (103) \end{aligned}$$

The form of any individual isotope equilibrium constant for ion pairs, if written from the free ions, will have the same form as Eqn. 103, with the logarithm of each fractionation factor multiplied by its stoichiometric coefficient in the free ion.

4.2. Individual Isotope Equilibrium Constants for Reactions of Bicarbonate Ion

The bicarbonate ion is asymmetric, with symmetry number 1 for all species. The algebra required to express the isotope ratios for bicarbonate is tedious, and too lengthy for presentation here (T&P provide the complete equations). Because of the algebraic complexity, a numerical method was used for the bicarbonate ion, and is discussed below.

Because all symmetry numbers are 1, the equilibrium constants of the intraspecies reactions (Eqn. 104) are unity, as shown in Eqn. 105:



$$1 = \frac{n_{1\text{H}^{12}\text{C}^{16}\text{O}_2{}^1\text{H}^{18}\text{O}_{2\text{aq}}^-}}{n_{1\text{H}^{12}\text{C}^{18}\text{O}_{3\text{aq}}^-} n_{1\text{H}^{12}\text{C}^{16}\text{O}_{3\text{aq}}^-}} = 1 = \frac{n_{1\text{H}^{12}\text{C}^{16}\text{O}^1\text{H}^{18}\text{O}_{2\text{aq}}^-}}{n_{1\text{H}^{12}\text{C}^{18}\text{O}_{3\text{aq}}^-} n_{1\text{H}^{12}\text{C}^{16}\text{O}_{3\text{aq}}^-}}. \quad (105)$$

There are three oxygen atoms in bicarbonate; thus, if the n^1 relation held, the intraspecies equilibrium constants would equal 27, and the isotope ratios, like those for the carbonate ion, would simplify to analogs of Eqns. 19 and 24. However, with $K = 1$ the terms do not cancel and the fractionation factor can no longer be expressed simply in terms of a concentration-based equilibrium constant for an isotope exchange reaction. Molality terms for individual ions still remain in the equations, and, as shown by T&P, the three primary individual isotope equilibrium constants for the reaction of $\text{CO}_{2\text{aq}}$ to $\text{HCO}_{3\text{aq}}^-$ are

$$\begin{aligned} \log K_{1\text{H}^{12}\text{C}^{16}\text{O}_2{}^1\text{H}^{18}\text{O}_{2\text{aq}}^-} &= \log K_{1\text{H}^{12}\text{C}^{16}\text{O}_{3\text{aq}}^-} + \log(1.5) \\ &\quad + \log (\alpha_{\text{HCO}_{3\text{aq}}^-}^{18\text{O}} - \text{CO}_{2\text{aq}}) + \log(\text{QQ1}) \\ &\quad + \log \left(\frac{\gamma_{1\text{H}^{12}\text{C}^{16}\text{O}_2{}^1\text{H}^{18}\text{O}_{2\text{aq}}^-} \gamma_{12}\text{C}^{16}\text{O}_{2\text{aq}}}{\gamma_{1\text{H}^{12}\text{C}^{16}\text{O}_{3\text{aq}}^-} \gamma_{12}\text{C}^{16}\text{O}_{18\text{O}_{2\text{aq}}^-}} \right)_{\text{exp}}, \quad (106) \end{aligned}$$

$$\begin{aligned} \log K_{\text{H}^{12}\text{C}^{16}\text{O}^{18}\text{O}_{2\text{aq}}^-} &= \log K_{\text{H}^{12}\text{C}^{16}\text{O}_{2\text{aq}}^-} + \log(3) \\ &+ 2\log(\alpha_{\text{HCO}_{3\text{aq}}^- - \text{CO}_{2\text{aq}}}) + \log(\text{QQ2}) \\ &+ \log\left(\frac{\gamma_{\text{H}^{12}\text{C}^{16}\text{O}^{18}\text{O}_{2\text{aq}}^-} \gamma_{\text{C}^{16}\text{O}_{2\text{aq}}}}{\gamma_{\text{H}^{12}\text{C}^{16}\text{O}_{3\text{aq}}^-} \gamma_{\text{C}^{18}\text{O}_{2\text{aq}}}}\right)_{\text{exp}}, \quad (107) \end{aligned}$$

and

$$\begin{aligned} \log K_{\text{H}^{12}\text{C}^{18}\text{O}_{3\text{aq}}^-} &= \log K_{\text{H}^{12}\text{C}^{16}\text{O}_{3\text{aq}}^-} - 3\log(2) \\ &+ 3\log(\alpha_{\text{HCO}_{3\text{aq}}^- - \text{CO}_{2\text{aq}}}) \\ &+ \log(\text{QQ3}) + \log\left(\frac{\gamma_{\text{H}^{12}\text{C}^{18}\text{O}_{3\text{aq}}^-} \gamma_{\text{C}^{16}\text{O}_{2\text{aq}}}^3}{\gamma_{\text{H}^{12}\text{C}^{16}\text{O}_{3\text{aq}}^-} \gamma_{\text{C}^{18}\text{O}_{3\text{aq}}^-}^3}\right)_{\text{exp}}, \quad (108) \end{aligned}$$

