

U.S. DEPARTMENT OF THE INTERIOR  
U.S. GEOLOGICAL SURVEY

# **CALCULATION OF INDIVIDUAL ISOTOPE EQUILIBRIUM CONSTANTS FOR IMPLEMENTATION IN GEOCHEMICAL MODELS**

***By Donald C. Thorstenson and David L. Parkhurst***

---

Water-Resources Investigations Report 02-4172

Denver, Colorado  
2002



**U.S. DEPARTMENT OF THE INTERIOR**

**GALE A. NORTON, Secretary**

**U.S. GEOLOGICAL SURVEY**

Charles G. Groat, Director

The use of trade, product, industry, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

---

For additional information write to:

Chief, Branch of Regional Research  
U.S. Geological Survey  
Box 25046, MS 418  
Denver Federal Center  
Denver, CO 80225

Copies of this report can be purchased from:

U.S. Geological Survey  
Branch of Information Services  
Open-File Reports Section  
Box 25286  
Denver Federal Center  
Denver, CO 80225

# CONTENTS

Abstract .....	1
Introduction .....	1
Isotope ratios in gaseous and aqueous CO <sub>2</sub> .....	3
Species and symmetry numbers .....	3
Equilibrium constants for intraspecies reactions among the CO <sub>2</sub> species .....	4
Isotope ratios .....	5
Calculation of individual isotope equilibrium constants for the reaction CO <sub>2(gas)</sub> - CO <sub>2(aqueous)</sub> .....	9
CO <sup>18</sup> O .....	9
C <sup>18</sup> O <sub>2</sub> .....	11
<sup>13</sup> CO <sub>2</sub> .....	12
<sup>13</sup> CO <sup>18</sup> O .....	12
<sup>13</sup> C <sup>18</sup> O <sub>2</sub> .....	13
<sup>14</sup> CO <sub>2</sub> , <sup>14</sup> CO <sup>18</sup> O, and <sup>14</sup> C <sup>18</sup> O <sub>2</sub> .....	14
Symmetry assumptions in the isotope ratios .....	14
Individual isotope equilibrium constants for bicarbonate .....	15
Individual isotope equilibrium constants for ion pairs.....	17
Application to other isotopes.....	19
Nonideality .....	20
Temperature dependence .....	22
Fundamental individual isotope equilibrium constants.....	23
Comparison of methods .....	24
Example calculation using PHREEQC .....	27
Summary .....	41
References cited .....	43

## TABLES

1. Symmetry numbers and isotope ratios .....	46
2. Reactions and equilibrium constants.....	55
3. Fractionation factors used in the PHREEQC example calculation .....	74

## APPENDICES

Appendix 1. Derivation of individual isotope equilibrium constants for the bicarbonate ion .....	78
Isotope ratios for bicarbonate.....	78
The <sup>18</sup> O/ <sup>16</sup> O ratio in terms of HCO <sub>2</sub> <sup>18</sup> O <sub>aq</sub> <sup>-</sup> .....	79
The <sup>18</sup> O/ <sup>16</sup> O ratio in terms of HCO <sup>18</sup> O <sub>2aq</sub> <sup>-</sup> .....	84
The <sup>18</sup> O/ <sup>16</sup> O ratio in terms of HC <sup>18</sup> O <sub>3aq</sub> <sup>-</sup> .....	87
The <sup>13</sup> C/ <sup>12</sup> C ratio.....	89
The <sup>2</sup> H/ <sup>1</sup> H ratio .....	90
Aqueous CO <sub>2</sub> -- bicarbonate ion equilibrium .....	90
Reaction to HCO <sub>2</sub> <sup>18</sup> O <sub>aq</sub> <sup>-</sup> .....	90
Reaction to HCO <sup>18</sup> O <sub>2aq</sub> <sup>-</sup> .....	92

Reaction to $\text{HC}^{18}\text{O}_{3\text{aq}}^-$ .....	93
Reaction to $\text{H}^{13}\text{CO}_{3\text{aq}}^-$ .....	94
Reaction to $\text{H}^{13}\text{CO}_2^{18}\text{O}_{\text{aq}}^-$ .....	95
Reaction to $\text{H}^{13}\text{CO}^{18}\text{O}_{2\text{aq}}^-$ .....	96
Reaction to $\text{H}^{13}\text{C}^{18}\text{O}_{3\text{aq}}^-$ .....	97
Reaction to $\text{DCO}_{3\text{aq}}^-$ .....	99
Reaction to $\text{DCO}_2^{18}\text{O}_{\text{aq}}^-$ .....	100
Reaction to $\text{DCO}^{18}\text{O}_{2\text{aq}}^-$ .....	101
Reaction to $\text{DC}^{18}\text{O}_{3\text{aq}}^-$ .....	103
Reaction to $\text{D}^{13}\text{CO}_{3\text{aq}}^-$ .....	104
Reaction to $\text{D}^{13}\text{CO}_2^{18}\text{O}_{\text{aq}}^-$ .....	105
Reaction to $\text{D}^{13}\text{CO}^{18}\text{O}_{2\text{aq}}^-$ .....	107
Reaction to $\text{D}^{13}\text{C}^{18}\text{O}_{3\text{aq}}^-$ .....	108
Appendix 2. Isotopic data input for PHREEQC .....	111
CALCULATE_VALUES .....	113
Example data block .....	113
Explanation .....	113
Notes .....	114
Example problems.....	114
Related keywords .....	114
ISOTOPES .....	115
Example data block .....	115
Explanation .....	115
Notes .....	116
Example problems.....	116
Related keywords .....	116
ISOTOPE_ALPHAS .....	117
Example data block .....	117
Explanation .....	117
Notes .....	118
Example problems.....	118
Related keywords .....	118
ISOTOPE_RATIOS .....	119
Example data block .....	119
Explanation .....	119
Notes .....	119
Example problems.....	120
Related keywords .....	120
NAMED_EXPRESSION .....	121
Example data block .....	121
Explanation .....	121
Notes .....	122
Example problems.....	123
Related keywords .....	123
PHASES .....	124
Example data block .....	124

Explanation.....	124
Notes.....	125
PRINT .....	126
Example data block .....	126
Explanation.....	126
SELECTED_OUTPUT .....	127
Example data block .....	127
Explanation.....	127
SOLUTION_SPECIES .....	128
Example data block .....	128
Explanation.....	128
Notes.....	129



# CALCULATION OF INDIVIDUAL ISOTOPE EQUILIBRIUM CONSTANTS FOR IMPLEMENTATION IN GEOCHEMICAL MODELS

by Donald C. Thorstenson and David L. Parkhurst

## Abstract

Theory is derived from the work of Urey 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  $\alpha = (K^{ex})^{1/n}$ , 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  $^1\text{H}^2\text{H}^{18}\text{O}$ , and to include the effects of nonideality. The equilibrium constants of the isotope exchange reactions provide a basis for calculating the individual isotope equilibrium constants for the geochemical modeling reactions. The temperature dependence of the individual isotope equilibrium constants can be calculated from the temperature dependence of the fractionation factors. Equilibrium constants are calculated for all species that can be formed from  $^1\text{H}$ ,  $^2\text{H}$ ,  $^{12}\text{C}$ ,  $^{13}\text{C}$ ,  $^{14}\text{C}$ ,  $^{16}\text{O}$ ,  $^{18}\text{O}$ , and selected species containing  $^3\text{H}$ , in the molecules  $\text{CO}_{2g}$ ,  $\text{CO}_{2aq}$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{CaCO}_{3s}$ ,  $\text{H}_2\text{O}_g$ ,  $\text{H}_2\text{O}_l$ ,  $\text{H}_3\text{O}^+$ ,  $\text{OH}^-$ , and the  $\text{OH}^-$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$  ion pairs with  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{+2}$ , and  $\text{Mg}^{+2}$ , where the subscripts  $g$ ,  $aq$ ,  $l$ , and  $s$  refer to gas, aqueous, liquid, and solid, respectively. These equilibrium constants are used in the geochemical model PHREEQC to produce an equilibrium and reaction-transport model that includes these isotopic species. Methods are presented for calculation of the individual isotope equilibrium constants for the asymmetric bicarbonate ion. An example calculates the equilibrium of multiple isotopes among multiple species and phases.

## INTRODUCTION

The theory relating isotope fractionation factors to the equilibrium constants of isotope exchange reactions was presented 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 equation 1, which holds for most isotope exchange reactions under conditions that are closely approximated by many geochemical systems:

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

where  $\alpha$  is the equilibrium isotope fractionation factor between reaction 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.

This report extends Urey's derivations to express the equilibrium constants of isotope exchange reactions as ratios of the equilibrium constants for individual isotope association or dissociation reactions that are commonly used in geochemical equilibrium and reaction-transport models. The Urey derivations are also extended to include mixed isotopic species such as  $^{13}\text{C}^{16}\text{O}^{18}\text{O}_{gas}$  and  $^1\text{H}^2\text{H}^{18}\text{O}_{liquid}$ . The individual isotope equilibrium constants for the association or dissociation reactions 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. This approach provides a method of geochemical modeling in which isotopic fractionation and chemical speciation are fully integrated, in contrast to the commonly used modeling approaches that perform chemical and isotopic calculations separately.

The purpose of this report is to relate the equilibrium constant of equation 1 to equilibrium constants for reactions convenient for geochemical modeling. The scope of the paper includes the derivation of individual isotope equilibrium constants, expressed as a function of fractionation factors, for reactions used in the reaction-transport model PHREEQC (Parkhurst and Appelo, 1999). The values of the equilibrium constants and their associated reactions can, however, be used as input data in any geochemical model. This report constructs a model in PHREEQC that contains all isotopic species that can be formed from  $^1\text{H}$ ,  $^2\text{H}$ ,  $^{12}\text{C}$ ,  $^{13}\text{C}$ ,  $^{14}\text{C}$ ,  $^{16}\text{O}$ , and  $^{18}\text{O}$  in the molecules/phases  $\text{CO}_{2g}$ ,  $\text{CO}_{2aq}$ ,  $\text{HCO}_{3aq}^-$ ,  $\text{CO}_{3aq}^{-2}$ ,  $\text{CaCO}_{3s}$ ,  $\text{H}_2\text{O}_g$ ,  $\text{H}_2\text{O}_l$ ,  $\text{H}_3\text{O}_{aq}^+$ ,  $\text{OH}_{aq}^-$ , and the  $\text{OH}_{aq}^-$ ,  $\text{HCO}_{3aq}^-$ , and  $\text{CO}_{3aq}^{-2}$  ion pairs with the cations  $\text{Na}_{aq}^+$ ,  $\text{K}_{aq}^+$ ,  $\text{Ca}_{aq}^{+2}$ , and  $\text{Mg}_{aq}^{+2}$ , where the subscripts  $g$ ,  $aq$ ,  $l$ , and  $s$  refer to gas, aqueous, liquid, and solid, respectively. Equilibrium constants for selected species containing  $^3\text{H}$  are also calculated. Derivations are presented in the text for reactions among  $\text{CO}_{2g}$  and  $\text{CO}_{2aq}$  species. The algebraically complex derivations for reactions involving  $\text{HCO}_{3aq}^-$  are presented in Appendix 1.

Symmetry numbers and isotope ratios, equations for all equilibrium constants, and fractionation factors are presented in tables 1, 2, and 3, respectively.

## ISOTOPE RATIOS IN GASEOUS AND AQUEOUS CO<sub>2</sub>

The Henry's Law equilibrium constants for the various isotopic species of CO<sub>2</sub> are used to illustrate the principles of the calculations. The subscript *j* denotes either gas or aqueous species. For notational convenience the most abundant isotope of each element, <sup>1</sup>H, <sup>12</sup>C, and <sup>16</sup>O will be used without superscripts. Thus, <sup>12</sup>C<sup>16</sup>O<sub>2</sub> is denoted CO<sub>2</sub>. Deuterium, <sup>2</sup>H, is denoted by *D*, and tritium, <sup>3</sup>H, is denoted by *T*.

### Species and Symmetry Numbers

Urey calculated equilibrium constants for the 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 the reactant or product molecules in a given reaction, for example formation of CO<sup>18</sup>O<sub>*j*</sub> from CO<sub>2*j*</sub> and C<sup>18</sup>O<sub>2*j*</sub>, 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,  $\sigma$ , can be determined by counting the number of indistinguishable orientations of a molecule that can be reached by rotational symmetry operations; for example,  $\sigma_{O_2} = 2$ ,  $\sigma_{CO} = 1$ , and  $\sigma_{CH_4} = 12$  (Atkins, 1982, p. 721). Symmetry numbers for the various CO<sub>2</sub> species follow and are tabulated for all species in table 1.

For the isotopes C, <sup>13</sup>C, <sup>14</sup>C, O, and <sup>18</sup>O, nine CO<sub>2</sub> species exist in the gas and aqueous phases. They are CO<sub>2*j*</sub>, CO<sup>18</sup>O<sub>2*j*</sub>, C<sup>18</sup>O<sub>2*j*</sub>, <sup>13</sup>CO<sub>2*j*</sub>, <sup>13</sup>CO<sup>18</sup>O<sub>*j*</sub>, <sup>13</sup>C<sup>18</sup>O<sub>2*j*</sub>, <sup>14</sup>CO<sub>2*j*</sub>, <sup>14</sup>CO<sup>18</sup>O<sub>*j*</sub>, and <sup>14</sup>C<sup>18</sup>O<sub>2*j*</sub>. The CO<sub>2</sub> molecule is linear, and thus the symmetry numbers of the isotopic species are

$$\sigma = 2, \quad \sigma = 1, \quad \sigma = 2, \quad \sigma = 2, \quad \sigma = 1, \quad \sigma = 2, \quad \sigma = 2, \quad \sigma = 1, \quad \text{and} \quad \sigma = 2.$$

## Equilibrium Constants for Intraspecies Reactions Among the CO<sub>2</sub> Species

The equilibrium constants for intraspecies isotopic reactions among the CO<sub>2</sub> species (gaseous or aqueous) are assumed to be determined by their symmetry numbers alone. Reactions are presented for C and <sup>13</sup>C; results for <sup>14</sup>C are identical to those for <sup>13</sup>C. The possible reactions are



The equilibrium constants for reactions 2- 6, calculated from symmetry numbers, with  $n_i$  = number of molecules of species  $i$ , are (Urey, 1947, p. 563-565)

$$K_{CO^{18}O_j} = \frac{n_{CO^{18}O_j}^2}{n_{CO_{2j}} n_{C^{18}O_{2j}}} = \frac{Q_{CO^{18}O_j}^2}{Q_{CO_{2j}} Q_{C^{18}O_{2j}}} = \frac{\left(\frac{1}{\sigma_{CO^{18}O_j}}\right)^2}{\left(\frac{1}{\sigma_{CO_{2j}}}\right)\left(\frac{1}{\sigma_{C^{18}O_{2j}}}\right)} = \frac{\sigma_{CO_{2j}} \sigma_{C^{18}O_{2j}}}{\sigma_{CO^{18}O_j}^2} = \frac{(2)(2)}{(1)^2} = 4, \quad (7)$$

$$K_{^{13}CO^{18}O_j} = \frac{n_{^{13}CO^{18}O_j}^2}{n_{^{13}CO_{2j}} n_{^{13}C^{18}O_{2j}}} = \frac{Q_{^{13}CO^{18}O_j}^2}{Q_{^{13}CO_{2j}} Q_{^{13}C^{18}O_{2j}}} = \frac{\left(\frac{1}{\sigma_{^{13}CO^{18}O_j}}\right)^2}{\left(\frac{1}{\sigma_{^{13}CO_{2j}}}\right)\left(\frac{1}{\sigma_{^{13}C^{18}O_{2j}}}\right)} = \frac{(2)(2)}{(1)^2} = 4, \quad (8)$$

$$K_{^{13}C^{18}O_{2j}} = \frac{n_{^{13}C^{18}O_{2j}} n_{CO_{2j}}}{n_{^{13}CO_{2j}} n_{C^{18}O_{2j}}} = \frac{Q_{^{13}C^{18}O_{2j}} Q_{CO_{2j}}}{Q_{^{13}CO_{2j}} Q_{C^{18}O_{2j}}} = \frac{\left(\frac{1}{\sigma_{^{13}C^{18}O_{2j}}}\right)\left(\frac{1}{\sigma_{CO_{2j}}}\right)}{\left(\frac{1}{\sigma_{^{13}CO_{2j}}}\right)\left(\frac{1}{\sigma_{C^{18}O_{2j}}}\right)} = \frac{(2)(2)}{(2)(2)} = 1, \quad (9)$$

$$K_{^{13}\text{CO}^{18}\text{O}_j} = \frac{n_{^{13}\text{CO}^{18}\text{O}_j} n_{\text{CO}_2j}}{n_{\text{CO}^{18}\text{O}_j} n_{^{13}\text{CO}_2j}} = \frac{Q_{^{13}\text{CO}^{18}\text{O}_j} Q_{\text{CO}_2j}}{Q_{\text{CO}^{18}\text{O}_j} Q_{^{13}\text{CO}_2j}} = \frac{\left(\frac{1}{\sigma_{^{13}\text{CO}^{18}\text{O}_j}}\right) \left(\frac{1}{\sigma_{\text{CO}_2j}}\right)}{\left(\frac{1}{\sigma_{\text{CO}^{18}\text{O}_j}}\right) \left(\frac{1}{\sigma_{^{13}\text{CO}_2j}}\right)} = \frac{(1)(2)}{(1)(2)} = 1, \text{ and} \quad (10)$$

$$K_{^{13}\text{CO}^{18}\text{O}_j} = \frac{n_{^{13}\text{CO}^{18}\text{O}_j} n_{\text{C}^{18}\text{O}_2j}}{n_{\text{CO}^{18}\text{O}_j} n_{^{13}\text{C}^{18}\text{O}_2j}} = \frac{Q_{^{13}\text{CO}^{18}\text{O}_j} Q_{\text{C}^{18}\text{O}_2j}}{Q_{\text{CO}^{18}\text{O}_j} Q_{^{13}\text{C}^{18}\text{O}_2j}} = \frac{\left(\frac{1}{\sigma_{^{13}\text{CO}^{18}\text{O}_j}}\right) \left(\frac{1}{\sigma_{\text{C}^{18}\text{O}_2j}}\right)}{\left(\frac{1}{\sigma_{\text{CO}^{18}\text{O}_j}}\right) \left(\frac{1}{\sigma_{^{13}\text{C}^{18}\text{O}_2j}}\right)} = \frac{(1)(2)}{(1)(2)} = 1. \quad (11)$$

where  $Q_i$  is the partition function and  $\sigma_i$  is the symmetry number for species  $i$  in equations 7 - 8.

Equations 7 - 8 provide the following relations:

$$\frac{n_{\text{CO}^{18}\text{O}_j}^2}{n_{\text{CO}_2j} n_{\text{C}^{18}\text{O}_2j}} = 4, \quad n_{\text{CO}^{18}\text{O}_j} = 2n_{\text{CO}_2j}^{\frac{1}{2}} n_{\text{C}^{18}\text{O}_2j}^{\frac{1}{2}}, \quad (12)$$

$$\frac{n_{^{13}\text{CO}^{18}\text{O}_j}^2}{n_{^{13}\text{CO}_2j} n_{^{13}\text{C}^{18}\text{O}_2j}} = 4, \quad n_{^{13}\text{CO}^{18}\text{O}_j} = 2n_{^{13}\text{CO}_2j}^{\frac{1}{2}} n_{^{13}\text{C}^{18}\text{O}_2j}^{\frac{1}{2}}, \quad (13)$$

$$\frac{n_{^{13}\text{C}^{18}\text{O}_2j}}{n_{^{13}\text{CO}_2j}} = \frac{n_{\text{C}^{18}\text{O}_2j}}{n_{\text{CO}_2j}}, \quad \frac{n_{^{13}\text{C}^{18}\text{O}_2j}}{n_{\text{C}^{18}\text{O}_2j}} = \frac{n_{^{13}\text{CO}_2j}}{n_{\text{CO}_2j}}, \quad (14)$$

$$\frac{n_{^{13}\text{CO}^{18}\text{O}_j}}{n_{^{13}\text{CO}_2j}} = \frac{n_{\text{CO}^{18}\text{O}_j}}{n_{\text{CO}_2j}}, \quad \frac{n_{^{13}\text{CO}^{18}\text{O}_j}}{n_{\text{CO}^{18}\text{O}_j}} = \frac{n_{^{13}\text{CO}_2j}}{n_{\text{CO}_2j}}, \quad (15)$$

$$\frac{n_{^{13}\text{CO}^{18}\text{O}_j}}{n_{^{13}\text{C}^{18}\text{O}_2j}} = \frac{n_{\text{CO}^{18}\text{O}_j}}{n_{\text{C}^{18}\text{O}_2j}}, \quad \text{and} \quad \frac{n_{^{13}\text{CO}^{18}\text{O}_j}}{n_{\text{CO}^{18}\text{O}_j}} = \frac{n_{^{13}\text{C}^{18}\text{O}_2j}}{n_{\text{C}^{18}\text{O}_2j}}. \quad (16)$$

Equations 7 - 16 allow calculation of isotope ratios for the  $\text{CO}_2j$  species.

## 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  $\text{CO}_2j$  is given by

$$R_{CO_{2j}}^{13C} = \frac{n_{13CO_{2j}} + n_{13CO^{18}O_j} + n_{13C^{18}O_{2j}}}{n_{CO_{2j}} + n_{CO^{18}O_j} + n_{C^{18}O_{2j}}}, \text{ or} \quad (17)$$

$$R_{CO_{2j}}^{13C} = \frac{n_{13CO_{2j}} \left( 1 + \frac{n_{13CO^{18}O_j} + n_{13C^{18}O_{2j}}}{n_{13CO_{2j}}} \right)}{n_{CO_{2j}} \left( 1 + \frac{n_{CO^{18}O_j} + n_{C^{18}O_{2j}}}{n_{CO_{2j}}} \right)} = \frac{n_{13CO_{2j}}}{n_{CO_{2j}}}. \quad (18)$$

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

$$R_{CO_{2j}}^{13C} = \frac{n_{13CO_{2j}}}{n_{CO_{2j}}} = \frac{n_{13CO^{18}O_j}}{n_{CO^{18}O_j}} = \frac{n_{13C^{18}O_{2j}}}{n_{C^{18}O_{2j}}}. \quad (19)$$

The  $^{18}O/^{16}O$  ratio in  $CO_{2j}$  is

$$R_{CO_{2j}}^{18O} = \frac{2n_{C^{18}O_{2j}} + n_{CO^{18}O_j} + 2n_{13C^{18}O_{2j}} + n_{13CO^{18}O_j}}{2n_{CO_{2j}} + n_{CO^{18}O_j} + 2n_{13CO_{2j}} + n_{13CO^{18}O_j}}. \quad (20)$$

An expression for  $R_{CO_{2j}}^{18O}$  can be derived in terms of  $C^{18}O_{2j}$  and  $CO_{2j}$ , as shown by Urey. Using equations 12

and 13 to substitute for  $n_{CO^{18}O_j}$  in equation 20 yields

$$R_{CO_{2j}}^{18O} = \frac{2n_{C^{18}O_{2j}} + 2n_{CO_{2j}}^{\frac{1}{2}} n_{C^{18}O_{2j}}^{\frac{1}{2}} + 2n_{13C^{18}O_{2j}} + 2n_{13CO_{2j}}^{\frac{1}{2}} n_{13C^{18}O_{2j}}^{\frac{1}{2}}}{2n_{CO_{2j}} + 2n_{CO_{2j}}^{\frac{1}{2}} n_{C^{18}O_{2j}}^{\frac{1}{2}} + 2n_{13CO_{2j}} + 2n_{13CO_{2j}}^{\frac{1}{2}} n_{13C^{18}O_{2j}}^{\frac{1}{2}}}$$

$$\begin{aligned}
& \left( \frac{2n_{C^{18}O_2j} \left( 1 + \frac{\frac{1}{2}}{n_{C^{18}O_2j}} \right) + 2n_{^{13}C^{18}O_2j} \left( 1 + \frac{\frac{1}{2}}{n_{^{13}C^{18}O_2j}} \right)}{2n_{CO_2j} \left( 1 + \frac{\frac{1}{2}}{n_{C^{18}O_2j}} \right) + 2n_{^{13}CO_2j} \left( 1 + \frac{\frac{1}{2}}{n_{^{13}CO_2j}} \right)} \left( n_{C^{18}O_2j} + n_{^{13}C^{18}O_2j} \right) \left( 1 + \frac{\frac{1}{2}}{n_{C^{18}O_2j}} \right)}{\left( n_{CO_2j} + n_{^{13}CO_2j} \right) \left( 1 + \frac{\frac{1}{2}}{n_{CO_2j}} \right)} \right) \\
& = \frac{n_{C^{18}O_2j} \left( 1 + \frac{n_{^{13}C^{18}O_2j}}{n_{C^{18}O_2j}} \right) \left( \frac{\frac{1}{2}}{n_{C^{18}O_2j}} + \frac{\frac{1}{2}}{n_{CO_2j}} \right)}{n_{CO_2j} \left( 1 + \frac{n_{^{13}CO_2j}}{n_{CO_2j}} \right) \left( \frac{\frac{1}{2}}{n_{CO_2j}} + \frac{\frac{1}{2}}{n_{C^{18}O_2j}} \right)} = \frac{n_{C^{18}O_2j} \left( \frac{\frac{1}{2}}{n_{CO_2j}} \right)}{\frac{1}{2} n_{CO_2j}} = \frac{n_{C^{18}O_2j}}{n_{CO_2j}}, \text{ or} \tag{21}
\end{aligned}$$

$$R_{CO_2j}^{18O} = \frac{\frac{1}{2} n_{C^{18}O_2j}}{\frac{1}{2} n_{CO_2j}}. \tag{22}$$

In addition to Urey's derivation of equation 22,  $R_{CO_2j}^{18O}$  can be expressed in terms of  $CO^{18}O_j$  by using equations 12 and 13 in the numerator of equation 20 to give

$$R_{CO_2j}^{18O} = \frac{n_{CO^{18}O_j} + 2 \left( \frac{n_{CO^{18}O_j}^2}{4n_{CO_2j}} \right) + n_{^{13}CO^{18}O_j} + 2 \left( \frac{n_{^{13}CO^{18}O_j}^2}{4n_{^{13}CO_2j}} \right)}{2n_{CO_2j} \left( 1 + \frac{n_{CO^{18}O_j}}{2n_{CO_2j}} \right) + 2n_{^{13}CO_2j} \left( 1 + \frac{n_{^{13}CO^{18}O_j}}{2n_{^{13}CO_2j}} \right)}$$

$$= \frac{\left(n_{CO^{18}O_j} + n_{^{13}CO^{18}O_j}\right)\left(1 + \frac{n_{CO^{18}O_j}}{2n_{CO_2j}}\right)}{2\left(n_{CO_2j} + n_{^{13}CO_2j}\right)\left(1 + \frac{n_{CO^{18}O_j}}{2n_{CO_2j}}\right)} = \frac{n_{CO^{18}O_j}\left(1 + \frac{n_{^{13}CO^{18}O_j}}{n_{CO^{18}O_j}}\right)\left(1 + \frac{n_{CO^{18}O_j}}{2n_{CO_2j}}\right)}{2n_{CO_2j}\left(1 + \frac{n_{^{13}CO_2j}}{n_{CO_2j}}\right)\left(1 + \frac{n_{CO^{18}O_j}}{2n_{CO_2j}}\right)}. \quad (23)$$

Equations 14 - 16 define the equality of the terms in parentheses in the numerator and denominator and allow the isotope ratio to be written as

$$R_{CO_2j}^{^{18}O} = \frac{n_{CO^{18}O_j}}{2n_{CO_2j}}. \quad (24)$$

Equation 24 can also be derived by substituting equation 12 into equation 22. Using equations 12 and 13 in equations 22 and 24 gives

$$R_{CO_2j}^{^{18}O} = \frac{\frac{1}{2}n_{C^{18}O_2j}}{\frac{1}{2}n_{CO_2j}} = \frac{\frac{1}{2}n_{^{13}C^{18}O_2j}}{\frac{1}{2}n_{^{13}CO_2j}} = \frac{n_{CO^{18}O_j}}{2n_{CO_2j}} = \frac{n_{^{13}CO^{18}O_j}}{2n_{^{13}CO_2j}}. \quad (25)$$

Equations 19 and 25 define the  $^{13}C/^{12}C$  and  $^{18}O/^{16}O$  ratios for  $CO_{2j}$ . 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.