where QQ1, QQ2, and QQ3 are quadratic functions of $(n_{\text{H}^{12}\text{C}^{16}\text{O}_2^{18}\text{O}_{3\text{aq}}^-} / 3n_{\text{H}^{12}\text{C}^{16}\text{O}_{3\text{aq}}^-})$, $(n_{\text{H}^{12}\text{C}^{16}\text{O}_2^{18}\text{O}_{2\text{aq}}^-} / 3n_{\text{H}^{12}\text{C}^{16}\text{O}_{2\text{aq}}^-})^{1/2}$, and $(n_{\text{H}^{12}\text{C}^{18}\text{O}_{3\text{aq}}^-} / n_{\text{H}^{12}\text{C}^{16}\text{O}_{3\text{aq}}^-})^{1/3}$, respectively. The three QQ factors are thus nonlinear functions of the calculated species distributions in PHREEQC simulations.

Values for the three parameters— $\log(\text{QQ1})$, $\log(\text{QQ2})$, and $\log(\text{QQ3})$ —were evaluated numerically by using UCODE (Poeter and Hill, 1998). Initial estimates for the QQ factors were used to calculate values of $\log K_{\text{H}^{12}\text{C}^{16}\text{O}_2^{18}\text{O}_{2\text{aq}}^-}$, $\log K_{\text{H}^{12}\text{C}^{16}\text{O}_2^{18}\text{O}_{3\text{aq}}^-}$, and $\log K_{\text{H}^{12}\text{C}^{18}\text{O}_{3\text{aq}}^-}$. An aqueous solution containing 10 mmol of carbon (^{12}C) at pH 6.3 and water with $\delta^{18}\text{O} = 0$ permil was speciated using the $\log K$ values. From the distribution of aqueous species, the fractionation factor $\alpha_{\text{HCO}_{3\text{aq}}^- - \text{CO}_{2\text{aq}}}$ and the quotients for equation 105 were calculated. UCODE was used to adjust the QQ factors until the calculated fractionation factor was equal to the assumed value of 1.0, and the quotients for equation 105 were equal to 1.0, the symmetry-derived equilibrium constants. The results are the values listed below for $\delta^{18}\text{O} = 0$.

The fractionation factor $\alpha_{\text{HCO}_{3\text{aq}}^- - \text{CO}_{2\text{aq}}}$ depends on the system oxygen-isotope composition because the expressions for the isotope ratios do not simplify. Values of the bicarbonate equilibrium constant were calculated as above for ^{18}O concentrations corresponding to $\delta^{18}\text{O} = \text{VSMOW} \pm 100$ permil, based on the $^{18}\text{O}/^{16}\text{O}$ isotope abundance ratio $R_{\text{VSMOW}} = 2.0052 \times 10^{-3}$ (Baertschi, 1976; Coplen et al., 2002). The values of the QQ factors for $\delta^{18}\text{O} = \text{VSMOW} \pm 100\text{‰}$ are also tabulated below.

$\delta^{18}\text{O}$ (permil)	$\log(\text{QQ1})$	$\log(\text{QQ2})$	$\log(\text{QQ3})$
+100	-3.9786×10^{-3}	0.46916	1.4194
0.0	-3.6178×10^{-3}	0.46989	1.4205
-100	-3.2568×10^{-3}	0.47061	1.4216

The variation is small, and the values calculated for R_{VSMOW} are used throughout this paper.

5. APPLICATION TO OTHER ISOTOPES

The methods described above can be readily extended to other molecular and isotopic species. The first, and most laborious, step in deriving the individual isotope equilibrium

constants is the derivation of the various expressions of the isotope ratios for each molecular species. However, if the new molecular species has the same stoichiometry and symmetry (identical structure is not required) as a species for which the isotope ratios have already been calculated, the new ratios can be written by inspection. The isotope ratios for H_2O , for example, can be obtained from the ratios for CO_2 by substituting throughout equations 19 and 24 the isotopes of O in H_2O for the isotopes of C in CO_2 and H_2 in H_2O for O_2 in CO_2 . The isotope ratios of H_2O and CO_2 are algebraically equivalent with these substitutions. Listed below are symmetry numbers and the corresponding species from T&P. On the right side of the list, other species of the same stoichiometry whose isotope ratios can be obtained by analogy are in parentheses, and species of differing stoichiometry for which derivations have not been done by T&P are in curly brackets. The molecular structures from which the symmetry numbers were obtained are from Wells (1984) and Purdue University (2002).