Inclusion of  $^{14}CO_{2j}$ ,  $^{14}CO^{18}O_j$ , and  $^{14}C^{18}O_{2j}$  as species, and as needed in equations 2 through 25 and their  $^{14}C$  analogs, yields

$$R_{CO_2j}^{^{18}O} = \frac{\frac{1}{2}n_{C^{18}O_2j}}{\frac{1}{2}n_{CO_2j}} = \frac{\frac{1}{2}n_{^{13}C^{18}O_2j}}{\frac{1}{2}n_{^{13}CO_2j}} = \frac{\frac{1}{2}n_{^{14}C^{18}O_2j}}{\frac{1}{2}n_{^{14}CO_2j}} = \frac{n_{CO^{18}O_j}}{2n_{CO_2j}} = \frac{n_{^{13}CO^{18}O_j}}{2n_{^{13}CO_2j}} = \frac{n_{^{14}CO^{18}O_j}}{2n_{^{14}CO_2j}}, \text{ and} \quad (26)$$

$$R_{CO_2j}^{^{14}C} = \frac{n_{^{14}CO_2j}}{n_{CO_2j}} = \frac{n_{^{14}CO^{18}O_j}}{n_{CO^{18}O_j}} = \frac{n_{^{14}C^{18}O_2j}}{n_{C^{18}O_2j}}. \quad (27)$$

Restating equation 19,

$$R_{CO_{2j}}^{13C} = \frac{n_{13CO_{2j}}}{n_{CO_{2j}}} = \frac{n_{13CO^{18}O_j}}{n_{CO^{18}O_j}} = \frac{n_{13C^{18}O_{2j}}}{n_{C^{18}O_{2j}}}. \quad (28)$$

The algebraic simplification of the isotope ratios that leads to equations 26 - 28 occurs if two or more atoms of the same element occupy equivalent positions in the molecule, and the equilibrium constants for the intraspecies reactions (equations 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,  $\sigma_{CO_2} = 2$ ,  $\sigma_{CO_3^{2-}} = 6$ , and so on. The intraspecies equilibrium constants are then equal to  $n^n$ . Table 1 contains symmetry numbers for all species and entries analogous to equations 26 - 28 for all species except bicarbonate. The bicarbonate ion is asymmetric and requires a different treatment, discussed shortly.

## CALCULATION OF INDIVIDUAL ISOTOPE EQUILIBRIUM CONSTANTS FOR THE REACTION $CO_{2gas} \rightleftharpoons CO_{2aqueous}$

The isotope ratios given in equations 26 - 28 form the basis for the algebraic expression of the fractionation factors for  $^{13}C$ ,  $^{14}C$ , and  $^{18}O$  between  $CO_{2g}$  and  $CO_{2aq}$ , thus permitting calculation of the individual isotope Henry's Law constants for the nine isotopic species of  $CO_2$ .

### $CO^{18}O$

For  $CO^{18}O$ , the reaction used in PHREEQC is

$$CO^{18}O_g = CO^{18}O_{aq}. \quad (29)$$

The first step is to express the fractionation factor in terms of the reactant and product species, choosing the appropriate ratios from equation 26. For equation 29, the appropriate expression of the fractionation factor is

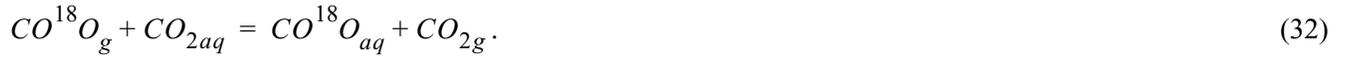
$$\alpha_{CO_{2aq}-CO_{2g}}^{18O} = \frac{R_{CO_{2aq}}^{18O}}{R_{CO_{2g}}^{18O}} = \frac{\left( \frac{n_{CO^{18}O_{aq}}}{2n_{CO_{2aq}}} \right)}{\left( \frac{n_{CO^{18}O_g}}{2n_{CO_{2g}}} \right)}. \quad (30)$$

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

$$\alpha_{CO_{2aq}-CO_{2g}}^{18O} = \frac{\left(\frac{n_{CO^{18}O_{aq}}}{2n_{CO_{2aq}}}\right)}{\left(\frac{n_{CO^{18}O_g}}{2n_{CO_{2g}}}\right)} = \frac{n_{CO^{18}O_{aq}} n_{CO_{2g}}}{n_{CO^{18}O_g} n_{CO_{2aq}}} = \frac{m_{CO^{18}O_{aq}} X_{CO_{2g}}}{X_{CO^{18}O_g} m_{CO_{2aq}}}, \quad (31)$$

where  $m_i$  is molality, and  $X_i$  is mole fraction.

The terms in equation 31 have the form of a concentration-based equilibrium constant for an isotope exchange reaction. The exchange reaction for equation 31 is



The next step is to write the equilibrium constant,  $K_{CO^{18}O_{aq}}^{ex}$ , for this reaction in terms of activities, then activity coefficients and concentrations (activity-concentration relations used here are from Garrels and Christ, 1965, p. 20-73):

$$K_{CO^{18}O_{aq}}^{ex} = \frac{a_{CO^{18}O_{aq}} a_{CO_{2g}}}{a_{CO^{18}O_g} a_{CO_{2aq}}} = \frac{\gamma_{CO^{18}O_{aq}} (\lambda_{CO_{2g}} P_{tot})^m}{\left(\lambda_{CO^{18}O_g} P_{tot}\right) \gamma_{CO_{2aq}} X_{CO^{18}O_g} m_{CO_{2aq}}}, \quad (33)$$

where  $P_{tot}$  is total gas pressure,  $a_i$  is activity, and  $\gamma_i$  and  $\lambda_i$  are activity coefficients. From equations 31 and 33

$$K_{CO^{18}O_{aq}}^{ex} = \left(\frac{\gamma_{CO^{18}O_{aq}} \lambda_{CO_{2g}}}{\gamma_{CO_{2aq}} \lambda_{CO^{18}O_g}}\right)_{exp} \left(\alpha_{CO_{2aq}-CO_{2g}}^{18O}\right), \quad (34)$$

where the subscript *exp* indicates that the true value of  $K_{CO^{18}O_{aq}}^{ex}$  can only be evaluated exactly if the parameters

in the brackets are known for the experiments in which  $\alpha_{CO_{2aq}-CO_{2g}}^{18O}$  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:

$$K_{CO^{18}O_{aq}}^{ex} = \frac{a_{CO^{18}O_{aq}} a_{CO_{2g}}}{a_{CO^{18}O_g} a_{CO_{2aq}}} = \frac{K_{CO^{18}O_{aq}}^H}{K_{CO_{2aq}}^H}, \quad (35)$$

where  $K_{CO^{18}O_{aq}}^H$  and  $K_{CO_{2aq}}^H$  are the equilibrium constants for the reactions



The value of  $K_{CO_{2aq}}^H$  is assumed to equal the standard thermochemical constant; this assumption is discussed in more detail later. From equations 34 and 35,

$$K_{CO^{18}O_{aq}}^H = K_{CO_{2aq}}^H K_{CO^{18}O_{aq}}^{ex} = K_{CO_{2aq}}^H \left( \frac{\gamma_{CO^{18}O_{aq}} \lambda_{CO_{2g}}}{\gamma_{CO_{2aq}} \lambda_{CO^{18}O_g}} \right)_{exp} \left( \alpha_{CO_{2aq} - CO_{2g}}^{18O} \right). \quad (37)$$

With known values of  $K_{CO_{2aq}}^H$  and the activity coefficients,  $K_{CO^{18}O_{aq}}^H$  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 equation 37,

$$\log K_{CO^{18}O_{aq}}^H = \log K_{CO_{2aq}}^H + \log \left( \alpha_{CO_{2aq} - CO_{2g}}^{18O} \right) + \log \left( \frac{\gamma_{CO^{18}O_{aq}} \lambda_{CO_{2g}}}{\gamma_{CO_{2aq}} \lambda_{CO^{18}O_g}} \right)_{exp}. \quad (38)$$

## $C^{18}O_2$

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

$$C^{18}O_{2g} = C^{18}O_{2aq}. \quad (39)$$

For reaction 39, the appropriate expression of the fractionation factor is

$$\left( \alpha_{CO_{2aq} - CO_{2g}}^{18O} \right)^2 = \left( \frac{R_{CO_{2aq}}^{18O}}{R_{CO_{2g}}^{18O}} \right)^2 = \frac{\left( \frac{n_{C^{18}O_{2aq}}}{n_{CO_{2aq}}} \right)}{\left( \frac{n_{C^{18}O_{2g}}}{n_{CO_{2g}}} \right)} = \frac{n_{C^{18}O_{2aq}} n_{CO_{2g}}}{n_{C^{18}O_{2g}} n_{CO_{2aq}}} = \frac{m_{C^{18}O_{2aq}} X_{CO_{2g}}}{X_{C^{18}O_{2g}} m_{CO_{2aq}}}. \quad (40)$$

The isotope exchange reaction for equation 39 is

$$C^{18}O_{2aq} + CO_{2aq} = C^{18}O_{2aq} + CO_{2g}, \quad (41)$$

and the equilibrium constant is

$$K_{C^{18}O_{2aq}}^{ex} = \frac{a_{C^{18}O_{2aq}} a_{CO_{2g}}}{a_{C^{18}O_{2g}} a_{CO_{2aq}}} = \frac{\gamma_{C^{18}O_{2aq}} (\lambda_{CO_{2g}} P_{tot})^m_{CO_{2g}} X_{CO_{2g}}}{(\lambda_{C^{18}O_{2g}} P_{tot}) \gamma_{CO_{2aq}} X_{C^{18}O_{2g}} m_{CO_{2aq}}}. \quad (42)$$

Following equations 33 - 38 yields

$$\log K_{C^{18}O_{2aq}}^H = \log K_{CO_{2aq}}^H + 2\log\left(\alpha_{CO_{2aq}-CO_{2g}}^{18O}\right) + \log\left(\frac{\gamma_{C^{18}O_{2aq}} \lambda_{CO_{2g}}}{\gamma_{CO_{2aq}} \lambda_{C^{18}O_{2g}}}\right)_{exp}. \quad (43)$$

### $^{13}CO_2$

For  $^{13}CO_2$ , the reaction is

$$^{13}CO_{2g} = ^{13}CO_{2aq}. \quad (44)$$

For reaction 44, the appropriate expression of the fractionation factor is

$$\alpha_{CO_{2aq}-CO_{2g}}^{13C} = \frac{R_{CO_{2aq}}^{13C}}{R_{CO_{2g}}^{13C}} = \frac{\left(\frac{n_{^{13}CO_{2aq}}}{n_{CO_{2aq}}}\right)}{\left(\frac{n_{^{13}CO_{2g}}}{n_{CO_{2g}}}\right)} = \frac{n_{^{13}CO_{2aq}} n_{CO_{2g}}}{n_{^{13}CO_{2g}} n_{CO_{2aq}}} = \frac{m_{^{13}CO_{2aq}} X_{CO_{2g}}}{X_{^{13}CO_{2g}} m_{CO_{2aq}}}. \quad (45)$$

The isotope exchange reaction is



and the equilibrium constant is

$$K_{^{13}CO_{2aq}}^{ex} = \frac{a_{^{13}CO_{2aq}} a_{CO_{2g}}}{a_{^{13}CO_{2g}} a_{CO_{2aq}}} = \frac{\gamma_{^{13}CO_{2aq}} (\lambda_{CO_{2g}} P_{tot})^{m_{^{13}CO_{2aq}}} X_{CO_{2g}}}{\left(\lambda_{^{13}CO_{2g}} P_{tot}\right) \gamma_{CO_{2aq}} X_{^{13}CO_{2g}} m_{CO_{2aq}}}. \quad (47)$$

Again following equations 33 - 38,

$$\log K_{^{13}CO_{2aq}}^H = \log K_{CO_{2aq}}^H + \log\left(\alpha_{CO_{2aq}-CO_{2g}}^{13C}\right) + \log\left(\frac{\gamma_{^{13}CO_{2aq}} \lambda_{CO_{2g}}}{\gamma_{CO_{2aq}} \lambda_{^{13}CO_{2g}}}\right)_{exp}. \quad (48)$$

### $^{13}CO^{18}O$

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

$$^{13}CO^{18}O_g = ^{13}CO^{18}O_{aq}. \quad (49)$$

In this case a product of fractionation factors is required to provide appropriate species; the algebra remains unchanged. Choosing appropriate ratios from equations 26 and 28 to define the fractionation factors gives

$$\left(\alpha_{CO_{2aq}-CO_{2g}}^{^{13}C}\right)\left(\alpha_{CO_{2aq}-CO_{2g}}^{^{18}O}\right) = \left(\frac{R_{CO_{2aq}}^{^{13}C}}{R_{CO_{2g}}^{^{13}C}}\right)\left(\frac{R_{CO_{2aq}}^{^{18}O}}{R_{CO_{2g}}^{^{18}O}}\right) = \frac{\left(\frac{n_{^{13}CO^{18}O_{aq}}}{n_{CO^{18}O_{aq}}}\right)\left(\frac{n_{CO^{18}O_{aq}}}{2n_{CO_{2aq}}}\right)}{\left(\frac{n_{^{13}CO^{18}O_g}}{n_{CO^{18}O_g}}\right)\left(\frac{n_{CO^{18}O_g}}{2n_{CO_{2g}}}\right)}. \quad (50)$$

Converting to concentration units yields

$$\left(\alpha_{CO_{2aq}-CO_{2g}}^{^{13}C}\right)\left(\alpha_{CO_{2aq}-CO_{2g}}^{^{18}O}\right) = \frac{n_{^{13}CO^{18}O_{aq}} n_{CO_{2g}}}{n_{^{13}CO^{18}O_g} n_{CO_{2aq}}} = \frac{m_{^{13}CO^{18}O_{aq}} X_{CO_{2g}}}{X_{^{13}CO^{18}O_g} m_{CO_{2aq}}}. \quad (51)$$

The isotope exchange reaction for equation 51 is



and the equilibrium constant is

$$K_{^{13}CO^{18}O_{aq}}^{ex} = \frac{a_{^{13}CO^{18}O_{aq}} a_{CO_{2g}}}{a_{^{13}CO^{18}O_g} a_{CO_{2aq}}} = \frac{\gamma_{^{13}CO^{18}O_{aq}} (\lambda_{CO_{2g}} P_{tot})^{m_{^{13}CO^{18}O_{aq}}} X_{CO_{2g}}}{\left(\lambda_{^{13}CO^{18}O_g} P_{tot}\right) \gamma_{CO_{2aq}} X_{^{13}CO^{18}O_g} m_{CO_{2aq}}}. \quad (53)$$

Again following equations 33 - 38,

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

## $^{13}C^{18}O_2$

The equations for  $^{13}C^{18}O_{2aq}$  are analogous to those for  $^{13}CO^{18}O_{aq}$ . The isotope ratios are

$$\left(\alpha_{CO_{2aq}-CO_{2g}}^{^{13}C}\right)\left(\alpha_{CO_{2aq}-CO_{2g}}^{^{18}O}\right)^2 = \left(\frac{R_{CO_{2aq}}^{^{13}C}}{R_{CO_{2g}}^{^{13}C}}\right)\left(\frac{R_{CO_{2aq}}^{^{18}O}}{R_{CO_{2g}}^{^{18}O}}\right)^2 = \frac{\left(\frac{n_{^{13}C^{18}O_{2aq}}}{n_{C^{18}O_{2aq}}}\right)\left(\frac{n_{C^{18}O_{2aq}}}{n_{CO_{2aq}}}\right)}{\left(\frac{n_{^{13}C^{18}O_{2g}}}{n_{C^{18}O_{2g}}}\right)\left(\frac{n_{C^{18}O_{2g}}}{n_{CO_{2g}}}\right)}, \text{ or} \quad (55)$$

$$\left(\alpha_{CO_{2aq}-CO_{2g}}^{^{13}C}\right)\left(\alpha_{CO_{2aq}-CO_{2g}}^{^{18}O}\right)^2 = \frac{n_{^{13}C^{18}O_{2aq}} n_{CO_{2g}}}{n_{^{13}C^{18}O_{2g}} n_{CO_{2aq}}} = \frac{m_{^{13}C^{18}O_{2aq}} X_{CO_{2g}}}{X_{^{13}C^{18}O_{2g}} m_{CO_{2aq}}}. \quad (56)$$

Familiar algebra leads to

$$\log K_{^{13}C^{18}O_{2aq}}^H = \log K_{CO_{2aq}}^H + \log\left(\alpha_{CO_{2aq}-CO_{2g}}^{^{13}C}\right) + 2\log\left(\alpha_{CO_{2aq}-CO_{2g}}^{^{18}O}\right) + \log\left(\frac{\gamma_{^{13}C^{18}O_{2aq}} \lambda_{CO_{2g}}}{\gamma_{CO_{2aq}} \lambda_{^{13}C^{18}O_{2g}}}\right)_{exp}. \quad (57)$$

### $^{14}CO_2$ , $^{14}CO^{18}O$ , and $^{14}C^{18}O_2$

The equations for  $^{14}CO_2$ ,  $^{14}CO^{18}O$ , and  $^{14}C^{18}O_2$  are exactly analogous to those for  $^{13}CO_2$ ,  $^{13}CO^{18}O$ , and  $^{13}C^{18}O_2$  (equations 48, 54, and 57), yielding

$$\log K_{^{14}CO_{2aq}}^H = \log K_{CO_{2aq}}^H + \log\left(\alpha_{CO_{2aq}-CO_{2g}}^{^{14}C}\right) + \log\left(\frac{\gamma_{^{14}CO_{2aq}} \lambda_{CO_{2g}}}{\gamma_{CO_{2aq}} \lambda_{^{14}CO_{2g}}}\right)_{exp}, \quad (58)$$

$$\log K_{^{14}CO^{18}O_{aq}}^H = \log K_{CO_{2aq}}^H + \log\left(\alpha_{CO_{2aq}-CO_{2g}}^{^{14}C}\right) + \log\left(\alpha_{CO_{2aq}-CO_{2g}}^{^{18}O}\right) + \log\left(\frac{\gamma_{^{14}CO^{18}O_{aq}} \lambda_{CO_{2g}}}{\gamma_{CO_{2aq}} \lambda_{^{14}CO^{18}O_g}}\right)_{exp} \quad (59)$$

and

$$\log K_{^{14}C^{18}O_{2aq}}^H = \log K_{CO_{2aq}}^H + \log\left(\alpha_{CO_{2aq}-CO_{2g}}^{^{14}C}\right) + 2\log\left(\alpha_{CO_{2aq}-CO_{2g}}^{^{18}O}\right) + \log\left(\frac{\gamma_{^{14}C^{18}O_{2aq}} \lambda_{CO_{2g}}}{\gamma_{CO_{2aq}} \lambda_{^{14}C^{18}O_{2g}}}\right)_{exp}. \quad (60)$$

The eight individual isotope equilibrium Henry's Law constants for  $CO_2$  can now be calculated given a value of the fundamental constant  $K_{^{12}C^{16}O_{2aq}}^H$  (denoted  $CO_2$  throughout the above discussion) and experimental or assumed fractionation factors.

### Symmetry Assumptions in the Isotope Ratios

The equilibrium constants for all of the reactions in the present model are listed in table 2. For all species except bicarbonate, the sequence of derivations follows that above. The fractionation factors used to derive each equilibrium constant can be recognized from the equations in table 2; the isotope ratios containing the appropriate

species are selected from table 1. The Urey relationship of equation 1,  $\alpha = (K^{ex})^{1/n}$  where  $K^{ex}$  is the equilibrium constant of the isotope exchange reaction, holds if equations 26 - 28 and their analogs for other species are valid. Urey points out that the above algebraic simplification does not occur for asymmetric molecules but does not calculate 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. The equilibrium constants for the reactions  $H_2O + D_2O = 2HDO$  and  $H_2O + T_2O = 2HTO$  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 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 was *calculating* fractionation effects in isotope exchange reactions; thus, errors 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 product molecules/phases. 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.

## INDIVIDUAL ISOTOPE EQUILIBRIUM CONSTANTS FOR BICARBONATE

The bicarbonate ion is asymmetric, with symmetry number 1 for all species. Thus, the equilibrium constants of the intraspecies reactions in equation 61 are unity, as shown in equation 62:



$$1 = \frac{n^3 HCO_2^{18}O^-}{n^2 HC^{18}O_3^- n HCO_3^-} \quad 1 = \frac{n^3 HCO^{18}O_2^-}{n^2 HC^{18}O_3^- n HCO_3^-} \quad (62)$$

There are three oxygen atoms in bicarbonate; thus, if the  $n^n$  relation held, the intraspecies equilibrium constants would equal 27, and the isotope ratios, like those for the carbonate ion, would simplify to analogs of equations 26 - 28. However, with  $K = 1$  the terms do not cancel and tedious algebra (Appendix 1) leads to the following equations for the three primary individual isotope equilibrium constants for bicarbonate:

$$\log K_{HCO_2^{18}O_{aq}^-} = \log K_{HCO_3aq^-} + \log(1.5) + \log\left(\alpha_{HCO_3aq^- - CO_{2aq}}^{18O}\right) + \log(QQ1) + \log\left(\frac{\gamma_{HCO_2^{18}O_{aq}^-} \gamma_{CO_{2aq}}}{\gamma_{HCO_3aq^-} \gamma_{CO^{18}O_{aq}}}\right)_{exp}, \quad (63)$$

$$\log K_{HCO^{18}O_{2aq}^-} = \log K_{HCO_3aq^-} + \log(3) + 2\log\left(\alpha_{HCO_3aq^- - CO_{2aq}}^{18O}\right) + \log(QQ2) + \log\left(\frac{\gamma_{HCO^{18}O_{2aq}^-} \gamma_{CO_{2g}}}{\gamma_{HCO_3aq^-} \gamma_{C^{18}O_{2g}}}\right)_{exp}, \text{ and} \quad (64)$$

$$\log K_{HC^{18}O_{3aq}^-} = \log K_{HCO_3aq^-} - 3\log(2) + 3\log\left(\alpha_{HCO_3aq^- - CO_{2aq}}^{18O}\right) + \log(QQ3) + \log\left(\frac{\gamma_{HC^{18}O_{3aq}^-} \gamma_{CO_{2aq}}^3}{\gamma_{HCO_3aq^-} \gamma_{CO^{18}O_{aq}}^3}\right)_{exp}, \quad (65)$$

where  $QQ1$ ,  $QQ2$ , and  $QQ3$  are complicated quadratic functions of  $\left(\frac{n_{HCO_2^{18}O_{aq}^-}}{3n_{HCO_3aq^-}}\right)$ ,  $\left(\frac{n_{HCO^{18}O_{2aq}^-}}{3n_{HCO_3aq^-}}\right)^{\frac{1}{2}}$ , and

$\left(\frac{n_{HC^{18}O_{3aq}^-}}{n_{HCO_3aq^-}}\right)^{\frac{1}{3}}$ , given by equations A1.18 and A1.58 for  $QQ1$ , A1.31 and A1.68 for  $QQ2$ , and A1.40 and A1.78

for  $QQ3$ , respectively. The three parameters are thus nonlinear functions of the calculated species distributions in PHREEQC simulations.

Values for the three parameters— $\log(QQ1)$ ,  $\log(QQ2)$ , and  $\log(QQ3)$ —were evaluated numerically by using UCODE (Poeter and Hill, 1998). Initial estimates for the QQ factors were used to calculate values of

$\log K_{HCO_2^{18}O_{aq}^-}$ ,  $\log K_{HCO^{18}O_{2aq}^-}$ , and  $\log K_{HC^{18}O_{3aq}^-}$ . An aqueous solution containing 10 mmol of carbon ( $^{12}C$ )

at pH 6.3 and water with  $\delta^{18}O = 0$  permil was speciated using the log K values. From the distribution of aqueous

species, the fractionation factor  $\alpha_{HCO_3aq^- - CO_{2aq}}^{18O}$  and the quotients for equation 62 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 62 were equal to 1.0, the symmetry-derived equilibrium constants. The resulting values are listed below.

The fractionation factor  $\left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O}\right)$  depends on system composition because the expressions for the isotope ratios do not simplify. The abundance ratio  $R_{VSMOW}$  is  $2.0052 \times 10^{-3}$ . Values of the three bicarbonate equilibrium constants calculated for  $^{18}O$  concentrations corresponding to  $\delta^{18}O = VSMOW \pm 100$  permil are tabulated below.

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

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

## 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  $CO_{2aq}$ , 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  $CaD^{13}C^{18}O_{3aq}^+$  ion pair requires the most complex algebra and 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 table 1):

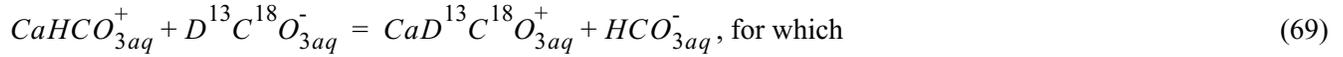
$$R_{HCO_{3aq}^-}^{18O} = \left( \frac{n_{D^{13}C^{18}O_{3aq}^-}}{n_{D^{13}CO_{3aq}^-}} \right)^{\frac{1}{3}} qq3 \quad R_{HCO_{3aq}^-}^{13C} = \frac{n_{D^{13}CO_{3aq}^-}}{n_{DCO_{3aq}^-}} \quad R_{HCO_{3aq}^-}^D = \frac{n_{DCO_{3aq}^-}}{n_{HCO_{3aq}^-}}, \quad (66)$$

$$R_{CaHCO_3^+}^{18O} = \left( \frac{n_{CaD^{13}C^{18}O_{3aq}^+}}{n_{CaD^{13}CO_{3aq}^+}} \right)^{\frac{1}{3}} qq3 \quad R_{CaHCO_3^+}^{13C} = \frac{n_{CaD^{13}CO_{3aq}^+}}{n_{CaDCO_{3aq}^+}} \quad R_{CaHCO_3^+}^D = \frac{n_{CaDCO_{3aq}^+}}{n_{CaHCO_{3aq}^+}}. \quad (67)$$

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

$$\begin{aligned} & \left( \alpha_{CaHCO_{3aq}^+ - HCO_{3aq}^-}^{18O} \right)^3 \left( \alpha_{CaHCO_{3aq}^+ - HCO_{3aq}^-}^{13C} \right) \left( \alpha_{CaHCO_{3aq}^+ - HCO_{3aq}^-}^D \right) \\ &= \frac{\left[ \left( \frac{n_{CaD^{13}C^{18}O_{3aq}^+}}{n_{CaD^{13}CO_{3aq}^+}} \right) (qq3)^3 \right] \left[ \left( \frac{n_{CaD^{13}CO_{3aq}^+}}{n_{CaDCO_{3aq}^+}} \right) \left( \frac{n_{CaDCO_{3aq}^+}}{n_{CaHCO_{3aq}^+}} \right) \right]}{\left[ \left( \frac{n_{D^{13}C^{18}O_{3aq}^-}}{n_{D^{13}CO_{3aq}^-}} \right) (qq3)^3 \right] \left[ \left( \frac{n_{D^{13}CO_{3aq}^-}}{n_{DCO_{3aq}^-}} \right) \left( \frac{n_{DCO_{3aq}^-}}{n_{HCO_{3aq}^-}} \right) \right]} = \frac{m_{CaD^{13}C^{18}O_{3aq}^+} m_{HCO_{3aq}^-}}{m_{CaHCO_{3aq}^+} m_{D^{13}C^{18}O_{3aq}^-}}. \end{aligned} \quad (68)$$

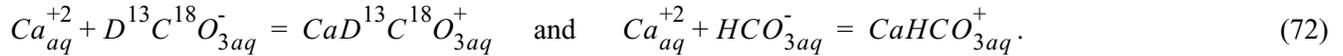
The isotope exchange reaction corresponding to equation 68 is



$$K_{CaD^{13}C^{18}O_{3aq}^+}^{ex} = \frac{a_{CaD^{13}C^{18}O_{3aq}^+} a_{HCO_{3aq}^-}}{a_{CaHCO_{3aq}^+} a_{D^{13}C^{18}O_{3aq}^-}} = \frac{m_{CaD^{13}C^{18}O_{3aq}^+} m_{HCO_{3aq}^-}}{m_{CaHCO_{3aq}^+} m_{D^{13}C^{18}O_{3aq}^-}} \frac{\gamma_{CaD^{13}C^{18}O_{3aq}^+}}{\gamma_{CaHCO_{3aq}^+}} \frac{\gamma_{HCO_{3aq}^-}}{\gamma_{D^{13}C^{18}O_{3aq}^-}}, \text{ or} \quad (70)$$

$$\begin{aligned} K_{CaD^{13}C^{18}O_{3aq}^+}^{ex} &= \left( \alpha_{CaHCO_{3aq}^+ - HCO_{3aq}^-}^{18O} \right)^3 \left( \alpha_{CaHCO_{3aq}^+ - HCO_{3aq}^-}^{13C} \right) \left( \alpha_{CaHCO_{3aq}^+ - HCO_{3aq}^-}^D \right) \times \\ & \quad \left( \frac{\gamma_{CaD^{13}C^{18}O_{3aq}^+} \gamma_{HCO_{3aq}^-}}{\gamma_{CaHCO_{3aq}^+} \gamma_{D^{13}C^{18}O_{3aq}^-}} \right)_{exp}. \end{aligned} \quad (71)$$

The reactions used in PHREEQC are



$$K_{CaD^{13}C^{18}O_{3aq}^+}^{ex} = \frac{a_{CaD^{13}C^{18}O_{3aq}^+} a_{HCO_{3aq}^-}}{a_{CaHCO_{3aq}^+} a_{D^{13}C^{18}O_{3aq}^-}} = \frac{a_{CaD^{13}C^{18}O_{3aq}^+} a_{Ca_{aq}^{+2}} a_{HCO_{3aq}^-}}{a_{Ca_{aq}^{+2}} a_{D^{13}C^{18}O_{3aq}^-} a_{CaHCO_{3aq}^+}} = \frac{K_{CaD^{13}C^{18}O_{3aq}^+}}{K_{CaHCO_{3aq}^+}}, \quad (73)$$

$$\begin{aligned} K_{CaD^{13}C^{18}O_{3aq}^+} &= K_{CaHCO_{3aq}^+} K_{CaD^{13}C^{18}O_{3aq}^+}^{ex} = K_{CaHCO_{3aq}^+} \left( \alpha_{CaHCO_{3aq}^+ - HCO_{3aq}^-}^{18O} \right)^3 \times \\ & \quad \left( \alpha_{CaHCO_{3aq}^+ - HCO_{3aq}^-}^{13C} \right) \left( \alpha_{CaHCO_{3aq}^+ - HCO_{3aq}^-}^D \right) \left( \frac{\gamma_{CaD^{13}C^{18}O_{3aq}^+} \gamma_{HCO_{3aq}^-}}{\gamma_{CaHCO_{3aq}^+} \gamma_{D^{13}C^{18}O_{3aq}^-}} \right)_{exp}, \text{ and} \end{aligned} \quad (74)$$

$$\log K_{CaD^{13}C^{18}O_{3aq}^+} = \log K_{CaHCO_{3aq}^+} + 3 \log \left( \alpha_{CaHCO_{3aq}^+ - HCO_{3aq}^-}^{18O} \right) + \log \left( \alpha_{CaHCO_{3aq}^+ - HCO_{3aq}^-}^{13C} \right) + \log \left( \alpha_{CaHCO_{3aq}^+ - HCO_{3aq}^-}^D \right) + \log \left( \frac{\gamma_{CaD^{13}C^{18}O_{3aq}^+} \gamma_{HCO_{3aq}^-}}{\gamma_{CaHCO_{3aq}^+} \gamma_{D^{13}C^{18}O_{3aq}^-}} \right)_{exp} \quad (75)$$

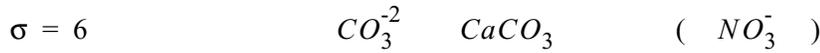
The form of any individual isotope equilibrium constant for ion pairs, if written from the free ions, will have the same form as equation 75, with each fractionation factor multiplied by its stoichiometric coefficient in the free ion.

## APPLICATION TO OTHER ISOTOPES

The methods described above are general and were applied systematically to generate all of the entries in tables 1 - 3. They 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 calculation of the various expressions of the isotope ratios for each molecular species. However, if the new molecular species has the same stoichiometry and symmetry 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 26 - 28 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  $CO_2$ . Table 1 shows the isotope ratios of  $H_2O$  and  $CO_2$  to be algebraically equivalent with these substitutions; identical structure is not required. Listed below are symmetry numbers and the corresponding species from table 1. To the right, 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 in this report are in brackets { }. The molecular structures from which the symmetry numbers were obtained are from Purdue University (2002).

$\sigma = 1$	$OH^-$	( $CO$ $NO$ )
	$HCO_3^-$	( $HNO_3$ )
		{ $NNO$ $HSO_4^-$ }
$\sigma = 2$	$CO_2$ $H_2O$	( $H_2S$ $NO_2$ $NO_2^-$ )
		{ $H_2$ $N_2$ $O_2$ }
$\sigma = 3$	$H_3O^+$	( $NH_3$ )



For the underived species, the procedure is analogous to equations 2 - 28 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 (equation 76) will be obtained as one of the isotope ratio expressions:

$$R_{AB_j}^i = \left( \frac{n_{A^i B_j}}{n_{AB_j}} \right)^{\frac{1}{j}}, \quad (76)$$

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

The remaining calculations of the individual isotope equilibrium constants are more straightforward and are analogous to equations 29 to 60 for  $CO_2$  and equations A1.49 - A1.185 for  $HCO_3^-$ . 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 isotope exchange reaction, and thus cancel.

## NONIDEALITY

The equation structure in PHREEQC assumes the presence of only one solvent, liquid  $H_2O$ . The other isotopic water species  $HDO_{aq}$ ,  $D_2O_{aq}$ ,  $H_2^{18}O_{aq}$ ,  $HD^{18}O_{aq}$ , and  $D_2^{18}O_{aq}$  are treated as electrically neutral solutes in PHREEQC. The concentration scale and the activity-concentration conventions differ for solute and solvent. The activity of water is defined by

$$a_{H_2O} = 1 - 0.017 \sum_i^{N_{aq}} \frac{n_i}{W_{aq}}, \quad (77)$$

where  $N_{aq}$  is the number of aqueous species 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  $\mu$  is the ionic strength. Therefore

$$a_i = (10^{b_i \mu}) m_i. \quad (78)$$

The reference state is infinite dilution, and the concentration scale is molal. If these conventions were used for the other isotopic water species, the activity of pure  $HDO$ , for example, would be  $\sim 53$ , whereas that of pure  $H_2O$  would be 1.0. In addition, as electrolyte concentrations increase,  $a_{H_2O}$  would decrease according to equation 77, whereas  $a_{HDO}/m_{HDO}$  would increase according to equation 78.

To make the concentration scales and the activity-concentration relations consistent for  $H_2O$  and for  $HDO_{aq}$ ,  $D_2O_{aq}$ ,  $H_2^{18}O_{aq}$ ,  $HD^{18}O_{aq}$ , and  $D_2O_{aq}$ , the activities and activity coefficients for the latter are defined as

$$a_i = \gamma_i m_i \quad \text{and} \quad \gamma_i = \frac{a_{H_2O}}{55.5}, \quad (79)$$

where  $i$  refers to the five species  $HDO_{aq}$ ,  $D_2O_{aq}$ ,  $H_2^{18}O_{aq}$ ,  $HD^{18}O_{aq}$ , and  $D_2O_{aq}$ .

Ratios of activity coefficients appear in all of the equations used to calculate the individual isotope equilibrium constants. For example, in the equations (table 2) for  $\log K_{HD_2O_{aq}^+}$ ,  $\log K_{^{13}C^{18}O_{3aq}^{-2}}$ , and  $\log K_{CaCO^{18}O_{2s}}$  are found

$$\text{the terms } \log \left( \frac{\gamma_{HD_2O_{aq}^+}}{\gamma_{H_3O_{aq}^+}} \right)_{exp}, \log \left( \frac{\gamma_{^{13}C^{18}O_{3aq}^{-2}} \gamma_{CO_{2aq}}^4}{\gamma_{CO_{3aq}^{-2}} \gamma_{CO^{18}O_{aq}}^3 \gamma_{^{13}CO_{2aq}}} \right)_{exp}, \text{ and } \log \left( \frac{\lambda_{CaCO_{3s}} \gamma_{C^{18}O_{2aq}}}{\lambda_{CaCO^{18}O_{2s}} \gamma_{CO_{2aq}}} \right)_{exp},$$

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 and/or phases 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. For gases and solids, this is an arbitrary assumption. For dissolved species, there is some fundamental justification provided by the fact that the PHREEQC aqueous model is an ion-interaction model in which the activity coefficients of aqueous species are based on the electrostatic-interaction Debye-Hückel equation

$$-\log \gamma_i = \frac{Az_i^2 \mu^{1/2}}{1 + a_i B \mu^{1/2}}. \quad (80)$$

There is no explicit mass dependence in the derivation of this equation and its included constants (Lewis and Randall, 1961, p. 332-343).

The activity-coefficient terms in each of the equations of 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. The individual isotope equilibrium constants should thus be applicable to calculations of evaporation from brines, for example. 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.

## TEMPERATURE DEPENDENCE

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

$$\log_{10} K = A_1 + A_2 T + \frac{A_3}{T} + A_4 \log_{10} T + \frac{A_5}{T^2}. \quad (81)$$

Fractionation factors are generally reported in equations of the form  $10^3 \ln \alpha = a \left( \frac{10^6}{T^2} \right) + b \left( \frac{10^3}{T} \right) + c$ , which will be written here as

$$10^3 \ln \alpha = A_1^\alpha + \frac{A_3^\alpha}{T} + \frac{A_5^\alpha}{T^2}. \quad (82)$$

Equation 82 is the form in which the fractionation factors are presented in table 3, which can be rewritten as equation 83

$$\log_{10} \alpha = \frac{A_1^\alpha}{10^3 \ln 10} + \frac{A_3^\alpha}{[10^3 \ln 10] T} + \frac{A_5^\alpha}{[10^3 \ln 10] T^2}. \quad (83)$$

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

Restating equation 38

$$\log K_{CO^{18}O_{aq}}^H = \log K_{CO_{2aq}}^H + \log \left( \alpha_{CO_{2aq} - CO_{2g}}^{^{18}O} \right) + \log \left( \frac{\gamma_{CO^{18}O_{aq}} \lambda_{CO_{2g}}}{\gamma_{CO_{2aq}} \lambda_{CO^{18}O_g}_{exp}} \right). \quad (84)$$

The fractionation factor temperature dependence is

$$10^3 \ln(\alpha_{CO_{2aq}-CO_{2g}}^{18O}) = A_1^\alpha + \frac{A_3^\alpha}{T} + \frac{A_5^\alpha}{T^2}, \text{ or} \quad (85)$$

$$\log(\alpha_{CO_{2aq}-CO_{2g}}^{18O}) = \frac{A_1^\alpha}{10^3 \ln 10} + \frac{A_3^\alpha}{[10^3 \ln 10]T} + \frac{A_5^\alpha}{[10^3 \ln 10]T^2}. \quad (86)$$

Assuming the activity coefficient term is unity, equations 81, 84, and 86 give

$$\log K_{CO^{18}O_{aq}}^H = \left( A_1 + \frac{A_1^\alpha}{10^3 \ln 10} \right) + A_2 T + \left( A_3 + \frac{A_3^\alpha}{10^3 \ln 10} \right) \left( \frac{1}{T} \right) + A_4 \log_{10} T + \left( A_5 + \frac{A_5^\alpha}{10^3 \ln 10} \right) \left( \frac{1}{T^2} \right). \quad (87)$$

The temperature dependence of  $\log K_{CO^{18}O_{aq}}^H$  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.

## FUNDAMENTAL INDIVIDUAL ISOTOPE EQUILIBRIUM CONSTANTS

Henry's Law is 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,  $CO_{2tot}$  is defined by equation 88:

$$K_{CO_{2tot}}^H \equiv \frac{\gamma_{CO_{2tot}} \left( m_{CO_{2aq}} + m_{CO^{18}O_{aq}} + m_{C^{18}O_{2aq}} + m_{^{13}CO_{2aq}} + m_{^{13}CO^{18}O_{aq}} + m_{^{13}C^{18}O_{2aq}} \right)}{\left( P_{CO_{2g}} + P_{CO^{18}O_g} + P_{C^{18}O_{2g}} + P_{^{13}CO_{2g}} + P_{^{13}CO^{18}O_g} + P_{^{13}C^{18}O_{2g}} \right)}. \quad (88)$$

The expression can be rewritten as follows:

$$K_{CO_{2tot}}^H \equiv \frac{\gamma_{CO_{2tot}} m_{CO_{2aq}} \left( 1 + \frac{m_{CO^{18}O_{aq}}}{m_{CO_{2aq}}} + \frac{m_{C^{18}O_{2aq}}}{m_{CO_{2aq}}} + \frac{m_{^{13}CO_{2aq}}}{m_{CO_{2aq}}} + \frac{m_{^{13}CO^{18}O_{aq}}}{m_{CO_{2aq}}} + \frac{m_{^{13}C^{18}O_{2aq}}}{m_{CO_{2aq}}} \right)}{P_{CO_{2g}} \left( 1 + \frac{P_{CO^{18}O_g}}{P_{CO_{2g}}} + \frac{P_{C^{18}O_{2g}}}{P_{CO_{2g}}} + \frac{P_{^{13}CO_{2g}}}{P_{CO_{2g}}} + \frac{P_{^{13}CO^{18}O_g}}{P_{CO_{2g}}} + \frac{P_{^{13}C^{18}O_{2g}}}{P_{CO_{2g}}} \right)}, \quad (89)$$

$$K_{CO_{2tot}}^H \equiv \frac{\gamma_{CO_{2tot}} \gamma_{CO_2} m_{CO_{2aq}} \left\{ 1 + 2R_{CO_{2aq}}^{18O} + \left( R_{CO_{2aq}}^{18O} \right)^2 + R_{CO_{2aq}}^{13C} \left[ 1 + 2R_{CO_{2aq}}^{18O} + \left( R_{CO_{2aq}}^{18O} \right)^2 \right] \right\}}{\gamma_{CO_2} P_{CO_{2g}} \left\{ \left( 1 + 2R_{CO_{2g}}^{18O} + \left( R_{CO_{2g}}^{18O} \right)^2 \right) + R_{CO_{2g}}^{13C} \left[ 1 + 2R_{CO_{2g}}^{18O} + \left( R_{CO_{2g}}^{18O} \right)^2 \right] \right\}}, \text{ and} \quad (90)$$

$$K_{CO_2}^H \equiv \frac{\gamma_{CO_2} K_{CO_2}^H}{\gamma_{CO_2}} \frac{\left(1 + R_{CO_2aq}^{13C}\right)\left(1 + R_{CO_2aq}^{18O}\right)^2}{\left(1 + R_{CO_2g}^{13C}\right)\left(1 + R_{CO_2g}^{18O}\right)^2}. \quad (91)$$

Using the definition of the fractionation factor gives

$$K_{CO_2}^H \equiv \frac{\gamma_{CO_2} K_{CO_2}^H}{\gamma_{CO_2}} \frac{\left(1 + \left[\alpha_{CO_2aq-CO_2g}^{13C}\right] R_{CO_2g}^{13C}\right)\left(1 + \left[\alpha_{CO_2aq-CO_2g}^{18O}\right] R_{CO_2g}^{18O}\right)^2}{\left(1 + R_{CO_2g}^{13C}\right)\left(1 + R_{CO_2g}^{18O}\right)^2}, \quad (92)$$

and thus solving for the fundamental constant  $K_{CO_2}^H$  gives

$$K_{CO_2}^H = K_{CO_2}^H \left(\frac{\gamma_{CO_2}}{\gamma_{CO_2}}\right) \frac{\left(1 + R_{CO_2g}^{13C}\right)\left(1 + R_{CO_2g}^{18O}\right)^2}{\left(1 + \left[\alpha_{CO_2aq-CO_2g}^{13C}\right] R_{CO_2g}^{13C}\right)\left(1 + \left[\alpha_{CO_2aq-CO_2g}^{18O}\right] R_{CO_2g}^{18O}\right)^2}. \quad (93)$$

If the parameters  $P_{CO_2g,tot}$ ,  $m_{CO_2aq,tot}$ ,  $R_{CO_2g}^{13C}$ ,  $R_{CO_2aq}^{13C}$ ,  $R_{CO_2g}^{18O}$  and  $R_{CO_2aq}^{18O}$  are all measured precisely *in the same experiment*, or extrapolated precisely to infinite dilution, then all of the parameters defined in equations 91 - 93 can be calculated exactly, provided the ratio of activity coefficients is known.  $K_{CO_2}^H$  could then be calculated from the standard thermochemical value of  $K_{CO_2}^H$ . However, experimental isotope studies determine the ratios  $R_{aq}$  and  $R_g$  (and thus  $\alpha$ ) precisely, with less emphasis on absolute solubilities, whereas the experimental solubility studies, from which the standard thermochemical properties of substances are calculated, measure  $K_{CO_2}^H$  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  $\alpha$  are usually not the same studies that define the values of  $K_{CO_2}^H$ .