$\sigma = 1$	OH^-	(CO NO)
	HCO_3^-	(HNO_3)
		{NNO HSO_4^- }
$\sigma = 2$	$\text{CO}_2 \text{H}_2\text{O}$	($\text{H}_2\text{S NO}_2 \text{NO}_2^-$)
		{ $\text{H}_2 \text{N}_2 \text{O}_2$ }
$\sigma = 3$	H_3O^+	(NH_3)
$\sigma = 6$	$\text{CO}_3^{2-} \text{CaCO}_3$	(NO_3^-)
$\sigma = 12$	none	{ $\text{CH}_4 \text{SO}_4^{2-} \text{NH}_4^+$ }

For the undervied species, the procedure is analogous to Eqns. 2–24 for CO_2 —calculation of the intraspecies equilibrium constants and substitution of these, for each species in turn, into the equations for the isotope ratios. The algebra becomes more cumbersome as the number of atoms of polyatomic elements increases, but as long as these atoms are structurally equivalent in the molecular species, the Urey relation (Eqn. 109) will be obtained as one of the isotope ratio expressions:

$$R_{\text{AB}_j}^i = \left(\frac{n_{\text{A}^i\text{B}_j}}{n_{\text{A}^k\text{B}_j}} \right)^{1/j}, \quad (109)$$

where ^iB is the isotope of element B of mass i in species AB_j , and ^kB is the most abundant isotope.

Calculation of the individual isotope equilibrium constants, once the isotope ratios are available, is more straightforward and is analogous to Eqn. 25–54 for CO_2 . The calculations require selection of the appropriate fractionation factors to provide isotope ratios for the species in the desired reactions, expression of these ratios as a concentration-based isotope exchange reaction and equilibrium constant, writing the thermodynamic equilibrium constant for the exchange reaction, and using the exchange reaction to define a ratio of PHREEQC reactions. The PHREEQC reactions can be of any type—association or dissociation, dissolution or precipitation, and acid-base or redox—because the activities of all species other than those in the isotope exchange reaction are introduced to both the numerator and denominator of the equilibrium constant for the isotope exchange reaction, and thus algebraically cancel in the exchange reaction equilibrium constant expression.

6. COMPARISON OF METHODS

Isotope calculations have been combined with geochemical reaction-path-modeling in earlier studies. Cheng and Long (1984) used the equations of Deines et al. (1974) and Wigley et al. (1978) in a subroutine to the reaction-path modeling program PHREEQE (Parkhurst et al., 1980). Bowers and Taylor (1985) applied equations for conservation of isotopic mass after each reaction increment in the geochemical reaction-path modeling program EQ3/6 (Wolery, 1978, 1979, 1983) to compute the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of fluid and mineral phases as a function of reaction progress. Similar equations were applied by Janecky and Shanks (1988) to sulfur isotopes, using EQ3/6, and by Bowers (1989) to ^{18}O , ^2H , and ^{34}S , also using EQ3/6. Böhlke and Shanks (1994) expanded the equations of Bowers and Taylor (1985) to include calculation of isotope effects in aqueous species and gases. The equations were applied as a post-processor to the reaction-modeling program CHILLER (Reed, 1982; Spycher and Reed, 1989). Lee (1993), Lee and Bethke (1996), and Bethke (1996) also extend the isotope-balance equations to include aqueous species and gases, by using a postprocessor to the program React (Bethke, 1996). Plummer et al. (1991, 1994) use the equations of Wigley et al. (1978, 1979) in the program NETPATH to solve Rayleigh calculations for reaction moletransfers determined by inverse modeling.

The term “postprocessor” is used in the following discussion to refer to any method, as in the above references, that performs the chemical and isotopic calculations separately. This definition is used whether the isotope calculations are applied after each individual step in a reaction-modeling calculation, after completion of an entire reaction-modeling calculation, or after reactions are determined by inverse modeling.

The method presented in this report differs fundamentally from that of the postprocessor calculations, although in practice both methods will yield isotopic speciation calculations that are indistinguishable in many natural systems. Calculation of the species distribution between $\text{CO}_{2\text{g}}$ and $\text{CO}_{2\text{aq}}$ can again be used for illustration. For ^{13}C , initially ignoring ^{18}O , at the completion of a species-distribution calculation, the postprocessor method uses the speciation-calculated values of $\text{CO}_{2\text{aq,tot}}$ and $\text{CO}_{2\text{g,tot}}$, the fractionation factor $\alpha_{\text{CO}_{2\text{aq}}-\text{CO}_{2\text{g}}}^{13\text{C}}$, and an isotope balance equation using $\delta^{13}\text{C}_{\text{system,tot}}$ (or more rigorously moles of $^{13}\text{C}_{\text{system,tot}}$) to calculate $\delta^{13}\text{C}_{\text{g,tot}}$ and $\delta^{13}\text{C}_{\text{aq,tot}}$, and thus $R_{\text{CO}_{2\text{g}}}^{13\text{C}}$ and $R_{\text{CO}_{2\text{aq}}}^{13\text{C}}$. Once $R_{\text{CO}_{2\text{g}}}^{13\text{C}}$ and $R_{\text{CO}_{2\text{aq}}}^{13\text{C}}$ are known simple mass-balance equations (110) allow calculation of the concentrations of $^{12}\text{C}^{16}\text{O}_{2\text{g}}$, $^{12}\text{C}^{16}\text{O}_{2\text{aq}}$, $^{13}\text{C}^{16}\text{O}_{2\text{g}}$, and $^{13}\text{C}^{16}\text{O}_{2\text{aq}}$:

$$\text{CO}_{2\text{g,tot}} = {}^{12}\text{C}^{16}\text{O}_{2\text{g}}(1 + R_{\text{CO}_{2\text{g}}}^{13\text{C}}) \\ \text{and } {}^{13}\text{C}^{16}\text{O}_{2\text{g}} = {}^{12}\text{C}^{16}\text{O}_{2\text{g}}(R_{\text{CO}_{2\text{g}}}^{13\text{C}}). \quad (110)$$

The thermodynamic model based on individual isotope equilibrium constants calculates values of $K_{12^{12}\text{C}^{16}\text{O}_{2\text{aq}}}^{\text{H}} = a_{12^{12}\text{C}^{16}\text{O}_{2\text{aq}}}/a_{12^{12}\text{C}^{16}\text{O}_{2\text{g}}}$ and $K_{13^{13}\text{C}^{16}\text{O}_{2\text{aq}}}^{\text{H}} = a_{13^{13}\text{C}^{16}\text{O}_{2\text{aq}}}/a_{13^{13}\text{C}^{16}\text{O}_{2\text{g}}}$, which are derived from the relation $\alpha_{\text{CO}_{2\text{aq}}-\text{CO}_{2\text{g}}}^{\text{H}} = K_{13^{13}\text{C}^{16}\text{O}_{2\text{aq}}}^{\text{H}}/K_{12^{12}\text{C}^{16}\text{O}_{2\text{aq}}}^{\text{H}}$, and uses the two individual isotope equilibrium constants in the species-distribution calculation to obtain concentrations of $^{12}\text{C}^{16}\text{O}_{2\text{g}}$, $^{12}\text{C}^{16}\text{O}_{2\text{aq}}$, $^{13}\text{C}^{16}\text{O}_{2\text{g}}$, and $^{13}\text{C}^{16}\text{O}_{2\text{aq}}$.

Both methods can be expanded to include mixed isotope species by using Eqns. 2–24. This paper uses Eqns. 2–24 to derive Eqns. 25–71, thus providing the individual isotope equi-

librium constants that permit the complete species-distribution calculation.

To calculate the complete species-distribution, the postprocessor method would again use the model-derived values of $\text{CO}_{2\text{aq,tot}}$ and $\text{CO}_{2\text{g,tot}}$, the fractionation factor $\alpha_{\text{CO}_{2\text{aq}}-\text{CO}_{2\text{g}}}^{13\text{C}}$, and an isotope-balance equation using $\delta^{13}\text{C}_{\text{system,tot}}$ (or more rigorously, moles of $^{13}\text{C}_{\text{system,tot}}$), to calculate $\delta^{13}\text{C}_{\text{g,tot}}$ and $\delta^{13}\text{C}_{\text{aq,tot}}$, and thus $R_{\text{CO}_{2\text{g}}}^{13\text{C}}$ and $R_{\text{CO}_{2\text{aq}}}^{13\text{C}}$. A mass-balance equation can then be written for each phase:

$$n_{\text{CO}_{2\text{g,tot}}} = n_{12^{12}\text{C}^{16}\text{O}_{2\text{g}}} + n_{12^{12}\text{C}^{16}\text{O}^{18}\text{O}_2} + n_{12^{12}\text{C}^{18}\text{O}_{2\text{g}}} \\ + n_{13^{13}\text{C}^{16}\text{O}_{2\text{g}}} + n_{13^{13}\text{C}^{16}\text{O}^{18}\text{O}_2} + n_{13^{13}\text{C}^{18}\text{O}_{2\text{g}}}. \quad (111)$$

The values of $\delta^{13}\text{C}_{\text{CO}_{2\text{g}}}$ are known, thus defining $R_{\text{CO}_{2\text{g}}}^{13\text{C}}$. Using Eqns. 19 and 24 allows Eqn. 111 to be written

$$n_{\text{CO}_{2\text{g,tot}}} = (n_{12^{12}\text{C}^{16}\text{O}_{2\text{g}}} + n_{12^{12}\text{C}^{16}\text{O}^{18}\text{O}_2} + n_{12^{12}\text{C}^{18}\text{O}_{2\text{g}}})(1 + R_{\text{CO}_{2\text{g}}}^{13\text{C}}). \quad (112)$$