## 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 and others (1974) and Wigley and others (1978) in a subroutine to the reaction-path modeling program PHREEQE (Parkhurst and others, 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  $\delta D$  and  $\delta^{18}O$  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  $^{18}O$ , D, and  $^{34}S$ , also using EQ3/6. Bohlke 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 postprocessor 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, using a postprocessor to the program React (Bethke, 1996). Plummer and others (1991, 1994) use the equations of Wigley and others (1978) in the program NETPATH to solve Rayleigh calculations for reaction mole-transfers 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  $CO_{2g}$  and  $CO_{2aq}$  can again be used for illustration. For  $^{13}C$ , for example, at the completion of a species-distribution calculation, the postprocessor method uses the speciation-calculated values of  $CO_{2aq, tot}$  and  $CO_{2g, tot}$ , the fractionation factor  $\alpha_{CO_{2aq} - CO_{2g}}^{^{13}C}$ , and an isotope balance equation using  $\delta^{13}C_{system, tot}$  (or more rigorously moles of  $^{13}C_{system, tot}$ ), to calculate  $\delta^{13}C_{g, tot}$  and  $\delta^{13}C_{aq, tot}$ , and thus  $R_{CO_{2g}}^{^{13}C}$  and  $R_{CO_{2aq}}^{^{13}C}$ . Once  $R_{CO_{2g}}^{^{13}C}$  and  $R_{CO_{2aq}}^{^{13}C}$  are known, simple mass-balance equations (94) allow calculation of  $CO_{2g}$ ,  $CO_{2aq}$ ,  $^{13}CO_{2g}$ , and  $^{13}CO_{2aq}$ :

$$CO_{2j, tot} = CO_{2j} \left( 1 + R_{CO_{2j}}^{^{13}C} \right) \quad \text{and} \quad ^{13}CO_{2j} = CO_{2j} \left( R_{CO_{2j}}^{^{13}C} \right). \quad (94)$$

The thermodynamic model based on individual isotope equilibrium constants calculates values of  $K_{CO_2}^H = a_{CO_{2aq}} / a_{CO_{2g}}$  and  $K_{^{13}CO_2}^H = a_{^{13}CO_{2aq}} / a_{^{13}CO_{2g}}$ , which are derived from from the relation

$$\alpha_{CO_{2aq} - CO_{2g}}^{^{13}C} = K_{^{13}CO_2}^H / K_{CO_2}^H, \quad \text{and uses the two individual isotope equilibrium constants in the species-}$$

distribution calculation to obtain concentrations of  $CO_{2g}$ ,  $CO_{2aq}$ ,  $^{13}CO_{2g}$ , and  $^{13}CO_{2aq}$ .

Both methods can be expanded to include mixed isotope species by using equations 2 - 28. This report then uses equations 29 - 57 to calculate the individual isotope equilibrium constants that permit the complete species-distribution calculation.

The postprocessor calculation would again use the speciation-calculated values of  $CO_{2aq,tot}$  and  $CO_{2g,tot}$ , the fractionation factor  $\alpha_{CO_{2aq}-CO_{2g}}^{^{13}C}$ , and an isotope-balance equation using  $\delta^{^{13}C}_{system,tot}$  (or more rigorously, moles of  $^{13}C_{system,tot}$ ), to calculate  $\delta^{^{13}C}_{g,tot}$  and  $\delta^{^{13}C}_{aq,tot}$ , and thus  $R_{CO_{2g}}^{^{13}C}$  and  $R_{CO_{2aq}}^{^{13}C}$ . A mass-balance equation can then be written for each phase:

$$n_{CO_{2j,tot}} = n_{CO_{2j}} + n_{CO^{18}O_j} + n_{C^{18}O_{2j}} + n_{^{13}CO_{2j}} + n_{^{13}CO^{18}O_j} + n_{^{13}C^{18}O_{2j}}. \quad (95)$$

The values of  $\delta^{^{13}C}_{CO_{2j}}$  are known, thus defining  $R_{CO_{2j}}^{^{13}C}$ . Using equation 28 allows equation 95 to be written

$$n_{CO_{2g,tot}} = \left( n_{CO_{2j}} + n_{CO^{18}O_j} + n_{C^{18}O_{2j}} \right) \left( 1 + R_{CO_{2j}}^{^{13}C} \right). \quad (96)$$

The values of  $\delta^{^{18}O}_{CO_{2j}}$  are known, thus defining  $R_{CO_{2j}}^{^{18}O}$ . Using equation 26 allows equation 96 to be written as

$$n_{CO_{2j,tot}} = n_{CO_{2j}} \left( 1 + 2R_{CO_{2j}}^{^{18}O} + \left[ R_{CO_{2j}}^{^{18}O} \right]^2 \right) \left( 1 + R_{CO_{2j}}^{^{13}C} \right) = n_{CO_{2j}} \left( 1 + R_{CO_{2j}}^{^{18}O} \right)^2 \left( 1 + R_{CO_{2j}}^{^{13}C} \right), \quad (97)$$

which allows calculation of  $n_{CO_{2j}}$ . Equations 26 and 28 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  $CO_{2,tot}$ , which is very slightly different from the individual Henry's Law constants (equation 93). 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  $K_{CO_2}^H$  is assumed to equal  $K_{CO_{2,tot}}^H$ , or equation 93 is used to calculate  $K_{CO_2}^H$ , 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 remains to be determined.

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. Kinetic fractionation factors can be used in both methods. The method presented here will calculate equilibrium constants corresponding to the values of the entered kinetic fractionation factors.

The advantage of the extra algebra for the individual isotope method in this report is that reaction and isotope calculations are performed simultaneously. In addition, the set of individual isotope equilibrium constants should prove useful in studies of reaction mechanisms, kinetics, and transport. An early version of this method was used to investigate gas-transport effects on isotopes in the unsaturated zone (Parkhurst and others, 2001). For isotopic phase equilibria studies that require a knowledge of the degree of saturation of each component, for example, the degree to which stoichiometric saturation is involved in isotope solutions, the individual isotope equilibrium constants appear to be a necessity.

## EXAMPLE CALCULATION USING PHREEQC

Descriptions of five new PHREEQC keyword data blocks for isotopic data input and the necessary modifications to existing keyword data blocks are found in Appendix 2. The example consists of constructing a solution of specified isotopic composition that is supersaturated with respect to calcite and allowing this solution to degas into an evacuated volume with attendant precipitation of calcite. The system attains complete isotopic equilibrium. The input data consist of the reactions and corresponding equilibrium constants of table 2 and the temperature coefficients of the fractionation factors in table 3. Internal consistency of the calculations is checked by comparing the values of  $10^3 \ln \alpha$  computed from the calculated species distribution and those input to the program at the temperature of the calculations.

```
Input file: example
Output file: example.out
Database file: iso.dat
```

```
-----
Reading data base.
-----
```

```
SOLUTION_MASTER_SPECIES
ISOTOPES
ISOTOPE_RATIOS
```

```

ISOTOPE_ALPHAS
NAMED_EXPRESSIONS
NAMED_EXPRESSIONS
SOLUTION_SPECIES
SOLUTION_SPECIES
SOLUTION_SPECIES
PHASES
SOLUTION_SPECIES
CALCULATE_VALUES
END

```

-----  
Reading input data for simulation 1.  
-----

```

SOLUTION 1
  pH      8.2
  Na      1      charge
  Ca      1      Calcite .1
  C       2
  [13C]   0      # permil
  [14C]   100    # pmc
  T       10     # TU
  D       0      # permil
  [18O]   0      # permil
END

```

-----  
Beginning of initial solution calculations.  
-----

Initial solution 1.

-----Isotopes-----

Isotope	Molality	Moles	Ratio	Units
H	1.10997e+02	1.10997e+02		
D	1.72889e-02	1.72889e-02	0.00000e+00	permil
T	5.55062e-16	5.55062e-16	1.00000e+01	TU
C	1.97789e-03	1.97789e-03		
[13C]	2.21132e-05	2.21132e-05	0.00000e+00	permil
[14C]	2.35178e-15	2.35178e-15	1.00000e+02	pmc
O	5.54011e+01	5.54011e+01		
[18O]	1.11090e-01	1.11090e-01	0.00000e+00	permil

-----Solution composition-----

Elements	Molality	Moles	
C	2.000e-03	2.000e-03	
Ca	3.909e-04	3.909e-04	Equilibrium with Calcite
Na	1.218e-03	1.218e-03	Charge balance

-----Description of solution-----

```

pH = 8.200
pe = 4.000
Activity of water = 1.000

```

```

      Ionic strength = 2.370e-03
      Mass of water (kg) = 1.000e+00
      Total alkalinity (eq/kg) = 2.000e-03
      Total CO2 (mol/kg) = 2.000e-03
      Temperature (deg C) = 25.000
      Electrical balance (eq) = 1.897e-12
      Percent error, 100*(Cat-|An|)/(Cat+|An|) = 0.00
      Iterations = 8
      Total H = 1.109971e+02
      Total O = 5.540110e+01

```

-----Distribution of species-----

	Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
	OH-	1.675e-06	1.586e-06	-5.776	-5.800	-0.023
	H3O+	6.632e-09	6.310e-09	-8.178	-8.200	-0.022
	H2O	5.551e+01	9.999e-01	-0.000	-0.000	0.000
C(4)	2.000e-03					
	HCO3-	1.941e-03	1.840e-03	-2.712	-2.735	-0.023
	CO2	2.609e-05	2.611e-05	-4.583	-4.583	0.000
	CO3-2	1.695e-05	1.368e-05	-4.771	-4.864	-0.093
	CaHCO3+	7.540e-06	7.154e-06	-5.123	-5.145	-0.023
	CaCO3	7.001e-06	7.005e-06	-5.155	-5.155	0.000
	NaHCO3	1.193e-06	1.193e-06	-5.924	-5.923	0.000
	NaCO3-	3.099e-07	2.937e-07	-6.509	-6.532	-0.023
Ca	3.909e-04					
	Ca+2	3.764e-04	3.049e-04	-3.424	-3.516	-0.091
	CaHCO3+	7.540e-06	7.154e-06	-5.123	-5.145	-0.023
	CaCO3	7.001e-06	7.005e-06	-5.155	-5.155	0.000
	CaOH+	8.470e-23	8.028e-23	-22.072	-22.095	-0.023
H(0)	5.634e-28					
	H2	2.817e-28	2.819e-28	-27.550	-27.550	0.000
Na	1.218e-03					
	Na+	1.216e-03	1.153e-03	-2.915	-2.938	-0.023
	NaHCO3	1.193e-06	1.193e-06	-5.924	-5.923	0.000
	NaCO3-	3.099e-07	2.937e-07	-6.509	-6.532	-0.023
	NaOH	1.208e-23	1.209e-23	-22.918	-22.918	0.000
O(0)	1.049e-37					
	O2	5.243e-38	5.246e-38	-37.280	-37.280	0.000

-----Saturation indices-----

Phase	SI	log IAP	log KT	
Calcite	0.10	8.30	8.20	CaCO3
CO2(g)	-3.12	-4.58	-1.47	CO2
H2O(g)	-1.51	-0.00	1.51	H2O

-----  
End of simulation.  
-----

-----  
Reading input data for simulation 2.  
-----

USE solution 1

```

GAS_PHASE
  fixed_volume 1
  H2O(g) 0
  HDO(g) 0
  D2O(g) 0
  H2[18O](g) 0
  HD[18O](g) 0
  D2[18O](g) 0
  HTO(g) 0
  HT[18O](g) 0
  DTO(g) 0
  CO2(g) 0
  CO[18O](g) 0
  C[18O]2(g) 0
  [13C]O2(g) 0
  [13C]O[18O](g) 0
  [13C][18O]2(g) 0
  [14C]O2(g) 0
  [14C]O[18O](g) 0
  [14C][18O]2(g) 0

```

```

SOLID_SOLUTION
Calcite
  component Calcite 0
  component CaCO2[180] 0
  component CaCO[180]2 0
  component CaC[180]3 0
  component Ca[13C]O3 0
  component Ca[13C]O2[180] 0
  component Ca[13C]O[180]2 0
  component Ca[13C][180]3 0
  component Ca[14C]O3 0
  component Ca[14C]O2[180] 0
  component Ca[14C]O[180]2 0
  component Ca[14C][180]3 0

```

END

-----  
Beginning of batch-reaction calculations.  
-----

Reaction step 1.

Using solution 1.

Using solid solution assemblage 1.

Using gas phase 1.

-----Gas phase-----

Total pressure: 0.0317 atmospheres  
Gas volume: 1.00e+00 liters

Component	log P	P	Moles in gas		
			Initial	Final	Delta
[13C][18O]2(g)	-10.41	3.907e-11	0.000e+00	1.597e-12	1.597e-12
[13C]O2(g)	-5.05	8.966e-06	0.000e+00	3.665e-07	3.665e-07
[13C]O[18O](g)	-7.43	3.743e-08	0.000e+00	1.530e-09	1.530e-09
[14C][18O]2(g)	-20.38	4.123e-21	0.000e+00	1.685e-22	1.685e-22
[14C]O2(g)	-15.02	9.464e-16	0.000e+00	3.868e-17	3.868e-17

[14C]O[18O](g)	-17.40	3.951e-18	0.000e+00	1.615e-19	1.615e-19
C[18O]2(g)	-8.45	3.521e-09	0.000e+00	1.439e-10	1.439e-10
CO2(g)	-3.09	8.081e-04	0.000e+00	3.303e-05	3.303e-05
CO[18O](g)	-5.47	3.374e-06	0.000e+00	1.379e-07	1.379e-07
D2[18O](g)	-11.89	1.276e-12	0.000e+00	5.214e-14	5.214e-14
D2O(g)	-9.19	6.421e-10	0.000e+00	2.625e-11	2.625e-11
DTO(g)	-22.42	3.820e-23	0.000e+00	1.561e-24	1.561e-24
H2[18O](g)	-4.21	6.125e-05	0.000e+00	2.504e-06	2.504e-06
H2O(g)	-1.51	3.083e-02	0.000e+00	1.260e-03	1.260e-03
HD[18O](g)	-7.75	1.768e-08	0.000e+00	7.226e-10	7.226e-10
HDO(g)	-5.05	8.899e-06	0.000e+00	3.637e-07	3.637e-07
HT[18O](g)	-21.28	5.259e-22	0.000e+00	2.149e-23	2.149e-23
HTO(g)	-18.58	2.647e-19	0.000e+00	1.082e-20	1.082e-20

-----Solid solutions-----

Solid solution	Component	Moles	Delta moles	Mole fract
Calcite		3.92e-05		
	Calcite	3.85e-05	3.85e-05	9.83e-01
	CaCO2[18O]	2.38e-07	2.38e-07	6.08e-03
	CaCO[18O]2	4.91e-10	4.91e-10	1.25e-05
	CaC[18O]3	3.37e-13	3.37e-13	8.61e-09
	Ca[13C]O3	4.32e-07	4.32e-07	1.10e-02
	Ca[13C]O2[18O]	2.67e-09	2.67e-09	6.81e-05
	Ca[13C]O[18O]2	5.50e-12	5.50e-12	1.40e-07
	Ca[13C][18O]3	3.78e-15	3.78e-15	9.65e-11
	Ca[14C]O3	4.60e-17	4.60e-17	1.17e-12
	Ca[14C]O2[18O]	2.84e-19	2.84e-19	7.26e-15
	Ca[14C]O[18O]2	5.86e-22	5.86e-22	1.50e-17
	Ca[14C][18O]3	4.03e-25	3.03e-25	1.03e-20

-----Isotope Ratios-----

Isotope Ratio	Ratio	Input Units
R(13C) Calcite	1.12049e-02	2.2079 permil
R(18O) Calcite	2.06136e-03	28.009 permil
R(13C) CO2(g)	1.10956e-02	-7.5676 permil
R(18O) CO2(g)	2.08734e-03	40.964 permil
R(13C) CO2(aq)	1.10863e-02	-8.4 permil
R(18O) CO2(aq)	2.08958e-03	42.08 permil
R(13C) HCO3-	1.11827e-02	0.22679 permil
R(D) HCO3-	1.55760e-04	0.0016832 permil
R(18O) HCO3-	2.08956e-03	42.072 permil
R(13C) CO3-2	1.11667e-02	-1.2086 permil
R(18O) CO3-2	2.08958e-03	42.08 permil
R(18O) H2O(l)	2.00519e-03	-0.0042574 permil
R(D) H2O(l)	1.55760e-04	0.0016832 permil
R(D) OH-	3.70889e-05	-761.88 permil
R(18O) OH-	1.93085e-03	-37.076 permil
R(D) H3O+	1.62250e-04	41.666 permil
R(18O) H3O+	2.05156e-03	23.119 permil
R(18O) H2O(g)	1.98657e-03	-9.2908 permil
R(D) H2O(g)	1.44310e-04	-73.512 permil
R(D)	1.55760e-04	0.0016729 permil
R(T)	1.00232e-17	10.023 TU
R(18O)	2.00520e-03	0.00010261 permil
R(13C)	1.11812e-02	0.0868 permil

R(14C)

1.17609e-12

100.02 pmc

## -----Isotope Alphas-----

Isotope Ratio	Solution alpha	1000ln(Alpha)	
		Solution	25.0 C
Alpha 18O CO2(aq)/CO2(g)	1.0011	1.0715	1.0715
Alpha 13C CO2(aq)/CO2(g)	0.99916	-0.83913	-0.83913
Alpha 18O CO2(aq)/H2O(l)	1.0421	41.223	41.223
Alpha D H2O(l)/H2O(g)	1.0793	76.356	76.356
Alpha 18O H2O(l)/H2O(g)	1.0094	9.33	9.33
Alpha 18O H3O+/H2O(l)	1.0231	22.86	22.86
Alpha D H3O+/H2O(l)	1.0417	40.82	40.82
Alpha 18O OH-/H2O(l)	0.96293	-37.777	-37.777
Alpha D OH-/H2O(l)	0.23812	-1435	-1435
Alpha 13C CO3-2/CO2(aq)	1.0073	7.2261	7.2261
Alpha 18O CO3-2/CO2(aq)	1	-1.5732e-09	0
Alpha 13C HCO3-/CO2(aq)	1.0087	8.6622	8.6622
Alpha 18O HCO3-/CO2(aq)	0.99999	-0.0076108	0
Alpha D HCO3-/H2O(l)	1	1.2044e-09	0
Alpha 13C CO2(aq)/Calcite	0.98942	-10.641	-10.641
Alpha 18O CO2(aq)/Calcite	1.0137	13.594	13.594

## -----Solution composition-----

Elements	Molality	Moles
[13C]	2.136e-05	2.131e-05
[14C]	2.272e-15	2.267e-15
[18O]	1.113e-01	1.111e-01
C	1.910e-03	1.906e-03
Ca	3.526e-04	3.517e-04
D	1.733e-02	1.729e-02
Na	1.221e-03	1.218e-03
T	5.563e-16	5.551e-16

## -----Description of solution-----

pH	= 8.157	Charge balance
pe	= -2.768	Adjusted to redox equilibrium
Activity of water	= 0.998	
Ionic strength	= 2.262e-03	
Mass of water (kg)	= 9.977e-01	
Total alkalinity (eq/kg)	= 1.926e-03	
Total CO2 (mol/kg)	= 1.910e-03	
Temperature (deg C)	= 25.000	
Electrical balance (eq)	= 1.897e-12	
Percent error, 100*(Cat- An )/(Cat+ An )	= 0.00	
Iterations	= 30	
Total H	= 1.109946e+02	
Total O	= 5.539966e+01	

## -----Distribution of species-----

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
---------	----------	----------	--------------	--------------	-----------

	OH-	1.509e-06	1.431e-06	-5.821	-5.844	-0.023
	H3O+	7.313e-09	6.964e-09	-8.136	-8.157	-0.021
	H2O	5.551e+01	9.978e-01	-0.001	-0.001	0.000
C(4)	1.910e-03					
	HCO3-	1.843e-03	1.749e-03	-2.734	-2.757	-0.023
	CO2	2.750e-05	2.751e-05	-4.561	-4.560	0.000
	CO3-2	1.450e-05	1.175e-05	-4.839	-4.930	-0.091
	HCO2[180]-	1.146e-05	1.087e-05	-4.941	-4.964	-0.023
	CaHCO3+	6.504e-06	6.178e-06	-5.187	-5.209	-0.022
	CaCO3	5.466e-06	5.469e-06	-5.262	-5.262	0.000
	NaHCO3	1.138e-06	1.138e-06	-5.944	-5.944	0.000
	DCO3-	2.871e-07	2.724e-07	-6.542	-6.565	-0.023
	NaCO3-	2.670e-07	2.533e-07	-6.574	-6.596	-0.023
	CO[180]	1.149e-07	1.150e-07	-6.940	-6.939	0.000
	CO2[180]-2	9.087e-08	7.368e-08	-7.042	-7.133	-0.091
	HCO[180]2-	7.123e-08	6.759e-08	-7.147	-7.170	-0.023
	CaHCO2[180]+	4.044e-08	3.841e-08	-7.393	-7.416	-0.022
	CaCO2[180]	3.426e-08	3.428e-08	-7.465	-7.465	0.000
	NaHCO2[180]	7.073e-09	7.076e-09	-8.150	-8.150	0.000
	DCO2[180]-	1.785e-09	1.693e-09	-8.748	-8.771	-0.023
	NaCO2[180]-	1.673e-09	1.588e-09	-8.776	-8.799	-0.023
	CaDCO3+	1.013e-09	9.623e-10	-8.994	-9.017	-0.022
	HC[180]3-	4.428e-10	4.202e-10	-9.354	-9.377	-0.023
	CaHCO[180]2+	2.514e-10	2.388e-10	-9.600	-9.622	-0.022
	CO[180]2-2	1.899e-10	1.540e-10	-9.722	-9.813	-0.091
	NaDCO3	1.772e-10	1.773e-10	-9.752	-9.751	0.000
	C[180]2	1.201e-10	1.201e-10	-9.921	-9.920	0.000
	CaCO[180]2	7.160e-11	7.164e-11	-10.145	-10.145	0.000
	NaHCO[180]2	4.397e-11	4.399e-11	-10.357	-10.357	0.000
	DCO[180]2-	1.109e-11	1.053e-11	-10.955	-10.978	-0.023
	CaDCO2[180]+	6.298e-12	5.982e-12	-11.201	-11.223	-0.022
	NaCO[180]2-	3.497e-12	3.318e-12	-11.456	-11.479	-0.023
	CaHC[180]3+	1.563e-12	1.484e-12	-11.806	-11.828	-0.022
	NaDCO2[180]	1.102e-12	1.102e-12	-11.958	-11.958	0.000
	NaHC[180]3	2.733e-13	2.735e-13	-12.563	-12.563	0.000
	C[180]3-2	1.323e-13	1.072e-13	-12.879	-12.970	-0.091
	DC[180]3-	6.897e-14	6.544e-14	-13.161	-13.184	-0.023
	CaC[180]3	4.987e-14	4.990e-14	-13.302	-13.302	0.000
	CaDCO[180]2+	3.915e-14	3.719e-14	-13.407	-13.430	-0.022
	NaDCO[180]2	6.849e-15	6.852e-15	-14.164	-14.164	0.000
	NaC[180]3-	2.436e-15	2.311e-15	-14.613	-14.636	-0.023
	CaDC[180]3+	2.434e-16	2.312e-16	-15.614	-15.636	-0.022
	NaDC[180]3	4.258e-17	4.260e-17	-16.371	-16.371	0.000
	TCO3-	9.216e-21	8.745e-21	-20.035	-20.058	-0.023
	TCO2[180]-	5.729e-23	5.437e-23	-22.242	-22.265	-0.023
	CaTCO3+	3.253e-23	3.090e-23	-22.488	-22.510	-0.022
	NaTCO3	5.689e-24	5.692e-24	-23.245	-23.245	0.000
	CaTCO2[180]+	2.022e-25	1.921e-25	-24.694	-24.717	-0.022
	NaTCO2[180]	3.537e-26	3.539e-26	-25.451	-25.451	0.000
Ca	3.526e-04					
	Ca+2	3.404e-04	2.770e-04	-3.468	-3.558	-0.089
	CaHCO3+	6.504e-06	6.178e-06	-5.187	-5.209	-0.022
	CaCO3	5.466e-06	5.469e-06	-5.262	-5.262	0.000
	CaH[13C]O3+	7.274e-08	6.909e-08	-7.138	-7.161	-0.022
	Ca[13C]O3	6.104e-08	6.107e-08	-7.214	-7.214	0.000
	CaHCO2[180]+	4.044e-08	3.841e-08	-7.393	-7.416	-0.022
	CaCO2[180]	3.426e-08	3.428e-08	-7.465	-7.465	0.000
	CaDCO3+	1.013e-09	9.623e-10	-8.994	-9.017	-0.022
	CaH[13C]O2[180]+	4.522e-10	4.295e-10	-9.345	-9.367	-0.022