The values of $\delta^{18}\text{O}_{\text{CO}_{2\text{g}}}$ are known, thus defining $R_{\text{CO}_{2\text{g}}}^{18\text{O}}$. Using Eqns. 19 and 24 allows Eqn. 112 to be written as

$$n_{\text{CO}_{2\text{g,tot}}} = n_{12^{12}\text{C}^{16}\text{O}_{2\text{g}}} (1 + 2R_{\text{CO}_{2\text{g}}}^{18\text{O}} + [R_{\text{CO}_{2\text{g}}}^{18\text{O}}]^2)(1 + R_{\text{CO}_{2\text{g}}}^{13\text{C}}) \\ = n_{12^{12}\text{C}^{16}\text{O}_{2\text{g}}} (1 + R_{\text{CO}_{2\text{g}}}^{18\text{O}})^2(1 + R_{\text{CO}_{2\text{g}}}^{13\text{C}}), \quad (113)$$

which allows calculation of $n_{12^{12}\text{C}^{16}\text{O}_{2\text{g}}}$. Equations 19 and 24 then allow calculation of the remaining CO_2 isotopic species.

There are fundamental differences in the calculation sequences of the two methods. In the postprocessor method the distribution of CO_2 between phases that precedes the isotopic speciation is based on the single Henry’s Law constant for $\text{CO}_{2\text{tot}}$, which is slightly different from the individual Henry’s Law constants (Eqn. 78). Using the individual isotope method, the calculated distribution is species-specific, but assumptions have been made in obtaining the individual Henry’s Law constant from existing thermochemical data. Either $K_{12^{12}\text{C}^{16}\text{O}_{2\text{aq}}}^{\text{H}}$ is assumed to equal $K_{\text{CO}_{2\text{aq,tot}}}^{\text{H}}$, or Eqn. 78 is used to calculate $K_{12^{12}\text{C}^{16}\text{O}_{2\text{aq}}}^{\text{H}}$, which requires assumptions about the isotope ratios of the CO_2 used in the experiments. If the standard thermochemical data were determined on substances of known isotopic composition, there would be no assumptions needed for the individual isotope equilibrium constant method. The numerical difference between the two methods would appear to be unimportant for speciation in any single iteration; whether this is so in extended reaction/transport calculations has not been determined in general.

Kinetic fractionation can be treated in both methods by introducing different values of the fractionation factors. Both methods would calculate this as an equilibrium fractionation to a different extent—the postprocessor explicitly through the direct use of the fractionation factors in equations, the individual isotope method implicitly through recalculation of the necessary equilibrium constants from the new values of the fractionation factors. The individual isotope approach, as implemented in PHREEQC, could, with additional work, treat kinetic fractionation processes in terms of relative forward and backward reaction rates.

The most obvious difference between the two methods is operational. To initiate isotope calculations, or to add new isotopic species, the postprocessor method requires that relatively simple computer programming be added to the reaction

modeling code. The individual isotope method requires that new data—definition of elements, species, and equilibrium constants—be added to the existing database, and that solid solutions can be treated adequately. Both methods require appropriate input/output coding for isotopic information.

The advantages of the extra algebra for the individual isotope method described in this paper are that reaction and isotope calculations are performed simultaneously, and that the total isotopic species distribution is obtained. For isotopic phase equilibria or kinetic studies that require a knowledge of the relative free energies of formation of individual isotopic species, the individual isotope equilibrium constants appear to be a necessity. Investigation, for example, of the dependence of the isotopic composition of precipitated calcite on the relative degree of supersaturation of the aqueous phase with respect to solid-phase components such as $\text{Ca}^{12}\text{C}^{16}\text{O}_{3\text{s}}$ and $\text{Ca}^{13}\text{C}^{16}\text{O}_{3\text{s}}$ would require the equations of the individual isotope method because the necessary aqueous ion activity products could only be calculated from a knowledge of the equilibrium constants for the dissolution reactions of the individual solid solution components, and the species distribution in the aqueous phase. This saturation-state study would be a subset of a potentially more general investigation of the degree to which stoichiometric saturation (Thorstenson and Plummer, 1977; Glynn and Reardon, 1990) plays a role in solid solutions of isotopic species. Another area of potential research that would require the individual isotope method is further investigation of salt effects on fractionation in terms not only of the effects of electrolyte concentration and ionic strength, but in terms of ion pair effects. Would, for example, ^{13}C fractionation in a highly associated uranyl carbonate solution be different from the ^{13}C fractionation in KCl solutions?

Another calculation that requires the speciation capability of the individual isotope approach is that of mass-dependent transport phenomena. Cerling (1984), for example, published equations depicting the steady-state relationship between the ^{13}C content of soil-resident CO_2 , the ^{13}C content of soil-respired CO_2 , the CO_2 respiration rate, and soil-zone depth. Parkhurst et al. (2000) made these calculations numerically with an early implementation of the individual isotope equations in PHREEQC. The numerical simulation, when carried to steady-state, matched the Cerling equations exactly. In addition, Parkhurst et al. (2000) were able to evaluate the effects of pore water composition, equilibrium with solids, and time dependence.

A second comparison with analytical results of fractionation calculations is provided by inverse modeling, as used in the code NETPATH (Plummer et al., 1994). NETPATH calculates fractionation factors analytically by applying the equations of Wigley et al. (1978) to mass transfers between phases obtained by inverse modeling. These are exact analytical solutions within the assumptions of the equations. In the process of preparing T&P, comparisons were made between calculations by NETPATH and the version of PHREEQC used in Parkhurst et al. (2000) for two geochemical reactions. The reactions, selected for conditions that adhere closely to the assumptions of the Wigley et al. (1978) equations, were (a) evasion of 25 mmol of dissolved CO_2 from a solution at pH = 2, and (b) reduction of 5 mmol of dissolved sulfate by organic carbon at neutral pH, maintaining equilibrium with calcite and a gas phase. Values of

Table 1. Logarithms of the molality, activity, and partial pressure of selected isotopic species of CO_2 and H_2O calculated in the PHREEQC example.

Aqueous species	Log molality	Log activity	Log partial pressure (atm)	Gaseous species
$^1\text{H}_2\text{}^{16}\text{O}_1$	+1.745	-0.001	-1.51	$^1\text{H}_2\text{}^{16}\text{O}_g$
$^1\text{H}^2\text{H}^{16}\text{O}_{\text{aq}}$	-1.762	-3.508	-5.05	$^1\text{H}^2\text{H}^{16}\text{O}_g$
$^2\text{H}_2\text{}^{16}\text{O}_{\text{aq}}$	-5.870	-7.616	-9.19	$^2\text{H}_2\text{}^{16}\text{O}_g$
$^1\text{H}_2\text{}^{18}\text{O}_{\text{aq}}$	-0.953	-2.699	-4.21	$^1\text{H}_2\text{}^{18}\text{O}_g$
$^1\text{H}^2\text{H}^{18}\text{O}_{\text{aq}}$	-4.460	-6.205	-7.75	$^1\text{H}^2\text{H}^{18}\text{O}_g$
$^2\text{H}_2\text{}^{18}\text{O}_{\text{aq}}$	-8.568	-10.314	-11.89	$^2\text{H}_2\text{}^{18}\text{O}_g$
$^{12}\text{C}^{16}\text{O}_{2\text{aq}}$	-4.974	-4.973	-3.51	$^{12}\text{C}^{16}\text{O}_{2g}$
$^{12}\text{C}^{16}\text{O}^{18}\text{O}_{\text{aq}}$	-7.353	-7.352	-5.88	$^{12}\text{C}^{16}\text{O}^{18}\text{O}_g$
$^{12}\text{C}^{18}\text{O}_{2\text{aq}}$	-10.334	-10.333	-8.87	$^{12}\text{C}^{18}\text{O}_{2g}$
$^{13}\text{C}^{16}\text{O}_{2\text{aq}}$	-6.929	-6.928	-5.46	$^{13}\text{C}^{16}\text{O}_{2g}$
$^{13}\text{C}^{16}\text{O}^{18}\text{O}_{\text{aq}}$	-9.308	-9.307	-7.84	$^{13}\text{C}^{16}\text{O}^{18}\text{O}_g$
$^{13}\text{C}^{18}\text{O}_{2\text{aq}}$	-12.289	-12.288	-10.82	$^{13}\text{C}^{18}\text{O}_{2g}$

$\delta^{13}\text{C}$ and the ^{14}C content in each phase calculated by the two methods agreed within the precision of the calculations for both reactions. The success of these examples does not prove the general case, but does strongly suggest that the individual isotope approach is fundamentally valid.