Ca[13C]O2[180]	3.826e-10	3.828e-10	-9.417	-9.417	0.000
CaHCO[180]2+	2.514e-10	2.388e-10	-9.600	-9.622	-0.022
CaCO[180]2	7.160e-11	7.164e-11	-10.145	-10.145	0.000
CaD[13C]O3+	1.133e-11	1.076e-11	-10.946	-10.968	-0.022
CaDCO2[180]+	6.298e-12	5.982e-12	-11.201	-11.223	-0.022
CaH[13C]O[180]2+	2.811e-12	2.670e-12	-11.551	-11.573	-0.022
CaHC[180]3+	1.563e-12	1.484e-12	-11.806	-11.828	-0.022
Ca[13C]O[180]2	7.995e-13	7.999e-13	-12.097	-12.097	0.000
CaD[13C]O2[180]+	7.043e-14	6.690e-14	-13.152	-13.175	-0.022
CaC[180]3	4.987e-14	4.990e-14	-13.302	-13.302	0.000
CaDCO[180]2+	3.915e-14	3.719e-14	-13.407	-13.430	-0.022
CaH[13C][180]3+	1.748e-14	1.660e-14	-13.758	-13.780	-0.022
Ca[13C][180]3	5.569e-16	5.572e-16	-15.254	-15.254	0.000
CaD[13C]O[180]2+	4.379e-16	4.159e-16	-15.359	-15.381	-0.022
CaDC[180]3+	2.434e-16	2.312e-16	-15.614	-15.636	-0.022
CaH[14C]O3+	7.737e-18	7.349e-18	-17.111	-17.134	-0.022
Ca[14C]O3	6.484e-18	6.487e-18	-17.188	-17.188	0.000
CaD[13C][180]3+	2.722e-18	2.585e-18	-17.565	-17.587	-0.022
CaH[14C]O2[180]+	4.810e-20	4.569e-20	-19.318	-19.340	-0.022
Ca[14C]O2[180]	4.064e-20	4.066e-20	-19.391	-19.391	0.000
CaD[14C]O3+	1.205e-21	1.145e-21	-20.919	-20.941	-0.022
CaH[14C]O[180]2+	2.990e-22	2.840e-22	-21.524	-21.547	-0.022
Ca[14C]O[180]2	8.493e-23	8.497e-23	-22.071	-22.071	0.000
CaOH+	6.932e-23	6.578e-23	-22.159	-22.182	-0.023
CaTCO3+	3.253e-23	3.090e-23	-22.488	-22.510	-0.022
CaD[14C]O2[180]+	7.492e-24	7.117e-24	-23.125	-23.148	-0.022
CaH[14C][180]3+	1.859e-24	1.766e-24	-23.731	-23.753	-0.022
CaT[13C]O3+	3.637e-25	3.455e-25	-24.439	-24.462	-0.022
CaTCO2[180]+	2.022e-25	1.921e-25	-24.694	-24.717	-0.022
Ca[180]H+	1.339e-25	1.270e-25	-24.873	-24.896	-0.023
Ca[14C][180]3	5.915e-26	5.918e-26	-25.228	-25.228	0.000
CaD[14C]O[180]2+	4.658e-26	4.424e-26	-25.332	-25.354	-0.022
CaOD+	2.571e-27	2.440e-27	-26.590	-26.613	-0.023
CaD[14C][180]3+	2.896e-28	2.750e-28	-27.538	-27.561	-0.022
Ca[180]D+	4.965e-30	4.711e-30	-29.304	-29.327	-0.023
CaOT+	0.000e+00	0.000e+00	-40.707	-40.729	-0.023
Ca[180]T+	0.000e+00	0.000e+00	-43.421	-43.444	-0.023
D	1.733e-02				
HDO	1.729e-02	3.108e-04	-1.762	-3.507	-1.745
HD[180]	3.467e-05	6.233e-07	-4.460	-6.205	-1.745
D2O	1.347e-06	2.421e-08	-5.871	-7.616	-1.745
DCO3-	2.871e-07	2.724e-07	-6.542	-6.565	-0.023
D[13C]O3-	3.210e-09	3.046e-09	-8.493	-8.516	-0.023
D2[180]	2.700e-09	4.854e-11	-8.569	-10.314	-1.745
DCO2[180]-	1.785e-09	1.693e-09	-8.748	-8.771	-0.023
CaDCO3+	1.013e-09	9.623e-10	-8.994	-9.017	-0.022
NaDCO3	1.772e-10	1.773e-10	-9.752	-9.751	0.000
OD-	5.596e-11	5.308e-11	-10.252	-10.275	-0.023
D[13C]O2[180]-	1.996e-11	1.894e-11	-10.700	-10.723	-0.023
CaD[13C]O3+	1.133e-11	1.076e-11	-10.946	-10.968	-0.022
DCO[180]2-	1.109e-11	1.053e-11	-10.955	-10.978	-0.023
CaDCO2[180]+	6.298e-12	5.982e-12	-11.201	-11.223	-0.022
H2DO+	3.560e-12	3.390e-12	-11.449	-11.470	-0.021
NaD[13C]O3	1.982e-12	1.983e-12	-11.703	-11.703	0.000
NaDCO2[180]	1.102e-12	1.102e-12	-11.958	-11.958	0.000
D[13C]O[180]2-	1.241e-13	1.177e-13	-12.906	-12.929	-0.023
[180]D-	1.080e-13	1.025e-13	-12.966	-12.989	-0.023
CaD[13C]O2[180]+	7.043e-14	6.690e-14	-13.152	-13.175	-0.022
DC[180]3-	6.897e-14	6.544e-14	-13.161	-13.184	-0.023

	CaDCO[180]2+	3.915e-14	3.719e-14	-13.407	-13.430	-0.022
	NaD[13C]O2[180]	1.232e-14	1.233e-14	-13.909	-13.909	0.000
	H2D[180]+	7.303e-15	6.954e-15	-14.137	-14.158	-0.021
	NaDCO[180]2	6.849e-15	6.852e-15	-14.164	-14.164	0.000
	D[13C][180]3-	7.712e-16	7.318e-16	-15.113	-15.136	-0.023
	HD20+	5.776e-16	5.500e-16	-15.238	-15.260	-0.021
	CaD[13C]O[180]2+	4.379e-16	4.159e-16	-15.359	-15.381	-0.022
	CaDC[180]3+	2.434e-16	2.312e-16	-15.614	-15.636	-0.022
	NaD[13C]O[180]2	7.659e-17	7.663e-17	-16.116	-16.116	0.000
	NaDC[180]3	4.258e-17	4.260e-17	-16.371	-16.371	0.000
	CaD[13C][180]3+	2.722e-18	2.585e-18	-17.565	-17.587	-0.022
	HD2[180]+	1.185e-18	1.128e-18	-17.926	-17.948	-0.021
	NaD[13C][180]3	4.761e-19	4.764e-19	-18.322	-18.322	0.000
	D[14C]O3-	3.415e-19	3.240e-19	-18.467	-18.489	-0.023
	DTO	8.647e-20	1.554e-21	-19.063	-20.808	-1.745
	D30+	3.124e-20	2.975e-20	-19.505	-19.527	-0.021
	D[14C]O2[180]-	2.123e-21	2.014e-21	-20.673	-20.696	-0.023
	CaD[14C]O3+	1.205e-21	1.145e-21	-20.919	-20.941	-0.022
	NaD[14C]O3	2.108e-22	2.109e-22	-21.676	-21.676	0.000
	D3[180]+	6.408e-23	6.102e-23	-22.193	-22.214	-0.021
	D[14C]O[180]2-	1.320e-23	1.252e-23	-22.880	-22.902	-0.023
	CaD[14C]O2[180]+	7.492e-24	7.117e-24	-23.125	-23.148	-0.022
	NaD[14C]O2[180]	1.311e-24	1.311e-24	-23.883	-23.882	0.000
	D[14C][180]3-	8.204e-26	7.785e-26	-25.086	-25.109	-0.023
	CaD[14C]O[180]2+	4.658e-26	4.424e-26	-25.332	-25.354	-0.022
	NaD[14C]O[180]2	8.147e-27	8.151e-27	-26.089	-26.089	0.000
	CaOD+	2.571e-27	2.440e-27	-26.590	-26.613	-0.023
	NaOD	4.057e-28	4.059e-28	-27.392	-27.392	0.000
	CaD[14C][180]3+	2.896e-28	2.750e-28	-27.538	-27.561	-0.022
	NaD[14C][180]3	5.065e-29	5.067e-29	-28.295	-28.295	0.000
	HDTO+	9.658e-30	9.197e-30	-29.015	-29.036	-0.021
	Ca[180]D+	4.965e-30	4.711e-30	-29.304	-29.327	-0.023
	Na[180]D	7.833e-31	7.837e-31	-30.106	-30.106	0.000
H(0)		2.373e-14				
	H2	1.186e-14	1.187e-14	-13.926	-13.926	0.000
Na		1.221e-03				
	Na+	1.219e-03	1.157e-03	-2.914	-2.936	-0.023
	NaHCO3	1.138e-06	1.138e-06	-5.944	-5.944	0.000
	NaCO3-	2.670e-07	2.533e-07	-6.574	-6.596	-0.023
	NaH[13C]O3	1.272e-08	1.273e-08	-7.895	-7.895	0.000
	NaHCO2[180]	7.073e-09	7.076e-09	-8.150	-8.150	0.000
	Na[13C]O3-	2.981e-09	2.829e-09	-8.526	-8.548	-0.023
	NaCO2[180]-	1.673e-09	1.588e-09	-8.776	-8.799	-0.023
	NaDCO3	1.772e-10	1.773e-10	-9.752	-9.751	0.000
	NaH[13C]O2[180]	7.909e-11	7.913e-11	-10.102	-10.102	0.000
	NaHCO[180]2	4.397e-11	4.399e-11	-10.357	-10.357	0.000
	Na[13C]O2[180]-	1.869e-11	1.773e-11	-10.728	-10.751	-0.023
	NaCO[180]2-	3.497e-12	3.318e-12	-11.456	-11.479	-0.023
	NaD[13C]O3	1.982e-12	1.983e-12	-11.703	-11.703	0.000
	NaDCO2[180]	1.102e-12	1.102e-12	-11.958	-11.958	0.000
	NaH[13C]O[180]2	4.917e-13	4.920e-13	-12.308	-12.308	0.000
	NaHC[180]3	2.733e-13	2.735e-13	-12.563	-12.563	0.000
	Na[13C]O[180]2-	3.905e-14	3.705e-14	-13.408	-13.431	-0.023
	NaD[13C]O2[180]	1.232e-14	1.233e-14	-13.909	-13.909	0.000
	NaDCO[180]2	6.849e-15	6.852e-15	-14.164	-14.164	0.000
	NaH[13C][180]3	3.057e-15	3.058e-15	-14.515	-14.515	0.000
	NaC[180]3-	2.436e-15	2.311e-15	-14.613	-14.636	-0.023
	NaD[13C]O[180]2	7.659e-17	7.663e-17	-16.116	-16.116	0.000
	NaDC[180]3	4.258e-17	4.260e-17	-16.371	-16.371	0.000

	Na[13C][18O]3-	2.720e-17	2.581e-17	-16.565	-16.588	-0.023
	NaH[14C]O3	1.353e-18	1.354e-18	-17.869	-17.868	0.000
	NaD[13C][18O]3	4.761e-19	4.764e-19	-18.322	-18.322	0.000
	Na[14C]O3-	3.167e-19	3.005e-19	-18.499	-18.522	-0.023
	NaH[14C]O2[18O]	8.414e-21	8.418e-21	-20.075	-20.075	0.000
	Na[14C]O2[18O]-	1.985e-21	1.884e-21	-20.702	-20.725	-0.023
	NaD[14C]O3	2.108e-22	2.109e-22	-21.676	-21.676	0.000
	NaH[14C]O[18O]2	5.231e-23	5.233e-23	-22.281	-22.281	0.000
	NaOH	1.094e-23	1.094e-23	-22.961	-22.961	0.000
	NaTCO3	5.689e-24	5.692e-24	-23.245	-23.245	0.000
	Na[14C]O[18O]2-	4.148e-24	3.936e-24	-23.382	-23.405	-0.023
	NaD[14C]O2[18O]	1.311e-24	1.311e-24	-23.883	-23.882	0.000
	NaH[14C][18O]3	3.252e-25	3.253e-25	-24.488	-24.488	0.000
	NaT[13C]O3	6.362e-26	6.366e-26	-25.196	-25.196	0.000
	NaTCO2[18O]	3.537e-26	3.539e-26	-25.451	-25.451	0.000
	Na[18O]H	2.112e-26	2.113e-26	-25.675	-25.675	0.000
	NaD[14C]O[18O]2	8.147e-27	8.151e-27	-26.089	-26.089	0.000
	Na[14C][18O]3-	2.889e-27	2.741e-27	-26.539	-26.562	-0.023
	NaOD	4.057e-28	4.059e-28	-27.392	-27.392	0.000
	NaD[14C][18O]3	5.065e-29	5.067e-29	-28.295	-28.295	0.000
	Na[18O]D	7.833e-31	7.837e-31	-30.106	-30.106	0.000
	NaOT	0.000e+00	0.000e+00	-41.508	-41.508	0.000
	Na[18O]T	0.000e+00	0.000e+00	-44.223	-44.222	0.000
O(0)	0.000e+00					
	O2	0.000e+00	0.000e+00	-64.531	-64.531	0.000
T	5.563e-16					
	HTO	5.551e-16	9.979e-18	-15.256	-17.001	-1.745
	HT[18O]	1.113e-18	2.001e-20	-17.953	-19.699	-1.745
	DTO	8.647e-20	1.554e-21	-19.063	-20.808	-1.745
	TCO3-	9.216e-21	8.745e-21	-20.035	-20.058	-0.023
	T[13C]O3-	1.031e-22	9.779e-23	-21.987	-22.010	-0.023
	TCO2[18O]-	5.729e-23	5.437e-23	-22.242	-22.265	-0.023
	CaTCO3+	3.253e-23	3.090e-23	-22.488	-22.510	-0.022
	NaTCO3	5.689e-24	5.692e-24	-23.245	-23.245	0.000
	OT-	4.278e-25	4.057e-25	-24.369	-24.392	-0.023
	CaT[13C]O3+	3.637e-25	3.455e-25	-24.439	-24.462	-0.022
	CaTCO2[18O]+	2.022e-25	1.921e-25	-24.694	-24.717	-0.022
	H2TO+	1.190e-25	1.134e-25	-24.924	-24.946	-0.021
	NaT[13C]O3	6.362e-26	6.366e-26	-25.196	-25.196	0.000
	NaTCO2[18O]	3.537e-26	3.539e-26	-25.451	-25.451	0.000
	[18O]T-	8.260e-28	7.834e-28	-27.083	-27.106	-0.023
	H2T[18O]+	2.442e-28	2.326e-28	-27.612	-27.633	-0.021
	HDTO+	9.658e-30	9.197e-30	-29.015	-29.036	-0.021
	CaOT+	0.000e+00	0.000e+00	-40.707	-40.729	-0.023
	NaOT	0.000e+00	0.000e+00	-41.508	-41.508	0.000
	Ca[18O]T+	0.000e+00	0.000e+00	-43.421	-43.444	-0.023
	Na[18O]T	0.000e+00	0.000e+00	-44.223	-44.222	0.000
[13C]	2.136e-05					
	H[13C]O3-	2.061e-05	1.956e-05	-4.686	-4.709	-0.023
	[13C]O2	3.049e-07	3.050e-07	-6.516	-6.516	0.000
	[13C]O3-2	1.619e-07	1.312e-07	-6.791	-6.882	-0.091
	H[13C]O2[18O]-	1.281e-07	1.216e-07	-6.892	-6.915	-0.023
	CaH[13C]O3+	7.274e-08	6.909e-08	-7.138	-7.161	-0.022
	Ca[13C]O3	6.104e-08	6.107e-08	-7.214	-7.214	0.000
	NaH[13C]O3	1.272e-08	1.273e-08	-7.895	-7.895	0.000
	D[13C]O3-	3.210e-09	3.046e-09	-8.493	-8.516	-0.023
	Na[13C]O3-	2.981e-09	2.829e-09	-8.526	-8.548	-0.023
	[13C]O[18O]	1.274e-09	1.275e-09	-8.895	-8.895	0.000
	[13C]O2[18O]-2	1.015e-09	8.227e-10	-8.994	-9.085	-0.091

H[13C]O[180]2-	7.965e-10	7.558e-10	-9.099	-9.122	-0.023
CaH[13C]O2[180]+	4.522e-10	4.295e-10	-9.345	-9.367	-0.022
Ca[13C]O2[180]	3.826e-10	3.828e-10	-9.417	-9.417	0.000
NaH[13C]O2[180]	7.909e-11	7.913e-11	-10.102	-10.102	0.000
D[13C]O2[180]-	1.996e-11	1.894e-11	-10.700	-10.723	-0.023
Na[13C]O2[180]-	1.869e-11	1.773e-11	-10.728	-10.751	-0.023
CaD[13C]O3+	1.133e-11	1.076e-11	-10.946	-10.968	-0.022
H[13C][180]3-	4.952e-12	4.699e-12	-11.305	-11.328	-0.023
CaH[13C]O[180]2+	2.811e-12	2.670e-12	-11.551	-11.573	-0.022
[13C]O[180]2-2	2.120e-12	1.719e-12	-11.674	-11.765	-0.091
NaD[13C]O3	1.982e-12	1.983e-12	-11.703	-11.703	0.000
[13C][180]2	1.331e-12	1.332e-12	-11.876	-11.876	0.000
Ca[13C]O[180]2	7.995e-13	7.999e-13	-12.097	-12.097	0.000
NaH[13C]O[180]2	4.917e-13	4.920e-13	-12.308	-12.308	0.000
D[13C]O[180]2-	1.241e-13	1.177e-13	-12.906	-12.929	-0.023
CaD[13C]O2[180]+	7.043e-14	6.690e-14	-13.152	-13.175	-0.022
Na[13C]O[180]2-	3.905e-14	3.705e-14	-13.408	-13.431	-0.023
CaH[13C][180]3+	1.748e-14	1.660e-14	-13.758	-13.780	-0.022
NaD[13C]O2[180]	1.232e-14	1.233e-14	-13.909	-13.909	0.000
NaH[13C][180]3	3.057e-15	3.058e-15	-14.515	-14.515	0.000
[13C][180]3-2	1.477e-15	1.197e-15	-14.831	-14.922	-0.091
D[13C][180]3-	7.712e-16	7.318e-16	-15.113	-15.136	-0.023
Ca[13C][180]3	5.569e-16	5.572e-16	-15.254	-15.254	0.000
CaD[13C]O[180]2+	4.379e-16	4.159e-16	-15.359	-15.381	-0.022
NaD[13C]O[180]2	7.659e-17	7.663e-17	-16.116	-16.116	0.000
Na[13C][180]3-	2.720e-17	2.581e-17	-16.565	-16.588	-0.023
CaD[13C][180]3+	2.722e-18	2.585e-18	-17.565	-17.587	-0.022
NaD[13C][180]3	4.761e-19	4.764e-19	-18.322	-18.322	0.000
T[13C]O3-	1.031e-22	9.779e-23	-21.987	-22.010	-0.023
CaT[13C]O3+	3.637e-25	3.455e-25	-24.439	-24.462	-0.022
NaT[13C]O3	6.362e-26	6.366e-26	-25.196	-25.196	0.000
[14C]	2.272e-15				
H[14C]O3-	2.192e-15	2.080e-15	-14.659	-14.682	-0.023
[14C]O2	3.215e-17	3.217e-17	-16.493	-16.493	0.000
[14C]O3-2	1.719e-17	1.394e-17	-16.765	-16.856	-0.091
H[14C]O2[180]-	1.363e-17	1.293e-17	-16.866	-16.888	-0.023
CaH[14C]O3+	7.737e-18	7.349e-18	-17.111	-17.134	-0.022
Ca[14C]O3	6.484e-18	6.487e-18	-17.188	-17.188	0.000
NaH[14C]O3	1.353e-18	1.354e-18	-17.869	-17.868	0.000
D[14C]O3-	3.415e-19	3.240e-19	-18.467	-18.489	-0.023
Na[14C]O3-	3.167e-19	3.005e-19	-18.499	-18.522	-0.023
[14C]O[180]	1.344e-19	1.344e-19	-18.872	-18.872	0.000
[14C]O2[180]-2	1.078e-19	8.739e-20	-18.967	-19.059	-0.091
H[14C]O[180]2-	8.473e-20	8.040e-20	-19.072	-19.095	-0.023
CaH[14C]O2[180]+	4.810e-20	4.569e-20	-19.318	-19.340	-0.022
Ca[14C]O2[180]	4.064e-20	4.066e-20	-19.391	-19.391	0.000
NaH[14C]O2[180]	8.414e-21	8.418e-21	-20.075	-20.075	0.000
D[14C]O2[180]-	2.123e-21	2.014e-21	-20.673	-20.696	-0.023
Na[14C]O2[180]-	1.985e-21	1.884e-21	-20.702	-20.725	-0.023
CaD[14C]O3+	1.205e-21	1.145e-21	-20.919	-20.941	-0.022
H[14C][180]3-	5.267e-22	4.998e-22	-21.278	-21.301	-0.023
CaH[14C]O[180]2+	2.990e-22	2.840e-22	-21.524	-21.547	-0.022
[14C]O[180]2-2	2.252e-22	1.826e-22	-21.647	-21.738	-0.091
NaD[14C]O3	2.108e-22	2.109e-22	-21.676	-21.676	0.000
[14C][180]2	1.404e-22	1.404e-22	-21.853	-21.852	0.000
Ca[14C]O[180]2	8.493e-23	8.497e-23	-22.071	-22.071	0.000
NaH[14C]O[180]2	5.231e-23	5.233e-23	-22.281	-22.281	0.000
D[14C]O[180]2-	1.320e-23	1.252e-23	-22.880	-22.902	-0.023
CaD[14C]O2[180]+	7.492e-24	7.117e-24	-23.125	-23.148	-0.022

	Na[14C]O[18O]2-	4.148e-24	3.936e-24	-23.382	-23.405	-0.023
	CaH[14C][18O]3+	1.859e-24	1.766e-24	-23.731	-23.753	-0.022
	NaD[14C]O2[18O]	1.311e-24	1.311e-24	-23.883	-23.882	0.000
	NaH[14C][18O]3	3.252e-25	3.253e-25	-24.488	-24.488	0.000
	[14C][18O]3-2	1.569e-25	1.272e-25	-24.804	-24.896	-0.091
	D[14C][18O]3-	8.204e-26	7.785e-26	-25.086	-25.109	-0.023
	Ca[14C][18O]3	5.915e-26	5.918e-26	-25.228	-25.228	0.000
	CaD[14C]O[18O]2+	4.658e-26	4.424e-26	-25.332	-25.354	-0.022
	NaD[14C]O[18O]2	8.147e-27	8.151e-27	-26.089	-26.089	0.000
	Na[14C][18O]3-	2.889e-27	2.741e-27	-26.539	-26.562	-0.023
	CaD[14C][18O]3+	2.896e-28	2.750e-28	-27.538	-27.561	-0.022
	NaD[14C][18O]3	5.065e-29	5.067e-29	-28.295	-28.295	0.000
[18O]	1.113e-01					
	H2[18O]	1.113e-01	2.001e-03	-0.954	-2.699	-1.745
	HD[18O]	3.467e-05	6.233e-07	-4.460	-6.205	-1.745
	HCO2[18O]-	1.146e-05	1.087e-05	-4.941	-4.964	-0.023
	H[13C]O2[18O]-	1.281e-07	1.216e-07	-6.892	-6.915	-0.023
	CO[18O]	1.149e-07	1.150e-07	-6.940	-6.939	0.000
	CO2[18O]-2	9.087e-08	7.368e-08	-7.042	-7.133	-0.091
	HCO[18O]2-	7.123e-08	6.759e-08	-7.147	-7.170	-0.023
	CaHCO2[18O]+	4.044e-08	3.841e-08	-7.393	-7.416	-0.022
	CaCO2[18O]	3.426e-08	3.428e-08	-7.465	-7.465	0.000
	NaHCO2[18O]	7.073e-09	7.076e-09	-8.150	-8.150	0.000
	[18O]H-	2.913e-09	2.763e-09	-8.536	-8.559	-0.023
	D2[18O]	2.700e-09	4.854e-11	-8.569	-10.314	-1.745
	DCO2[18O]-	1.785e-09	1.693e-09	-8.748	-8.771	-0.023
	NaCO2[18O]-	1.673e-09	1.588e-09	-8.776	-8.799	-0.023
	[13C]O[18O]	1.274e-09	1.275e-09	-8.895	-8.895	0.000
	[13C]O2[18O]-2	1.015e-09	8.227e-10	-8.994	-9.085	-0.091
	H[13C]O[18O]2-	7.965e-10	7.558e-10	-9.099	-9.122	-0.023
	CaH[13C]O2[18O]+	4.522e-10	4.295e-10	-9.345	-9.367	-0.022
	HC[18O]3-	4.428e-10	4.202e-10	-9.354	-9.377	-0.023
	Ca[13C]O2[18O]	3.826e-10	3.828e-10	-9.417	-9.417	0.000
	CaHCO[18O]2+	2.514e-10	2.388e-10	-9.600	-9.622	-0.022
	CO[18O]2-2	1.899e-10	1.540e-10	-9.722	-9.813	-0.091
	C[18O]2	1.201e-10	1.201e-10	-9.921	-9.920	0.000
	NaH[13C]O2[18O]	7.909e-11	7.913e-11	-10.102	-10.102	0.000
	CaCO[18O]2	7.160e-11	7.164e-11	-10.145	-10.145	0.000
	NaHCO[18O]2	4.397e-11	4.399e-11	-10.357	-10.357	0.000
	D[13C]O2[18O]-	1.996e-11	1.894e-11	-10.700	-10.723	-0.023
	Na[13C]O2[18O]-	1.869e-11	1.773e-11	-10.728	-10.751	-0.023
	H3[18O]+	1.500e-11	1.429e-11	-10.824	-10.845	-0.021
	DCO[18O]2-	1.109e-11	1.053e-11	-10.955	-10.978	-0.023
	CaDCO2[18O]+	6.298e-12	5.982e-12	-11.201	-11.223	-0.022
	H[13C][18O]3-	4.952e-12	4.699e-12	-11.305	-11.328	-0.023
	NaCO[18O]2-	3.497e-12	3.318e-12	-11.456	-11.479	-0.023
	CaH[13C]O[18O]2+	2.811e-12	2.670e-12	-11.551	-11.573	-0.022
	[13C]O[18O]2-2	2.120e-12	1.719e-12	-11.674	-11.765	-0.091
	CaHC[18O]3+	1.563e-12	1.484e-12	-11.806	-11.828	-0.022
	[13C][18O]2	1.331e-12	1.332e-12	-11.876	-11.876	0.000
	NaDCO2[18O]	1.102e-12	1.102e-12	-11.958	-11.958	0.000
	Ca[13C]O[18O]2	7.995e-13	7.999e-13	-12.097	-12.097	0.000
	NaH[13C]O[18O]2	4.917e-13	4.920e-13	-12.308	-12.308	0.000
	NaHC[18O]3	2.733e-13	2.735e-13	-12.563	-12.563	0.000
	C[18O]3-2	1.323e-13	1.072e-13	-12.879	-12.970	-0.091
	D[13C]O[18O]2-	1.241e-13	1.177e-13	-12.906	-12.929	-0.023
	[18O]D-	1.080e-13	1.025e-13	-12.966	-12.989	-0.023
	CaD[13C]O2[18O]+	7.043e-14	6.690e-14	-13.152	-13.175	-0.022
	DC[18O]3-	6.897e-14	6.544e-14	-13.161	-13.184	-0.023