7. EXAMPLE CALCULATION USING PHREEQC

The example calculates the equilibrium state between an acidic aqueous solution containing dissolved CO_2 and a gas phase consisting of CO_{2g} and H_2O_g . The initial solution composition is specified as pH = 2.0 by addition of HCl, $P_{\text{CO}_{2\text{aq,tot}}} = 10^{-3.5}$ atm, $\delta_{\text{aqueous phase,tot}}^{18\text{O}} = 0.0$ permil, $\delta_{\text{aqueous phase,tot}}^{2\text{H}} = 0.0$ permil, $\delta_{\text{aqueous phase,tot}}^{13\text{C}} = -7.0$, and $T = 25\text{C}$. Specifying $\delta_{\text{aqueous phase,tot}}^{18\text{O}} = 0.0$ permil, for example, refers to the ^{18}O content of the combined solvent and solute species. The low pH was chosen to minimize the contribution of bicarbonate and carbonate species, leaving the predominant aqueous solute species as $^{12}\text{C}^{16}\text{O}_{2\text{aq}}$ and its isotopic variants. The isotope ratios of the standards are needed to implement the mole balance equations in PHREEQC; those used here are $(^2\text{H}/^1\text{H})_{\text{VSMOW}} = 0.00015576$ and $(^{18}\text{O}/^{16}\text{O})_{\text{VSMOW}} = 0.0020052$, calculated from mole fractions cited in Coplen et al. (2002), and $(^{13}\text{C}/^{12}\text{C})_{\text{VPDB}} = 0.0111802$, calculated from Chang and Li (1990) by using the convention (Coplen, 1994) that $\delta^{13}\text{C}_{\text{NBS 19}} = +1.95\text{‰}$ relative to VPDB.

To calculate the composition of a gas phase in equilibrium with this solution in PHREEQC, 1 kg of the specified solution is equilibrated with 1 μL of initially evacuated gas space. The gas evolution required to fill this small space is small enough that the solution composition is minimally altered. This PHREEQC model contains 49 aqueous species and 12 gaseous species. The molalities, activities, and partial pressures for the 12 volatile aqueous species and their gas counterparts are presented in Table 1. The isotopic composition of the PHREEQC-calculated solution, the PHREEQC-calculated fractionation factors, and the input fractionation factors at 25C are presented in Table 2. The equality of the species-calculated and input

Table 2. Selected isotope ratios and fractionation factors calculated from the species distribution in the PHREEQC example.

Isotope ratio	Ratio	δ (‰) ^a	Fractionation factor ^b	Value of α	1000ln α calculated ^c	1000ln α input ^d
$R_{H_2O_1}^2$	1.55758e-04	-0.0124				
$R_{H_2O_g}^2$	1.44308e-04	-73.525	$\alpha_{H_2O_1 - H_2O_g}^2$	1.0793	76.356	76.356
$R_{H_2O_1}^{18O}$	2.00519e-03	-0.0046				
$R_{H_2O_g}^{18O}$	1.98657e-03	-9.2911	$\alpha_{H_2O_1 - H_2O_g}^{18O}$	1.0094	9.330	9.330
$R_{CO_{2aq}}^{18O}$	2.08958e-03	42.079	$\alpha_{CO_{2aq} - H_2O_1}^{18O}$	1.0421	41.223	41.223
$R_{CO_{2g}}^{18O}$	2.08734e-03	40.963	$\alpha_{CO_{2aq} - CO_{2g}}^{18O}$	1.0011	1.0715	1.0715
$R_{CO_{2aq}}^{13C}$	1.11019e-02	-7.0004				
$R_{CO_{2g}}^{13C}$	1.11113e-02	-6.1668	$\alpha_{CO_{2aq} - CO_{2g}}^{13C}$	0.99916	-0.83913	-0.83913
$R_{aq,total}^D$	1.55760e-04	0.0				
$R_{aq,total}^{18O}$	2.00520e-03	0.0				
$R_{aq,total}^{13C}$	1.11019e-02	7.0000				

^a For an isotope of mass i of element M , delta is defined by $\delta_i^M_{sample} = (R_{sample}^i/R_{standard}^i - 1) 1000$.

^b The fractionation factor between two molecular species A and B is defined by $\alpha_{A-B}^i = (R_A^i/R_B^i)$.

^c Calculated from the species distribution in the PHREEQC model.

^d Calculated from the analytical expression for α used as input to the PHREEQC model.

fractionation factors is a necessary, but not sufficient, condition for the internal consistency of the individual isotope speciation calculation. Two other such criteria are the equality of aqueous and gaseous partial pressures (Table 1) and the equality of the species-calculated and input values of $\delta_{aqueous\ phase,tot}^{18O} = 0.0$ permil, $\delta_{aqueous\ phase,tot}^{2H} = 0.0$ permil, and $\delta_{aqueous\ phase,tot}^{13C} = -7.0$ permil (Table 2). The analytical expressions for the fractionation factors are presented in Table 3.

The results in Table 2 show the expected isotopic behavior. For H_2O the vapor phase is substantially depleted in ^{18}O and 2H relative to the aqueous phase, as shown by the isotope ratios and delta values in Table 2. For CO_2 the gas-phase species are also depleted in ^{18}O , but are slightly enriched in ^{13}C , an often-unappreciated phenomenon in acidic solutions.