CaC[18O]3	4.987e-14	4.990e-14	-13.302	-13.302	0.000
CaDCO[18O]2+	3.915e-14	3.719e-14	-13.407	-13.430	-0.022
Na[13C]O[18O]2-	3.905e-14	3.705e-14	-13.408	-13.431	-0.023
CaH[13C][18O]3+	1.748e-14	1.660e-14	-13.758	-13.780	-0.022
NaD[13C]O2[18O]	1.232e-14	1.233e-14	-13.909	-13.909	0.000
H2D[18O]+	7.303e-15	6.954e-15	-14.137	-14.158	-0.021
NaDCO[18O]2	6.849e-15	6.852e-15	-14.164	-14.164	0.000
NaH[13C][18O]3	3.057e-15	3.058e-15	-14.515	-14.515	0.000
NaC[18O]3-	2.436e-15	2.311e-15	-14.613	-14.636	-0.023
[13C][18O]3-2	1.477e-15	1.197e-15	-14.831	-14.922	-0.091
D[13C][18O]3-	7.712e-16	7.318e-16	-15.113	-15.136	-0.023
Ca[13C][18O]3	5.569e-16	5.572e-16	-15.254	-15.254	0.000
CaD[13C]O[18O]2+	4.379e-16	4.159e-16	-15.359	-15.381	-0.022
CaDC[18O]3+	2.434e-16	2.312e-16	-15.614	-15.636	-0.022
NaD[13C]O[18O]2	7.659e-17	7.663e-17	-16.116	-16.116	0.000
NaDC[18O]3	4.258e-17	4.260e-17	-16.371	-16.371	0.000
Na[13C][18O]3-	2.720e-17	2.581e-17	-16.565	-16.588	-0.023
H[14C]O2[18O]-	1.363e-17	1.293e-17	-16.866	-16.888	-0.023
CaD[13C][18O]3+	2.722e-18	2.585e-18	-17.565	-17.587	-0.022
HD2[18O]+	1.185e-18	1.128e-18	-17.926	-17.948	-0.021
HT[18O]	1.113e-18	2.001e-20	-17.953	-19.699	-1.745
NaD[13C][18O]3	4.761e-19	4.764e-19	-18.322	-18.322	0.000
[14C]O[18O]	1.344e-19	1.344e-19	-18.872	-18.872	0.000
[14C]O2[18O]-2	1.078e-19	8.739e-20	-18.967	-19.059	-0.091
H[14C]O[18O]2-	8.473e-20	8.040e-20	-19.072	-19.095	-0.023
CaH[14C]O2[18O]+	4.810e-20	4.569e-20	-19.318	-19.340	-0.022
Ca[14C]O2[18O]	4.064e-20	4.066e-20	-19.391	-19.391	0.000
NaH[14C]O2[18O]	8.414e-21	8.418e-21	-20.075	-20.075	0.000
D[14C]O2[18O]-	2.123e-21	2.014e-21	-20.673	-20.696	-0.023
Na[14C]O2[18O]-	1.985e-21	1.884e-21	-20.702	-20.725	-0.023
H[14C][18O]3-	5.267e-22	4.998e-22	-21.278	-21.301	-0.023
CaH[14C]O[18O]2+	2.990e-22	2.840e-22	-21.524	-21.547	-0.022
[14C]O[18O]2-2	2.252e-22	1.826e-22	-21.647	-21.738	-0.091
[14C][18O]2	1.404e-22	1.404e-22	-21.853	-21.852	0.000
Ca[14C]O[18O]2	8.493e-23	8.497e-23	-22.071	-22.071	0.000
D3[18O]+	6.408e-23	6.102e-23	-22.193	-22.214	-0.021
TCO2[18O]-	5.729e-23	5.437e-23	-22.242	-22.265	-0.023
NaH[14C]O[18O]2	5.231e-23	5.233e-23	-22.281	-22.281	0.000
D[14C]O[18O]2-	1.320e-23	1.252e-23	-22.880	-22.902	-0.023
CaD[14C]O2[18O]+	7.492e-24	7.117e-24	-23.125	-23.148	-0.022
Na[14C]O[18O]2-	4.148e-24	3.936e-24	-23.382	-23.405	-0.023
CaH[14C][18O]3+	1.859e-24	1.766e-24	-23.731	-23.753	-0.022
NaD[14C]O2[18O]	1.311e-24	1.311e-24	-23.883	-23.882	0.000
NaH[14C][18O]3	3.252e-25	3.253e-25	-24.488	-24.488	0.000
CaTCO2[18O]+	2.022e-25	1.921e-25	-24.694	-24.717	-0.022
[14C][18O]3-2	1.569e-25	1.272e-25	-24.804	-24.896	-0.091
Ca[18O]H+	1.339e-25	1.270e-25	-24.873	-24.896	-0.023
D[14C][18O]3-	8.204e-26	7.785e-26	-25.086	-25.109	-0.023
Ca[14C][18O]3	5.915e-26	5.918e-26	-25.228	-25.228	0.000
CaD[14C]O[18O]2+	4.658e-26	4.424e-26	-25.332	-25.354	-0.022
NaTCO2[18O]	3.537e-26	3.539e-26	-25.451	-25.451	0.000
Na[18O]H	2.112e-26	2.113e-26	-25.675	-25.675	0.000
NaD[14C]O[18O]2	8.147e-27	8.151e-27	-26.089	-26.089	0.000
Na[14C][18O]3-	2.889e-27	2.741e-27	-26.539	-26.562	-0.023
[18O]T-	8.260e-28	7.834e-28	-27.083	-27.106	-0.023
CaD[14C][18O]3+	2.896e-28	2.750e-28	-27.538	-27.561	-0.022
H2T[18O]+	2.442e-28	2.326e-28	-27.612	-27.633	-0.021
NaD[14C][18O]3	5.065e-29	5.067e-29	-28.295	-28.295	0.000
Ca[18O]D+	4.965e-30	4.711e-30	-29.304	-29.327	-0.023

Na[180]D	7.833e-31	7.837e-31	-30.106	-30.106	0.000
Ca[180]T+	0.000e+00	0.000e+00	-43.421	-43.444	-0.023
Na[180]T	0.000e+00	0.000e+00	-44.223	-44.222	0.000

-----Saturation indices-----

Phase	SI	log IAP	log KT	
[13C][180]2(g)	-10.41	-11.91	-1.50	[13C][180]2
[13C]O2(g)	-5.05	-6.52	-1.47	[13C]O2
[13C]O[180](g)	-7.43	-9.21	-1.79	[13C]O[180]
[14C][180]2(g)	-20.38	-21.89	-1.50	[14C][180]2
[14C]O2(g)	-15.02	-16.49	-1.47	[14C]O2
[14C]O[180](g)	-17.40	-19.19	-1.79	[14C]O[180]
C[180]2(g)	-8.45	-9.96	-1.50	C[180]2
Ca[13C][180]3	-10.02	-1.86	8.16	Ca[13C][180]3
Ca[13C]O2[180]	-4.17	3.54	7.71	Ca[13C]O2[180]
Ca[13C]O3	-1.96	6.24	8.20	Ca[13C]O3
Ca[13C]O[180]2	-6.85	0.84	7.70	Ca[13C]O[180]2
Ca[14C][180]3	-19.99	-11.83	8.16	Ca[14C][180]3
Ca[14C]O2[180]	-14.14	-6.44	7.70	Ca[14C]O2[180]
Ca[14C]O3	-11.93	-3.74	8.19	Ca[14C]O3
Ca[14C]O[180]2	-16.82	-9.13	7.69	Ca[14C]O[180]2
CaC[180]3	-8.07	0.10	8.16	CaC[180]3
CaCO2[180]	-2.22	5.50	7.71	CaCO2[180]
CaCO[180]2	-4.90	2.80	7.70	CaCO[180]2
Calcite	-0.01	8.19	8.20	CaCO3
CO2(g)	-3.09	-4.56	-1.47	CO2
CO[180](g)	-5.47	-7.26	-1.79	CO[180]
D2[180](g)	-11.89	-10.31	1.58	D2[180]
D2O(g)	-9.19	-7.62	1.58	D2O
DTO(g)	-22.42	-20.81	1.61	DTO
H2[180](g)	-4.21	-2.70	1.51	H2[180]
H2O(g)	-1.51	-0.00	1.51	H2O
HD[180](g)	-7.75	-6.51	1.25	HD[180]
HDO(g)	-5.05	-3.81	1.24	HDO
HT[180](g)	-21.28	-19.70	1.58	HT[180]
HTO(g)	-18.58	-17.00	1.58	HTO

-----  
End of simulation.  
-----

-----  
Reading input data for simulation 3.  
-----

-----  
End of run.  
-----

The initial 1 kilogram of solution has a pH of 8.2, contains 2.0 mmole dissolved carbon with  $\delta^{13}\text{C} = 0.0$  permil and  $^{14}\text{C} = 100.0$  pmc,  $m_{\text{Ca}^{+2}} = 0.3909e-03$ , adjusted to provide a saturation index of +0.1 with respect

to calcite, and  $m_{Na^+} = 1.218e - 03$ , adjusted for charge balance. The isotopic composition of the water is

$\delta^{18}O = 0.0$  permil,  $\delta D = 0.0$  permil, and  $^3H = 10.0$  tritium units.

This solution is allowed to evaporate water, degas  $CO_2$ , and precipitate calcite. The gases evolve into an evacuated volume of 1 liter until equilibrium is achieved. The calculation is performed in a single step, attaining equilibrium among all isotopic species in all phases. The equilibrium gas pressure is 0.0317 atm and the gas consists of roughly 97 percent water vapor and 3 percent  $CO_2$  (p. 31). There has been 0.0392 mmole of calcite precipitated. The molar compositions of the gas and calcite are given on pages 30-31; the isotope ratios in all three phases are given on pages 31-32. The last five entries in the isotope ratio table, R(D), R(T), R(18O), R(13C), R(14C), and their corresponding values in permil, TU, and pmc represent the total isotopic composition of the solution. These are the values that would be measured. Pages 32-40 tabulate the total species distribution for the aqueous phase.

The results agree with qualitative expectations. The aqueous phase has become slightly enriched in the heavy isotopes of each element. For D, T, and  $^{18}O$  this results from evaporation of water, with water vapor enriched in the lighter isotopes.  $CO_{2g}$  is enriched in the light carbon isotopes while calcite is enriched in the heavy carbon isotopes. The amount of  $CO_2$  degassed is more than an order of magnitude greater than the amount of calcite formed; thus, the aqueous phase is enriched in the heavier isotopes.

## SUMMARY

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  $HD^{18}O$ . The equilibrium constants for isotope exchange reactions that are calculated from fractionation factors can be expressed as ratios of 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 effects of nonideality have been included in the derivations, although the effects are minimal because of the chemical similarity of the isotopic variants of the same molecule or ion. The individual isotope equilibrium constant for the molecular species composed of the most abundant isotope of each element can be calculated from, or assumed to equal, the standard thermochemical equilibrium constant. This 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 constants.

Methods are presented for calculation of the individual isotope equilibrium constants for the asymmetric bicarbonate ion. Calculation of the isotope ratios for the asymmetric bicarbonate ion do not simplify to the Urey generalizations, and the algebraic expressions for them are complex. Numerical methods are used to calculate three factors that allow calculations of the individual equilibrium constants for bicarbonate.

Equilibrium constants are calculated for all species that can be formed from  $H$ ,  $^2H$ ,  $^{12}C$ ,  $^{13}C$ ,  $^{14}C$ ,  $^{16}O$ , and  $^{18}O$  in the molecules  $CO_{2g}$ ,  $CO_{2aq}$ ,  $HCO_{3aq}^-$ ,  $CO_{3aq}^{2-}$ ,  $CaCO_{3s}$ ,  $H_2O_g$ ,  $H_2O_l$ ,  $H_3O_{aq}^+$ ,  $OH_{aq}^-$ , and the  $OH_{aq}^-$ ,  $HCO_{3aq}^-$  and  $CO_{3aq}^{2-}$  ion pairs with the cations  $Na_{aq}^+$ ,  $K_{aq}^+$ ,  $Ca_{aq}^{+2}$ , and  $Mg_{aq}^{+2}$ . Equilibrium constants for selected species containing  $^3H$  are also calculated. These equilibrium constants are used in the geochemical model PHREEQC to produce an equilibrium and reaction-transport model that includes these isotopic species.

The example calculates the equilibrium distribution of  $H$ ,  $^2H$ ,  $^{12}C$ ,  $^{13}C$ ,  $^{14}C$ ,  $^{16}O$ ,  $^{18}O$ , and  $^3H$  in all molecular combinations in the gas, solution, and calcite phases. The calculated species distribution reproduces the fractionation factors input to the model. The simultaneous equilibrium of multiple isotopes among multiple species and phases is a new modeling capability.

## REFERENCES CITED

- Atkins, P.W., 1982, *Physical chemistry* (2d ed.): San Francisco, W.H. Freeman and Co., 1095 p.
- Bethke, C.M., 1996, *Geochemical reaction modeling—Concepts and applications*: New York, Oxford University Press, 397 p.
- Bigeleisen, J., 1955, Statistical mechanics of isotopic systems with small quantum corrections. I. General considerations and the rule of the geometric mean: *Journal of Chemical Physics*, v. 23, p. 2264-2267.
- Bohlke, J. K. and Shanks, W.C., III, 1994, Stable isotope study of hydrothermal vents at Escanaba Trough—Observed and calculated effects of sediment-seawater interaction, *in* J.L. Morton and others, eds., *Geologic, hydrothermal, and biologic studies at Escanaba Trough, Gorda Ridge, Offshore Northern California*: U.S. Geological Survey Bulletin 2022, p. 223-239.
- Bottinga, Y., 1968, Calculation of fractionation factors for carbon and oxygen exchange in the system calcite-carbon dioxide-water: *Journal of Physical Chemistry*, v.72, p. 800-808.
- Bowers, T.S., 1989, Stable isotope signatures of water-rock interaction in mid-ocean ridge hydrothermal systems—Sulfur, oxygen, and hydrogen: *Journal of Geophysical Research*, v. 94, p. 5775-5786.
- Bowers, T.S., and Taylor, H.P., Jr., 1985, An integrated chemical and stable-isotope model of the origin of midocean ridge hot spring systems: *Journal of Geophysical Research*, v. 90, p. 12583-12606.
- Cheng, S., and Long, A., 1984, Implementation of carbon isotope subroutine to computer program PHREEQE and their application to C-14 ground-water dating, *in* *Proceedings of Hydrology and Water Resources in Arizona and the Southwest*, American Water Resources Association and Arizona-Nevada Academy of Science, v. 14, p. 121-135.
- Cotton, F.A., and Wilkinson, F.R.S., 1966, *Advanced inorganic chemistry* (2d ed.): New York, Interscience, 1136 p.
- Deines, P., Langmuir, D., and Harmon, R.S., 1974, Stable carbon isotope ratios and the existence of a gas phase in the evolution of carbonate ground waters: *Geochimica et Cosmochimica Acta*, v. 38, p. 1147-1164.
- Friedman, I., and O'Neil, J.R., 1977, Compilation of stable isotope fractionation factors of geochemical interest, chap. KK *in* Fleischer, M., ed., *Data of geochemistry* (6th ed.): U.S. Geological Survey Professional Paper 440, 12 p.
- Garrels, R.M., and Christ, C.L., 1965, *Solutions, minerals, and equilibria*: New York, Harper and Row, 450 p.
- Heinzinger, K., and Weston, R.E., Jr., 1964a, Isotopic fractionation of hydrogen between water and the aqueous hydroxide ion: *Journal of Physical Chemistry*, v. 68, no. 8, p. 2170-2183.
- Heinzinger, K., and Weston, R.E., Jr., 1964b, Isotopic fractionation of hydrogen between water and the aqueous hydrogen ion: *Journal of Physical Chemistry*, v. 68, no. 4, p. 744-751.

- Janecky, D.R., and Shanks, W.C., III., 1988, Computational modeling of chemical and sulfur isotopic reaction processes in seafloor hydrothermal systems: Chimneys, massive sulfides, and subjacent alteration zones: *Canadian Mineralogist*, v. 26, p. 805-825.
- Lee, M.-K., 1993, Quantitative models of fluid flow, chemical reaction, and stable isotopic fractionation and their application to sediment diagenesis and hydrothermal alteration: University of Illinois at Urbana-Champaign, Ph.D. dissertation, 179 p.
- Lee, M.-K., and Bethke, C.M., 1996, A model of isotope fractionation in reacting geochemical systems: *American Journal of Science*, v. 296, p. 965-988.
- Lewis, G.N., and Randall, M., revised by Pitzer, K.S., and Brewer, L., 1961, *Thermodynamics* (2d ed.): New York, McGraw-Hill, 723 p.
- Majzoub, M., 1971, Fractionnement en oxygen-18 et en deuterium entre l'eau et sa vapeur: *Jour. Chim. Phys.*, v. 68, p. 1423-1436 (cited in Friedman and O'Neil, 1977).
- Parkhurst, D.L., Thorstenson, D.C., and Plummer, L.N., 1980, PHREEQE—A computer program for geochemical calculations: U.S. Geological Survey Water-Resources Investigations Report 80-96, 210 p.
- Parkhurst, D.L., and Appelo, C.A.J., 1999, User's guide to PHREEQC (version 2)--A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Water-Resources Investigations Report 99-4259, 312 p.
- Parkhurst, D.L., Thorstenson, D.C., and Kipp, K.L., 2001, Calculating carbon-isotope compositions in an unsaturated zone with seasonally varying CO<sub>2</sub> production *in* Yanxin Wang, ed., *Hydrogeology and the environment*: Wuhan, China, China Environmental Science Press, p. 220-224.
- Plummer, L.N., Prestemon, E.C., and Parkhurst, D.L., 1991, An interactive code (NETPATH) for modeling NET geochemical reactions along a flow PATH: U.S. Geological Survey Water-Resources Investigations Report 91-4078, 227 p.
- Plummer, L.N., Prestemon, E.C., and Parkhurst, D.L., 1994, An interactive code (NETPATH) for modeling NET geochemical reactions along a flow PATH, Version 2.0: U.S. Geological Survey Water Resources-Investigations Report 94-4169, 130 p.
- Poeter, E.P., and Hill, M.C., 1998, Documentation of UCODE, a computer code for universal inverse modeling: U.S. Geological Survey Water-Resources Investigation Report 98-4080, 122 p.
- Purdue University, 2002, Department of Chemistry, The molecular structure pages: accessed January 4, 2002 at URL <http://www.chem.purdue.edu/gchelp/molecules/>
- Reed, M.H., 1982, Calculation of multicomponent chemical equilibria and reaction processes in systems involving minerals, gases, and an aqueous phase: *Geochimica et Cosmochimica Acta*, v. 56, p. 2025-2040.

- Spycher, N.F., and Reed, M.H., 1989, CHILLER—A program for calculating water-rock reactions, boiling, mixing, and other reaction processes in aqueous-mineral-gas systems: Eugene, University of Oregon, 63 p.
- Thornton, E.R., 1962, Solvent isotope effects in H<sub>2</sub>O<sup>16</sup> and H<sub>2</sub>O<sup>18</sup>: *American Chemical Society Journal*, v. 84, p. 2474-2475.
- Urey, H.C., 1947, The thermodynamic properties of isotopic substances: *Journal of the Chemical Society*, p. 562-581.
- Vogel, J.C., Grootes, P.M., and Mook, W.G., 1970, Isotopic fractionation between gaseous and dissolved carbon dioxide: *Zeitschrift. Physik*, v. 230, p. 225-238 (cited in Friedman and O'Neil, 1977).
- Wells, A.F., 1984, *Structural inorganic chemistry* (5th ed.): Oxford, Clarendon Press, 1382 p.
- Wigley, T.M.L., Plummer, L.N., and Pearson, F.J., Jr., 1978, Mass transfer and carbon isotope evolution in natural water systems: *Geochimica et Cosmochimica Acta*, v. 42, p. 1117-1139.
- \_\_\_\_\_ 1979, Errata: *Geochimica et Cosmochimica Acta*, v. 43, p. 1395.
- Wolery, T.J., 1978, Some chemical aspects of hydrothermal processes at mid-ocean ridges—a theoretical study I. Basalt-seawater reaction and chemical cycling between the oceanic crust and the oceans. II. Calculation of equilibrium between aqueous solutions and minerals: Evanston, Illinois, Northwestern University, Ph.D. thesis.
- Wolery, T.J., 1979, Calculation of chemical equilibrium between aqueous solution and minerals: the EQ3/6 software package: Livermore, Calif., Lawrence Livermore National Laboratory publication UCRL-52658.
- Wolery, T.J., 1983, EQ3NR: A computer program for geochemical aqueous speciation-solubility calculations: User's guide and documentation: Livermore, Calif., Lawrence Livermore National Laboratory publication UCRL-53414.

**Table 1.** Symmetry numbers and isotope ratios

---

$H_2O_j$	The molecule is planar triangular (Wells, 1984, p. 653); 9 of 12 possible isotopic species are considered. $j$ denotes either gas or aqueous species.								
Species:	$H_2O_j$	$HDO_j$	$D_2O_j$	$H_2^{18}O_j$	$HD^{18}O_j$	$D_2^{18}O_j$	$HTO_j$	$HT^{18}O_j$	$DTO_j$
Symmetry no.	$\sigma = 2$	$\sigma = 1$	$\sigma = 2$	$\sigma = 2$	$\sigma = 1$	$\sigma = 2$	$\sigma = 1$	$\sigma = 1$	$\sigma = 1$
Isotope ratios are presented for completeness, but concentrations of the following species will be negligible and they are not included in the aqueous model.									
Species:	$DT^{18}O_j$	$T_2O_j$	$T_2^{18}O_j$						
Symmetry no.	$\sigma = 1$	$\sigma = 2$	$\sigma = 2$						
Isotope ratios:	$R_{H_2O_j}^D = \frac{\frac{1}{2}}{\frac{1}{2}} \frac{n_{D_2O_j}}{n_{H_2O_j}} = \frac{\frac{1}{2}}{\frac{1}{2}} \frac{n_{D_2^{18}O_j}}{n_{H_2^{18}O_j}} = \frac{n_{HDO_j}}{2n_{H_2O_j}} = \frac{n_{HD^{18}O_j}}{2n_{H_2^{18}O_j}} = \frac{n_{DTO_j}}{n_{HTO_j}} = \frac{n_{DT^{18}O_j}}{n_{HT^{18}O_j}}$ $R_{H_2O_j}^T = \frac{\frac{1}{2}}{\frac{1}{2}} \frac{n_{T_2O_j}}{n_{H_2O_j}} = \frac{\frac{1}{2}}{\frac{1}{2}} \frac{n_{T_2^{18}O_j}}{n_{H_2^{18}O_j}} = \frac{n_{HTO_j}}{2n_{H_2O_j}} = \frac{n_{HT^{18}O_j}}{2n_{H_2^{18}O_j}} = \frac{n_{TDO_j}}{n_{HDO_j}} = \frac{n_{TD^{18}O_j}}{n_{HD^{18}O_j}}$ $R_{H_2O_j}^{18O} = \frac{n_{H_2^{18}O_j}}{n_{H_2O_j}} = \frac{n_{HD^{18}O_j}}{n_{HDO_j}} = \frac{n_{HT^{18}O_j}}{n_{HTO_j}} = \frac{n_{DT^{18}O_j}}{n_{DTO_j}} = \frac{n_{D_2^{18}O_j}}{n_{D_2O_j}} = \frac{n_{T_2^{18}O_j}}{n_{T_2O_j}}$								

**Table 1.** Symmetry numbers and isotope ratios—continued

$OH^-$  The ion is linear; 6 isotopic species are considered.