8. SUMMARY AND CONCLUSIONS

The Urey relationship $\alpha = (K^{ex})^{1/n}$, where n is the number of atoms exchanged in an exchange reaction for a single isotope,

has been extended to include species containing multiple isotopes, for example $^{13}C^{16}O^{18}O$ and $^1H^2H^{18}O$. The equilibrium constants for isotope exchange reactions that are calculated from fractionation factors can be expressed as ratios of individual isotope equilibrium constants for the various reactions (dissolution, precipitation, association, dissociation, acid-base, redox, and so on) commonly used in geochemical equilibrium and reaction-transport models. The individual isotope equilibrium constant for the molecular species composed of the most abundant terrestrial isotope of each element is nearly equal to the standard thermochemical equilibrium constant, and can be calculated to a close approximation from that constant if desired. This approximation provides a basis for calculating the individual isotope equilibrium constants for each isotopic species. The temperature dependence of the individual isotope equilibrium constants can be calculated from the temperature dependence of the fractionation factors and the temperature dependence of the standard thermochemical equilibrium con-

Table 3. Fractionation factors used in the PHREEQC example calculation.

Fractionation factor	$10^3 \ln(\alpha) = A_1^\alpha + A_3^\alpha/T_K + A_5^\alpha/T_K^2$			$10^3 \ln(\alpha)$ at 25°C	Range (°C)	Source
	A_1^α	A_3^α	A_5^α			
$\alpha_{H_2O_1 - H_2O_g}^2$	52.612	-76.248×10^3	24.844×10^6	76.4	0-100	Majzoub (1971)
$\alpha_{H_2O_1 - H_2O_g}^{18O}$	-2.0667	-0.4156×10^3	1.137×10^6	9.3	0-100	Majzoub (1971)
$\alpha_{CO_{2aq} - H_2O_1}^{18O}$	-21.9285	19.43596×10^3	-0.181115×10^6	41.2	0-100	Bottinga (1968); Friedman and O'Neil (1977); Vogel et al. (1970)
$\alpha_{CO_{2aq} - CO_{2g}}^{18O}$	-1.9585	1.44176×10^3	-0.160515×10^6	1.07	0-60	Vogel et al. (1970)
$\alpha_{CO_{2aq} - CO_{2g}}^{13C}$	-0.91	0.0	0.0063×10^6	-0.8	0-100	Deines et al. (1974)

¹ Coefficients are from Majzoub (1971) as presented in Friedman and O'Neil (1977).

² Coefficients are from Majzoub (1971) as presented in Friedman and O'Neil (1977).

³ Calculated from $(\alpha_{CO_{2g} - H_2O_1}^{18O})(\alpha_{CO_{2aq} - CO_{2g}}^{18O})$. Coefficients for $\alpha_{CO_{2g} - H_2O_1}^{18O}$ are from Bottinga (1968) as corrected and presented in Friedman and O'Neil (1977); coefficients for $\alpha_{CO_{2aq} - CO_{2g}}^{18O}$ are from Vogel et al. (1970), this table.

⁴ Calculated from $(\alpha_{CO_{2g} - CO_{2aq}}^{18O})$ with coefficients for $\alpha_{CO_{2g} - CO_{2aq}}^{18O}$ obtained by regression of data from Vogel et al. (1970) as presented in Friedman and O'Neil (1977).

stants. The derivations presented here can be extended to other species, such as ion pairs, and would also be applicable to other reaction types, such as redox reactions.

The effects of nonideality have been included in the derivations. Activity coefficients have been included in all equations, the conventions necessary to model the water-like species in the solvent $^1\text{H}_2^{16}\text{O}_1$ have been presented, and isotope salt effects have been included in the equations where applicable. The effects of nonideality are generally presumed to be small because of the chemical similarity of the different isotopic species of the same molecule or ion.

The equilibrium distribution of species is thermodynamically defined at constant temperature and pressure, and thus the isotopic content of phases, or of individual reactants or products within phases, should be the same whether calculated by the individual isotope techniques or the existing postprocessor methods. Calculations using the individual isotope method produce the same results as obtained from NETPATH (Plummer et al., 1994) for two model calculations. The individual isotope method provides the complete distribution for all species in all phases included in the calculation. The knowledge of the concentrations of individual isotope species will permit calculation of mass effects in transport phenomena (for example, Parkhurst et al., 2000). In addition, species-specific isotope information should stimulate research in areas such as the effect of solution composition (ionic strength and ion-pairing) on fractionation processes, the use of isotopes in evaluation of kinetic processes, and in ways yet to be recognized.

The individual isotope equilibrium constants are used in the geochemical model PHREEQC to produce an equilibrium and reaction-transport model that includes these isotopic species. An example calculation of gas-water equilibrium for CO_2 in an acidic aqueous solution is presented in this paper. Thorstenson and Parkhurst (2002) present a more complex calculation involving gas-water-solid equilibrium between CO_2 , a near-neutral-pH solution, and calcite.

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