Species:	$OH^-$	$OD^-$	$OT^-$	$^{18}OH^-$	$^{18}OD^-$	$^{18}OT^-$
Symmetry no.	$\sigma = 1$					

Isotope ratios:

$$R_{OH^-}^D = \frac{n_{OD^-}}{n_{OH^-}} = \frac{n_{^{18}OD^-}}{n_{^{18}OH^-}} \quad R_{OH^-}^T = \frac{n_{OT^-}}{n_{OH^-}} = \frac{n_{^{18}OT^-}}{n_{^{18}OH^-}}$$

$$R_{OH^-}^{^{18}O} = \frac{n_{^{18}OH^-}}{n_{OH^-}} = \frac{n_{^{18}OD^-}}{n_{OD^-}} = \frac{n_{^{18}OT^-}}{n_{OT^-}}$$

$H_3O_{aq}^+$  The ion is a flattened triangular pyramid (Cotton and Wilkinson, 1966, p. 199); 11 of 20 possible isotopic species are considered.

Species:	$H_3O_{aq}^+$	$H_2DO_{aq}^+$	$HD_2O_{aq}^+$	$D_3O_{aq}^+$	$H_3^{18}O_{aq}^+$	$H_2D^{18}O_{aq}^+$	$HD_2^{18}O_{aq}^+$	$D_3^{18}O_{aq}^+$
Symmetry no.	$\sigma = 3$	$\sigma = 1$	$\sigma = 1$	$\sigma = 3$	$\sigma = 3$	$\sigma = 1$	$\sigma = 1$	$\sigma = 3$

Species:	$H_2TO_{aq}^+$	$HDTO_{aq}^+$	$H_2T^{18}O_{aq}^+$
Symmetry no.	$\sigma = 1$	$\sigma = 1$	$\sigma = 1$

Isotope ratios are presented for completeness, but concentrations of the following species will be negligible and they are not included in the aqueous model.

Species:	$D_2TO_{aq}^+$	$DT_2O_{aq}^+$	$D_2T^{18}O_{aq}^+$	$DT_2^{18}O_{aq}^+$	$HT_2O_{aq}^+$	$T_3O_{aq}^+$
Symmetry no.	$\sigma = 1$	$\sigma = 1$	$\sigma = 1$	$\sigma = 1$	$\sigma = 1$	$\sigma = 3$

Species:	$HT_2^{18}O_{aq}^+$	$T_3^{18}O_{aq}^+$	$HDT^{18}O_{aq}^+$
Symmetry no.	$\sigma = 1$	$\sigma = 3$	$\sigma = 1$

Isotope ratios:

$$\begin{aligned}
 R_{H_3O_{aq}^+}^D &= \frac{\frac{1}{3} n_{D_3O_{aq}^+}}{\frac{1}{3} n_{H_3O_{aq}^+}} = \frac{\frac{1}{2} n_{HD_2O_{aq}^+}}{3 \frac{1}{2} \frac{1}{2} n_{H_3O_{aq}^+}} = \frac{n_{H_2DO_{aq}^+}}{3 n_{H_3O_{aq}^+}} = \frac{\frac{1}{2} n_{D_2TO_{aq}^+}}{\frac{1}{2} n_{H_2TO_{aq}^+}} = \frac{n_{DT_2O_{aq}^+}}{n_{HT_2O_{aq}^+}} = \frac{n_{HDTO_{aq}^+}}{n_{H_2TO_{aq}^+}} \\
 &= \frac{\frac{1}{3} n_{D_3^{18}O_{aq}^+}}{\frac{1}{3} n_{H_3^{18}O_{aq}^+}} = \frac{\frac{1}{2} n_{HD_2^{18}O_{aq}^+}}{3 \frac{1}{2} \frac{1}{2} n_{H_3^{18}O_{aq}^+}} = \frac{n_{H_2D^{18}O_{aq}^+}}{3 n_{H_3^{18}O_{aq}^+}} = \frac{\frac{1}{2} n_{D_2T^{18}O_{aq}^+}}{\frac{1}{2} n_{H_2T^{18}O_{aq}^+}} = \frac{n_{DT_2^{18}O_{aq}^+}}{n_{HT_2^{18}O_{aq}^+}} = \frac{n_{HDT^{18}O_{aq}^+}}{n_{H_2T^{18}O_{aq}^+}} \\
 R_{H_3O_{aq}^+}^T &= \frac{\frac{1}{3} n_{T_3O_{aq}^+}}{\frac{1}{3} n_{H_3O_{aq}^+}} = \frac{\frac{1}{2} n_{HT_2O_{aq}^+}}{3 \frac{1}{2} \frac{1}{2} n_{H_3O_{aq}^+}} = \frac{n_{H_2TO_{aq}^+}}{3 n_{H_3O_{aq}^+}} = \frac{\frac{1}{2} n_{DT_2O_{aq}^+}}{\frac{1}{2} n_{DH_2O_{aq}^+}} = \frac{n_{D_2TO_{aq}^+}}{n_{D_2HO_{aq}^+}} \\
 &= \frac{\frac{1}{3} n_{T_3^{18}O_{aq}^+}}{\frac{1}{3} n_{H_3^{18}O_{aq}^+}} = \frac{\frac{1}{2} n_{HT_2^{18}O_{aq}^+}}{3 \frac{1}{2} \frac{1}{2} n_{H_3^{18}O_{aq}^+}} = \frac{n_{H_2T^{18}O_{aq}^+}}{3 n_{H_3^{18}O_{aq}^+}} = \frac{\frac{1}{2} n_{DT_2^{18}O_{aq}^+}}{\frac{1}{2} n_{DH_2^{18}O_{aq}^+}} = \frac{n_{D_2T^{18}O_{aq}^+}}{n_{D_2H^{18}O_{aq}^+}} \\
 R_{H_3O_{aq}^+}^{18O} &= \frac{n_{H_3^{18}O_{aq}^+}}{n_{H_3O_{aq}^+}} = \frac{n_{H_2D^{18}O_{aq}^+}}{n_{H_2DO_{aq}^+}} = \frac{n_{HD_2^{18}O_{aq}^+}}{n_{HD_2O_{aq}^+}} = \frac{n_{D_3^{18}O_{aq}^+}}{n_{D_3O_{aq}^+}} = \frac{n_{H_2T^{18}O_{aq}^+}}{n_{H_2TO_{aq}^+}} \\
 &= \frac{n_{HT_2^{18}O_{aq}^+}}{n_{HT_2O_{aq}^+}} = \frac{n_{T_3^{18}O_{aq}^+}}{n_{T_3O_{aq}^+}} = \frac{n_{D_2T^{18}O_{aq}^+}}{n_{H_2TO_{aq}^+}} = \frac{n_{DT_2^{18}O_{aq}^+}}{n_{HT_2O_{aq}^+}} = \frac{n_{HDT^{18}O_{aq}^+}}{n_{HDTO_{aq}^+}}
 \end{aligned}$$

**Table 1.** Symmetry numbers and isotope ratios—continued

$CO_{2j}$  The molecule is linear (Wells, 1984, p. 925); 9 isotopic species are considered.

$j$  denotes either gas or aqueous species.

Species:	$CO_{2j}$	$CO^{18}O_j$	$C^{18}O_{2j}$	$^{13}CO_{2j}$	$^{13}CO^{18}O_j$	$^{13}C^{18}O_{2j}$
Symmetry no.	$\sigma = 2$	$\sigma = 1$	$\sigma = 2$	$\sigma = 2$	$\sigma = 1$	$\sigma = 2$

Species:	$^{14}CO_{2j}$	$^{14}CO^{18}O_j$	$^{14}C^{18}O_{2j}$
Symmetry no.	$\sigma = 2$	$\sigma = 1$	$\sigma = 2$

Isotope ratios:

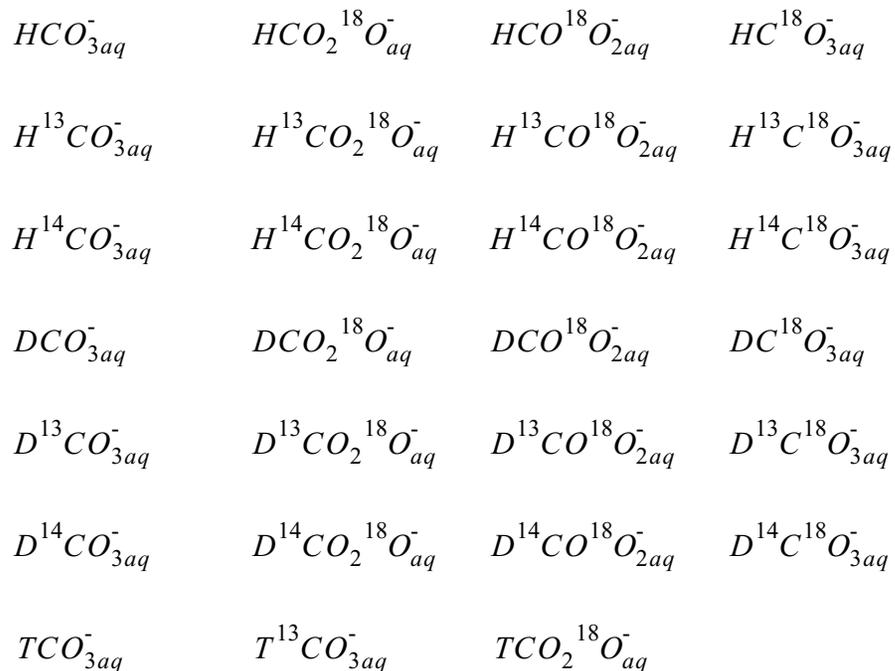
$$R_{CO_{2j}}^{18O} = \frac{\frac{1}{2} n_{C^{18}O_{2j}}}{n_{CO_{2j}}} = \frac{\frac{1}{2} n_{^{13}C^{18}O_{2j}}}{n_{^{13}CO_{2j}}} = \frac{\frac{1}{2} n_{^{14}C^{18}O_{2j}}}{n_{^{14}CO_{2j}}} = \frac{n_{CO^{18}O_j}}{2n_{CO_{2j}}} = \frac{n_{^{13}CO^{18}O_j}}{2n_{^{13}CO_{2j}}} = \frac{n_{^{14}CO^{18}O_j}}{2n_{^{14}CO_{2j}}}$$

$$R_{CO_{2j}}^{13C} = \frac{n_{^{13}CO_{2j}}}{n_{CO_{2j}}} = \frac{n_{^{13}CO^{18}O_j}}{n_{CO^{18}O_j}} = \frac{n_{^{13}C^{18}O_{2j}}}{n_{C^{18}O_{2j}}}$$

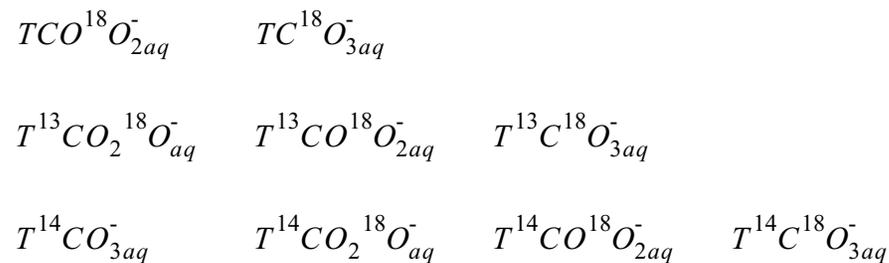
$$R_{CO_{2j}}^{14C} = \frac{n_{^{14}CO_{2j}}}{n_{CO_{2j}}} = \frac{n_{^{14}CO^{18}O_j}}{n_{CO^{18}O_j}} = \frac{n_{^{14}C^{18}O_{2j}}}{n_{C^{18}O_{2j}}}$$

**Table 1.** Symmetry numbers and isotope ratios—continued

$HCO_3^-$  The  $HCO_3^-$  ion is planar and the C-O-H bond is nonlinear (Purdue University, 2002). The ion is asymmetric with all symmetry numbers = 1; 27 of 36 possible isotopic species are considered.



Isotope ratios are presented for completeness, but concentrations of the following species will be negligible and they are not included in the aqueous model.



**Table 1.** Symmetry numbers and isotope ratios—continued

Isotope ratios:

$$R_{HCO_3aq}^{13C} = \frac{n_{H^{13}CO_3aq^-}}{n_{HCO_3aq^-}} = \frac{n_{H^{13}CO_2^{18}O_{aq}^-}}{n_{HCO_2^{18}O_{aq}^-}} = \frac{n_{H^{13}CO^{18}O_{2aq}^-}}{n_{HCO^{18}O_{2aq}^-}} = \frac{n_{H^{13}C^{18}O_{3aq}^-}}{n_{HC^{18}O_{3aq}^-}}$$

$$= \frac{n_{D^{13}CO_3aq^-}}{n_{DCO_3aq^-}} = \frac{n_{D^{13}CO_2^{18}O_{aq}^-}}{n_{DCO_2^{18}O_{aq}^-}} = \frac{n_{D^{13}CO^{18}O_{2aq}^-}}{n_{DCO^{18}O_{2aq}^-}} = \frac{n_{D^{13}C^{18}O_{3aq}^-}}{n_{DC^{18}O_{3aq}^-}} = \frac{n_{T^{13}CO_3aq^-}}{n_{TCO_3aq^-}} = \frac{n_{T^{13}CO_2^{18}O_{aq}^-}}{n_{TCO_2^{18}O_{aq}^-}} = \frac{n_{T^{13}CO^{18}O_{2aq}^-}}{n_{TCO^{18}O_{2aq}^-}} = \frac{n_{T^{13}C^{18}O_{3aq}^-}}{n_{TC^{18}O_{3aq}^-}}$$

$$R_{HCO_3aq}^{14C} = \frac{n_{H^{14}CO_3aq^-}}{n_{HCO_3aq^-}} = \frac{n_{H^{14}CO_2^{18}O_{aq}^-}}{n_{HCO_2^{18}O_{aq}^-}} = \frac{n_{H^{14}CO^{18}O_{2aq}^-}}{n_{HCO^{18}O_{2aq}^-}} = \frac{n_{H^{14}C^{18}O_{3aq}^-}}{n_{HC^{18}O_{3aq}^-}}$$

$$= \frac{n_{D^{14}CO_3aq^-}}{n_{DCO_3aq^-}} = \frac{n_{D^{14}CO_2^{18}O_{aq}^-}}{n_{DCO_2^{18}O_{aq}^-}} = \frac{n_{D^{14}CO^{18}O_{2aq}^-}}{n_{DCO^{18}O_{2aq}^-}} = \frac{n_{D^{14}C^{18}O_{3aq}^-}}{n_{DC^{18}O_{3aq}^-}} = \frac{n_{T^{14}CO_3aq^-}}{n_{TCO_3aq^-}} = \frac{n_{T^{14}CO_2^{18}O_{aq}^-}}{n_{TCO_2^{18}O_{aq}^-}} = \frac{n_{T^{14}CO^{18}O_{2aq}^-}}{n_{TCO^{18}O_{2aq}^-}} = \frac{n_{T^{14}C^{18}O_{3aq}^-}}{n_{TC^{18}O_{3aq}^-}}$$

$$R_{HCO_3aq}^D = \frac{n_{DCO_3aq^-}}{n_{HCO_3aq^-}} = \frac{n_{DCO_2^{18}O_{aq}^-}}{n_{HCO_2^{18}O_{aq}^-}} = \frac{n_{DCO^{18}O_{2aq}^-}}{n_{HCO^{18}O_{2aq}^-}} = \frac{n_{DC^{18}O_{3aq}^-}}{n_{HC^{18}O_{3aq}^-}}$$

$$= \frac{n_{D^{13}CO_3aq^-}}{n_{HCO_3aq^-}} = \frac{n_{D^{13}CO_2^{18}O_{aq}^-}}{n_{HCO_2^{18}O_{aq}^-}} = \frac{n_{D^{13}CO^{18}O_{2aq}^-}}{n_{HCO^{18}O_{2aq}^-}} = \frac{n_{D^{13}C^{18}O_{3aq}^-}}{n_{HC^{18}O_{3aq}^-}} = \frac{n_{D^{14}CO_3aq^-}}{n_{HCO_3aq^-}} = \frac{n_{D^{14}CO_2^{18}O_{aq}^-}}{n_{HCO_2^{18}O_{aq}^-}} = \frac{n_{D^{14}CO^{18}O_{2aq}^-}}{n_{HCO^{18}O_{2aq}^-}} = \frac{n_{D^{14}C^{18}O_{3aq}^-}}{n_{HC^{18}O_{3aq}^-}}$$

$$R_{HCO_3aq}^T = \frac{n_{TCO_3aq^-}}{n_{HCO_3aq^-}} = \frac{n_{TCO_2^{18}O_{aq}^-}}{n_{HCO_2^{18}O_{aq}^-}} = \frac{n_{TCO^{18}O_{2aq}^-}}{n_{HCO^{18}O_{2aq}^-}} = \frac{n_{TC^{18}O_{3aq}^-}}{n_{HC^{18}O_{3aq}^-}}$$

$$= \frac{n_{T^{13}CO_3aq^-}}{n_{HCO_3aq^-}} = \frac{n_{T^{13}CO_2^{18}O_{aq}^-}}{n_{HCO_2^{18}O_{aq}^-}} = \frac{n_{T^{13}CO^{18}O_{2aq}^-}}{n_{HCO^{18}O_{2aq}^-}} = \frac{n_{T^{13}C^{18}O_{3aq}^-}}{n_{HC^{18}O_{3aq}^-}} = \frac{n_{T^{14}CO_3aq^-}}{n_{HCO_3aq^-}} = \frac{n_{T^{14}CO_2^{18}O_{aq}^-}}{n_{HCO_2^{18}O_{aq}^-}} = \frac{n_{T^{14}CO^{18}O_{2aq}^-}}{n_{HCO^{18}O_{2aq}^-}} = \frac{n_{T^{14}C^{18}O_{3aq}^-}}{n_{HC^{18}O_{3aq}^-}}$$

The oxygen-18 isotope ratios are complicated functions of composition. See Appendix 1.

From equation A1.19

$$\begin{aligned} R_{HCO_3aq}^{18O} &= \left( \frac{n_{HCO_2^{18}O_{aq}}}{3n_{HCO_3aq}} \right) qq1 = \left( \frac{n_{H^{13}CO_2^{18}O_{aq}}}{3n_{H^{13}CO_3aq}} \right) qq1 = \left( \frac{n_{DCO_2^{18}O_{aq}}}{3n_{DCO_3aq}} \right) qq1 = \left( \frac{n_{D^{13}CO_2^{18}O_{aq}}}{3n_{D^{13}CO_3aq}} \right) qq1 \\ &= \left( \frac{n_{H^{14}CO_2^{18}O_{aq}}}{3n_{H^{14}CO_3aq}} \right) qq1 = \left( \frac{n_{D^{14}CO_2^{18}O_{aq}}}{3n_{D^{14}CO_3aq}} \right) qq1 = \left( \frac{n_{TCO_2^{18}O_{aq}}}{3n_{TCO_3aq}} \right) qq1 \end{aligned}$$

From equation A1.32

$$\begin{aligned} R_{HCO_3aq}^{18O} &= \left( \frac{n_{HCO^{18}O_{2aq}}}{3n_{HCO_3aq}} \right)^{\frac{1}{2}} qq2 = \left( \frac{n_{H^{13}CO^{18}O_{2aq}}}{3n_{H^{13}CO_3aq}} \right)^{\frac{1}{2}} qq2 = \left( \frac{n_{DCO^{18}O_{2aq}}}{3n_{DCO_3aq}} \right)^{\frac{1}{2}} qq2 = \left( \frac{n_{D^{13}CO^{18}O_{2aq}}}{3n_{D^{13}CO_3aq}} \right)^{\frac{1}{2}} qq2 \\ &= \left( \frac{n_{H^{14}CO^{18}O_{2aq}}}{3n_{H^{14}CO_3aq}} \right)^{\frac{1}{2}} qq2 = \left( \frac{n_{D^{14}CO^{18}O_{2aq}}}{3n_{D^{14}CO_3aq}} \right)^{\frac{1}{2}} qq2 \end{aligned}$$

From equation A1.41

$$\begin{aligned} R_{HCO_3aq}^{18O} &= \left( \frac{n_{HC^{18}O_{3aq}}}{n_{HCO_3aq}} \right)^{\frac{1}{3}} qq3 = \left( \frac{n_{H^{13}C^{18}O_{3aq}}}{n_{H^{13}CO_3aq}} \right)^{\frac{1}{3}} qq3 = \left( \frac{n_{DC^{18}O_{3aq}}}{n_{DCO_3aq}} \right)^{\frac{1}{3}} qq3 = \left( \frac{n_{D^{13}C^{18}O_{3aq}}}{n_{D^{13}CO_3aq}} \right)^{\frac{1}{3}} qq3 \\ &= \left( \frac{n_{H^{14}C^{18}O_{3aq}}}{n_{H^{14}CO_3aq}} \right)^{\frac{1}{3}} qq3 = \left( \frac{n_{D^{14}C^{18}O_{3aq}}}{n_{D^{14}CO_3aq}} \right)^{\frac{1}{3}} qq3 \end{aligned}$$

**Table 1.** Symmetry numbers and isotope ratios—continued

$CO_{3aq}^{-2}$  The carbonate ion is planar (Wells, 1984, p. 921); 12 isotopic species are considered.

Species:	$CO_{3aq}^{-2}$	$CO_2^{18}O_{aq}^{-2}$	$CO^{18}O_{2aq}^{-2}$	$C^{18}O_{3aq}^{-2}$	$^{13}CO_{3aq}^{-2}$	$^{13}CO_2^{18}O_{aq}^{-2}$
Symmetry no.	$\sigma = 6$	$\sigma = 2$	$\sigma = 2$	$\sigma = 6$	$\sigma = 6$	$\sigma = 2$
Species:	$^{13}CO^{18}O_{2aq}^{-2}$	$^{13}C^{18}O_{3aq}^{-2}$	$^{14}CO_{3aq}^{-2}$	$^{14}CO_2^{18}O_{aq}^{-2}$	$^{14}CO^{18}O_{2aq}^{-2}$	$^{14}C^{18}O_{3aq}^{-2}$
Symmetry no.	$\sigma = 2$	$\sigma = 6$	$\sigma = 6$	$\sigma = 2$	$\sigma = 2$	$\sigma = 6$

Isotope ratios:

$$\begin{aligned}
 R_{CO_{3aq}^{-2}}^{18O} &= \frac{\frac{1}{3} n_{C^{18}O_{3aq}^{-2}}}{\frac{1}{3} n_{CO_{3aq}^{-2}}} = \frac{\frac{1}{2} n_{CO^{18}O_{2aq}^{-2}}}{3 \frac{1}{2} \frac{1}{2} n_{CO_{3aq}^{-2}}} = \frac{n_{CO_2^{18}O_{aq}^{-2}}}{3 n_{CO_{3aq}^{-2}}} = \frac{\frac{1}{3} n_{^{13}C^{18}O_{3aq}^{-2}}}{\frac{1}{3} n_{^{13}CO_{3aq}^{-2}}} = \frac{\frac{1}{2} n_{^{13}CO^{18}O_{2aq}^{-2}}}{3 \frac{1}{2} \frac{1}{2} n_{^{13}CO_{3aq}^{-2}}} = \frac{n_{^{13}CO_2^{18}O_{aq}^{-2}}}{3 n_{^{13}CO_{3aq}^{-2}}} \\
 &= \frac{\frac{1}{3} n_{^{14}C^{18}O_{3aq}^{-2}}}{\frac{1}{3} n_{^{14}CO_{3aq}^{-2}}} = \frac{\frac{1}{2} n_{^{14}CO^{18}O_{2aq}^{-2}}}{3 \frac{1}{2} \frac{1}{2} n_{^{14}CO_{3aq}^{-2}}} = \frac{n_{^{14}CO_2^{18}O_{aq}^{-2}}}{3 n_{^{14}CO_{3aq}^{-2}}} \\
 R_{CO_{3aq}^{-2}}^{13C} &= \frac{n_{^{13}CO_{3aq}^{-2}}}{n_{CO_{3aq}^{-2}}} = \frac{n_{^{13}CO_2^{18}O_{aq}^{-2}}}{n_{CO_2^{18}O_{aq}^{-2}}} = \frac{n_{^{13}CO^{18}O_{2aq}^{-2}}}{n_{CO^{18}O_{2aq}^{-2}}} = \frac{n_{^{13}C^{18}O_{3aq}^{-2}}}{n_{C^{18}O_{3aq}^{-2}}} \\
 R_{CO_{3aq}^{-2}}^{14C} &= \frac{n_{^{14}CO_{3aq}^{-2}}}{n_{CO_{3aq}^{-2}}} = \frac{n_{^{14}CO_2^{18}O_{aq}^{-2}}}{n_{CO_2^{18}O_{aq}^{-2}}} = \frac{n_{^{14}CO^{18}O_{2aq}^{-2}}}{n_{CO^{18}O_{2aq}^{-2}}} = \frac{n_{^{14}C^{18}O_{3aq}^{-2}}}{n_{C^{18}O_{3aq}^{-2}}}
 \end{aligned}$$

$CaCO_{3s}$  The carbonate ion is planar (Wells, 1984, p. 921); 12 isotopic species are considered.

Species:	$CaCO_{3s}$	$CaCO_2^{18}O_s$	$CaCO^{18}O_{2s}$	$CaC^{18}O_{3s}$
Symmetry no.	$\sigma = 6$	$\sigma = 2$	$\sigma = 2$	$\sigma = 6$
Species:	$Ca^{13}CO_{3s}$	$Ca^{13}CO_2^{18}O_s$	$Ca^{13}CO^{18}O_{2s}$	$Ca^{13}C^{18}O_{3s}$
Symmetry no.	$\sigma = 6$	$\sigma = 2$	$\sigma = 2$	$\sigma = 6$
Species:	$Ca^{14}CO_{3s}$	$Ca^{14}CO_2^{18}O_s$	$Ca^{14}CO^{18}O_{2s}$	$Ca^{14}C^{18}O_{3s}$
Symmetry no.	$\sigma = 6$	$\sigma = 2$	$\sigma = 2$	$\sigma = 6$

$$\begin{aligned}
 R_{CaCO_{3s}}^{18O} &= \frac{n_{CaC^{18}O_{3s}} \frac{1}{3}}{n_{CaCO_{3s}} \frac{1}{3}} = \frac{n_{CaCO_2^{18}O_s} \frac{1}{2}}{3 n_{CaCO_{3s}} \frac{1}{2} \frac{1}{2}} = \frac{n_{CaCO_2^{18}O_s}}{3 n_{CaCO_{3s}}} = \frac{n_{Ca^{13}C^{18}O_{3s}} \frac{1}{3}}{n_{Ca^{13}CO_{3s}} \frac{1}{3}} = \frac{n_{Ca^{13}CO^{18}O_{2s}} \frac{1}{2}}{3 n_{Ca^{13}CO_{3s}} \frac{1}{2} \frac{1}{2}} = \frac{n_{Ca^{13}CO_2^{18}O_s}}{3 n_{Ca^{13}CO_{3s}}} \\
 &= \frac{n_{Ca^{14}C^{18}O_{3s}} \frac{1}{3}}{n_{Ca^{14}CO_{3s}} \frac{1}{3}} = \frac{n_{Ca^{14}CO^{18}O_{2s}} \frac{1}{2}}{3 n_{Ca^{14}CO_{3s}} \frac{1}{2} \frac{1}{2}} = \frac{n_{Ca^{14}CO_2^{18}O_s}}{3 n_{Ca^{14}CO_{3s}}} \\
 R_{CaCO_{3s}}^{13C} &= \frac{n_{Ca^{13}CO_{3s}}}{n_{CaCO_{3s}}} = \frac{n_{Ca^{13}CO_2^{18}O_s}}{n_{CaCO_2^{18}O_s}} = \frac{n_{Ca^{13}CO^{18}O_{2s}}}{n_{CaCO^{18}O_{2s}}} = \frac{n_{Ca^{13}C^{18}O_{3s}}}{n_{CaC^{18}O_{3s}}} \\
 R_{CaCO_{3s}}^{14C} &= \frac{n_{Ca^{14}CO_{3s}}}{n_{CaCO_{3s}}} = \frac{n_{Ca^{14}CO_2^{18}O_s}}{n_{CaCO_2^{18}O_s}} = \frac{n_{Ca^{14}CO^{18}O_{2s}}}{n_{CaCO^{18}O_{2s}}} = \frac{n_{Ca^{14}C^{18}O_{3s}}}{n_{CaC^{18}O_{3s}}}
 \end{aligned}$$


---

**Table 2.** Reactions and equilibrium constants

[ $K$  is the equilibrium constant of the reaction listed;  $\alpha$  is the fractionation factor;  $K^H$  is the Henry's Law equilibrium constant;  $K_w$  is the dissociation constant of water;  $\gamma$  is the activity coefficient of aqueous (aq) species;  $\lambda$  is the activity coefficient of gaseous (g) or solid (s) species; and  $\epsilon$  refers to experimental conditions under which  $\alpha$  was measured]

---

**Species**                      **Reaction and log of the equilibrium constant**

**H<sub>2</sub>O (liquid) — H<sub>2</sub>O (liquid)**

$D_2^{18}O_{aq}$	$H_2^{18}O_{aq} + D_2O_{aq} = D_2^{18}O_{aq} + H_2O_l$ $\log K = 0$
$HDO_{aq}$	$0.5H_2O_l + 0.5D_2O_{aq} = HDO_{aq}$ $\log K = \log(2)$
$HD^{18}O_{aq}$	$0.5H_2^{18}O_{aq} + 0.5D_2^{18}O_{aq} = HD^{18}O_{aq}$ $\log K = \log(2)$
$DTO_{aq}$	$HTO_{aq} + HDO_{aq} = DTO_{aq} + H_2O_l$ $\log K = -\log(2)$
$HT^{18}O_{aq}$	$HTO_{aq} + H_2^{18}O_{aq} = HT^{18}O_{aq} + H_2O_l$ $\log K = 0$

**CO<sub>2</sub> (aqueous) — CO<sub>2</sub>(aqueous)**

$CO^{18}O_{aq}$	$0.5CO_{2aq} + 0.5C^{18}O_{2aq} = CO^{18}O_{aq}$ $\log K = \log(2)$
$^{13}C^{18}O_{2aq}$	$^{13}CO_{2aq} + C^{18}O_{2aq} = ^{13}C^{18}O_{2aq} + CO_{2aq}$ $\log K = 0$

56 **Table 2.** Reactions and equilibrium constants—continued

Calculation of Individual Isotope Equilibrium Constants

**Species**                      **Reaction and log of the equilibrium constant**

$$^{13}\text{CO}^{18}\text{O}_{aq} \quad 0.5\ ^{13}\text{CO}_{2aq} + 0.5\ ^{13}\text{C}^{18}\text{O}_{2aq} = ^{13}\text{CO}^{18}\text{O}_{aq}$$

$$\log K = \log(2)$$

$$^{14}\text{C}^{18}\text{O}_{2aq} \quad ^{14}\text{CO}_{2aq} + \text{C}^{18}\text{O}_{2aq} = ^{14}\text{C}^{18}\text{O}_{2aq} + \text{CO}_{2aq}$$

$$\log K = 0$$

$$^{14}\text{CO}^{18}\text{O}_{aq} \quad 0.5\ ^{14}\text{CO}_{2aq} + 0.5\ ^{14}\text{C}^{18}\text{O}_{2aq} = ^{14}\text{CO}^{18}\text{O}_{aq}$$

$$\log K = \log(2)$$

**H<sub>2</sub>O(liquid) — CO<sub>2</sub>(aqueous)**

$$\text{C}^{18}\text{O}_{2aq} \quad \text{CO}_{2aq} + 2\text{H}_2\ ^{18}\text{O}_{aq} = \text{C}^{18}\text{O}_{2aq} + 2\text{H}_2\text{O}_l$$

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

**H<sub>2</sub>O(gas) — H<sub>2</sub>O(liquid)**

**PHREEQC reference reaction:**  $\text{H}_2\text{O}_g = \text{H}_2\text{O}_l$ ,       $K_{\text{H}_2\text{O}_g}^H$

$$\text{HDO}_g \quad \text{HDO}_g = \text{HDO}_{aq}$$

$$\log K_{\text{HDO}_g}^H = \log K_{\text{H}_2\text{O}_g}^H + \log(\alpha_{\text{H}_2\text{O}_l-\text{H}_2\text{O}_g}^D) + \log\left(\frac{\lambda_{\text{H}_2\text{O}_g}}{\lambda_{\text{HDO}_g}}\right)_{exp}$$

$$\text{D}_2\text{O}_g \quad \text{D}_2\text{O}_g = \text{D}_2\text{O}_{aq}$$

$$\log K_{\text{D}_2\text{O}_g}^H = \log K_{\text{H}_2\text{O}_g}^H + 2\log(\alpha_{\text{H}_2\text{O}_l-\text{H}_2\text{O}_g}^D) + \log\left(\frac{\lambda_{\text{H}_2\text{O}_g}}{\lambda_{\text{D}_2\text{O}_g}}\right)_{exp}$$

**Table 2.** Reactions and equilibrium constants—continued

<b>Species</b>	<b>Reaction and log of the equilibrium constant</b>
$H_2^{18}O_g$	$H_2^{18}O_g = H_2^{18}O_{aq}$ $\log K_{H_2^{18}O_g}^H = \log K_{H_2O_g}^H + \log(\alpha_{H_2O_l-H_2O_g}^{18O}) + \log\left(\frac{\lambda_{H_2O_g}}{\lambda_{H_2^{18}O_g}}\right)_{exp}$
$HD^{18}O_g$	$HD^{18}O_g = HD^{18}O_{aq}$ $\log K_{HD^{18}O_g}^H = \log K_{H_2O_g}^H + \log(\alpha_{H_2O_l-H_2O_g}^{18O}) + \log(\alpha_{H_2O_l-H_2O_g}^D) + \log\left(\frac{\lambda_{H_2O_g}}{\lambda_{HD^{18}O_g}}\right)_{exp}$
$D_2^{18}O_g$	$D_2^{18}O_g = D_2^{18}O_{aq}$ $\log K_{D_2^{18}O_g}^H = \log K_{H_2O_g}^H + \log(\alpha_{H_2O_l-H_2O_g}^{18O}) + 2\log(\alpha_{H_2O_l-H_2O_g}^D) + \log\left(\frac{\lambda_{H_2O_g}}{\lambda_{D_2^{18}O_g}}\right)_{exp}$
$HTO_g$	$HTO_g = HTO_{aq}$ $\log K_{HTO_g}^H = \log K_{H_2O_g}^H + \log(\alpha_{H_2O_l-H_2O_g}^T) + \log\left(\frac{\lambda_{H_2O_g}}{\lambda_{HTO_g}}\right)_{exp}$
$HT^{18}O_g$	$HT^{18}O_g = HT^{18}O_{aq}$ $\log K_{HT^{18}O_g}^H = \log K_{H_2O_g}^H + \log(\alpha_{H_2O_l-H_2O_g}^{18O}) + \log(\alpha_{H_2O_l-H_2O_g}^T) + \log\left(\frac{\lambda_{H_2O_g}}{\lambda_{HT^{18}O_g}}\right)_{exp}$
$DTO_g$	$DTO_g = DTO_{aq}$ $\log K_{DTO_g}^H = \log K_{H_2O_g}^H + \log(\alpha_{H_2O_l-H_2O_g}^D) + \log(\alpha_{H_2O_l-H_2O_g}^T) + \log\left(\frac{\lambda_{H_2O_g}}{\lambda_{DTO_g}}\right)_{exp}$

58 **Table 2.** Reactions and equilibrium constants—continued

<u>Species</u>	<u>Reaction and log of the equilibrium constant</u>
	<b>H<sub>2</sub>O(liquid) — OH<sup>-</sup>(aqueous)</b>
	<b>PHREEQC reference reaction:</b> $H_2O_l + H_2O_l = OH_{aq}^- + H_3O_{aq}^+$ , $K_w = K_{OH_{aq}^-} = K_{H_3O_{aq}^+}$
$OD_{aq}^-$	$H_2O_l + HDO_{aq} = OD_{aq}^- + H_3O_{aq}^+$ $\log K_{OD_{aq}^-} = \log K_w - \log(2) + \log(\alpha_{OH_{aq}^- - H_2O_l}^D) + \log\left(\frac{\gamma_{OD_{aq}^-}}{\gamma_{OH_{aq}^-}}\right)_{exp}$
$^{18}OH_{aq}^-$	$H_2O_l + H_2^{18}O_{aq} = ^{18}OH_{aq}^- + H_3O_{aq}^+$ $\log K_{^{18}OH_{aq}^-} = \log K_w + \log\left(\alpha_{OH_{aq}^- - H_2O_l}^{^{18}O}\right) + \log\left(\frac{\gamma_{^{18}OH_{aq}^-}}{\gamma_{OH_{aq}^-}}\right)_{exp}$
$^{18}OD_{aq}^-$	$H_2O_l + HD^{18}O_{aq} = ^{18}OD_{aq}^- + H_3O_{aq}^+$ $\log K_{^{18}OD_{aq}^-} = \log K_w - \log(2) + \log\left(\alpha_{OH^- - H_2O_l}^{^{18}O}\right) + \log(\alpha_{OH^- - H_2O_l}^D) + \log\left(\frac{\gamma_{^{18}OD_{aq}^-}}{\gamma_{OH_{aq}^-}}\right)_{exp}$
$OT_{aq}^-$	$H_2O_l + HTO_{aq} = OT_{aq}^- + H_3O_{aq}^+$ $\log K_{OT_{aq}^-} = \log K_w - \log(2) + \log(\alpha_{OH_{aq}^- - H_2O_l}^T) + \log\left(\frac{\gamma_{OT_{aq}^-}}{\gamma_{OH_{aq}^-}}\right)_{exp}$
$^{18}OT_{aq}^-$	$H_2O_l + HT^{18}O_{aq} = ^{18}OT_{aq}^- + H_3O_{aq}^+$ $\log K_{^{18}OT_{aq}^-} = \log K_w - \log(2) + \log\left(\alpha_{OH^- - H_2O_l}^{^{18}O}\right) + \log(\alpha_{OH^- - H_2O_l}^T) + \log\left(\frac{\gamma_{^{18}OT_{aq}^-}}{\gamma_{OH_{aq}^-}}\right)_{exp}$

**Table 2.** Reactions and equilibrium constants—continued

<b>Species</b>	<b>Reaction and log of the equilibrium constant</b>
<b>H<sub>2</sub>O(liquid) — H<sub>3</sub>O<sup>+</sup>(aqueous)</b>	
<b>PHREEQC reference reaction:</b> $H_2O_l + H_2O_l = H_3O_{aq}^+ + OH_{aq}^-$ , $K_w = K_{H_3O_{aq}^+} = K_{OH_{aq}^-}$	
$H_2DO_{aq}^+$	$H_2O_l + HDO_{aq} = H_2DO_{aq}^+ + OH_{aq}^-$ $\log K_{H_2DO_{aq}^+} = \log K_w + \log(1.5) + \log(\alpha_{H_3O_{aq}^+ - H_2O_l}^D) + \log\left(\frac{\gamma_{H_2DO_{aq}^+}}{\gamma_{H_3O_{aq}^+}}\right)_{exp}$
$HD_2O_{aq}^+$	$H_2O_l + D_2O_{aq} = HD_2O_{aq}^+ + OH_{aq}^-$ $\log K_{HD_2O_{aq}^+} = \log K_w + \log(3) + 2\log(\alpha_{H_3O_{aq}^+ - H_2O_l}^D) + \log\left(\frac{\gamma_{HD_2O_{aq}^+}}{\gamma_{H_3O_{aq}^+}}\right)_{exp}$
$D_3O_{aq}^+$	$3HDO_{aq} = D_3O_{aq}^+ + OH_{aq}^- + H_2O_l$ $\log K_{D_3O_{aq}^+} = \log K_w - 3\log(2) + 3\log(\alpha_{H_3O_{aq}^+ - H_2O_l}^D) + \log\left(\frac{\gamma_{D_3O_{aq}^+}}{\gamma_{H_3O_{aq}^+}}\right)_{exp}$
$H_3^{18}O_{aq}^+$	$H_2O_l + H_2^{18}O_{aq} = H_3^{18}O_{aq}^+ + OH_{aq}^-$ $\log K_{H_3^{18}O_{aq}^+} = \log K_w + \log(\alpha_{H_3O_{aq}^+ - H_2O_l}^{18O}) + \log\left(\frac{\gamma_{H_3^{18}O_{aq}^+}}{\gamma_{H_3O_{aq}^+}}\right)_{exp}$
$H_2D^{18}O_{aq}^+$	$H_2O_l + HD^{18}O_{aq} = H_2D^{18}O_{aq}^+ + OH_{aq}^-$ $\log K_{H_2D^{18}O_{aq}^+} = \log K_w + \log(1.5) + \log(\alpha_{H_3O_{aq}^+ - H_2O_l}^{18O}) + \log(\alpha_{H_3O_{aq}^+ - H_2O_l}^D) + \log\left(\frac{\gamma_{H_2D^{18}O_{aq}^+}}{\gamma_{H_3O_{aq}^+}}\right)_{exp}$

60 **Table 2.** Reactions and equilibrium constants—continued

<b>Species</b>	<b>Reaction and log of the equilibrium constant</b>
$HD_2^{18}O_{aq}^+$	$H_2O_l + D_2^{18}O_{aq} = HD_2^{18}O_{aq}^+ + OH_{aq}^-$ $\log K_{HD_2^{18}O_{aq}^+} = \log K_w + \log(3) + \log\left(\alpha_{H_3O_{aq}^+ - H_2O_l}^{18O}\right) + 2\log\left(\alpha_{H_3O_{aq}^+ - H_2O_l}^D\right) + \log\left(\frac{\gamma_{HD_2^{18}O_{aq}^+}}{\gamma_{H_3O_{aq}^+}}\right)_{exp}$
$D_3^{18}O_{aq}^+$	$3HDO_{aq} + H_2^{18}O_{aq} = D_3^{18}O_{aq}^+ + OH_{aq}^- + 2H_2O_l$ $\log K_{D_3^{18}O_{aq}^+} = \log K_w - 3\log(2) + \log\left(\alpha_{H_3O_{aq}^+ - H_2O_l}^{18O}\right) + 3\log\left(\alpha_{H_3O_{aq}^+ - H_2O_l}^D\right) + \log\left(\frac{\gamma_{D_3^{18}O_{aq}^+}}{\gamma_{H_3O_{aq}^+}}\right)_{exp}$
$H_2TO_{aq}^+$	$H_2O_l + HTO_{aq} = H_2TO_{aq}^+ + OH_{aq}^-$ $\log K_{H_2TO_{aq}^+} = \log K_w + \log(1.5) + \log\left(\alpha_{H_3O_{aq}^+ - H_2O_l}^T\right) + \log\left(\frac{\gamma_{H_2TO_{aq}^+}}{\gamma_{H_3O_{aq}^+}}\right)_{exp}$
$H_2T^{18}O_{aq}^+$	$H_2O_l + HT^{18}O_{aq} = H_2T^{18}O_{aq}^+ + OH_{aq}^-$ $\log K_{H_2T^{18}O_{aq}^+} = \log K_w + \log(1.5) + \log\left(\alpha_{H_3O_{aq}^+ - H_2O_l}^{18O}\right) + \log\left(\alpha_{H_3O_{aq}^+ - H_2O_l}^T\right) + \log\left(\frac{\gamma_{H_2T^{18}O_{aq}^+}}{\gamma_{H_3O_{aq}^+}}\right)_{exp}$
$HDTO_{aq}^+$	$H_2O_l + DTO_{aq} = HDTO_{aq}^+ + OH_{aq}^-$ $\log K_{HDTO_{aq}^+} = \log K_w + \log(0.75) + \log\left(\alpha_{H_3O_{aq}^+ - H_2O_l}^D\right) + \log\left(\alpha_{H_3O_{aq}^+ - H_2O_l}^T\right) + \log\left(\frac{\gamma_{HDTO_{aq}^+}}{\gamma_{H_3O_{aq}^+}}\right)_{exp}$

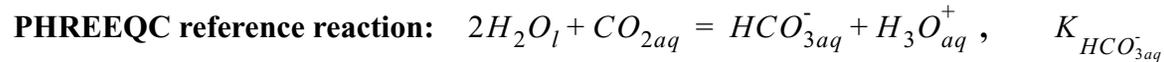
**Table 2.** Reactions and equilibrium constants—continued

<u>Species</u>	<u>Reaction and log of the equilibrium constant</u>	<u>Species</u>
	<b>CO<sub>2</sub>(gas) — CO<sub>2</sub>(aqueous)</b>	
	<b>PHREEQC reference reaction:</b> $CO_{2g} = CO_{2aq}$ , $K_{CO_{2g}}^H$	
$CO^{18}O_g$	$CO^{18}O_g = CO^{18}O_{aq}$	
	$\log K_{CO^{18}O_g}^H = \log K_{CO_{2g}}^H + \log(\alpha_{CO_{2aq}-CO_{2g}}^{18O}) + \log\left(\frac{\gamma_{CO^{18}O_{aq}} \lambda_{CO_{2g}}}{\gamma_{CO_{2aq}} \lambda_{CO^{18}O_g}}\right)_{exp}$	
$C^{18}O_{2g}$	$C^{18}O_{2g} = C^{18}O_{2aq}$	
	$\log K_{C^{18}O_{2g}}^H = \log K_{CO_{2g}}^H + 2\log(\alpha_{CO_{2aq}-CO_{2g}}^{18O}) + \log\left(\frac{\gamma_{C^{18}O_{2aq}} \lambda_{CO_{2g}}}{\gamma_{CO_{2aq}} \lambda_{C^{18}O_{2g}}}\right)_{exp}$	
$^{13}CO_{2g}$	$^{13}CO_{2g} = ^{13}CO_{2aq}$	
	$\log K_{^{13}CO_{2g}}^H = \log K_{CO_{2g}}^H + \log(\alpha_{CO_{2aq}-CO_{2g}}^{13C}) + \log\left(\frac{\gamma_{^{13}CO_{2aq}} \lambda_{CO_{2g}}}{\gamma_{CO_{2aq}} \lambda_{^{13}CO_{2g}}}\right)_{exp}$	
$^{13}CO^{18}O_g$	$^{13}CO^{18}O_g = ^{13}CO^{18}O_{aq}$	
	$\log K_{^{13}CO^{18}O_g}^H = \log K_{CO_{2g}}^H + \log(\alpha_{CO_{2aq}-CO_{2g}}^{13C}) + \log(\alpha_{CO_{2aq}-CO_{2g}}^{18O}) + \log\left(\frac{\gamma_{^{13}CO^{18}O_{aq}} \lambda_{CO_{2g}}}{\gamma_{CO_{2aq}} \lambda_{^{13}CO^{18}O_g}}\right)_{exp}$	
$^{13}C^{18}O_{2g}$	$^{13}C^{18}O_{2g} = ^{13}C^{18}O_{2aq}$	
	$\log K_{^{13}C^{18}O_{2g}}^H = \log K_{CO_{2g}}^H + \log(\alpha_{CO_{2aq}-CO_{2g}}^{13C}) + 2\log(\alpha_{CO_{2aq}-CO_{2g}}^{18O}) + \log\left(\frac{\gamma_{^{13}C^{18}O_{2aq}} \lambda_{CO_{2g}}}{\gamma_{CO_{2aq}} \lambda_{^{13}C^{18}O_{2g}}}\right)_{exp}$	

62 **Table 2.** Reactions and equilibrium constants—continued

<b>Species</b>	<b>Reaction and log of the equilibrium constant</b>
$^{14}\text{CO}_{2g}$	$^{14}\text{CO}_{2g} = ^{14}\text{CO}_{2aq}$ $\log K_{^{14}\text{CO}_{2g}}^H = \log K_{\text{CO}_{2g}}^H + \log(\alpha_{\text{CO}_{2aq}-\text{CO}_{2g}}^{^{14}\text{C}}) + \log\left(\frac{\gamma_{^{14}\text{CO}_{2aq}} \lambda_{\text{CO}_{2g}}}{\gamma_{\text{CO}_{2aq}} \lambda_{^{14}\text{CO}_{2g}}}\right)_{exp}$
$^{14}\text{CO}^{18}\text{O}_g$	$^{14}\text{CO}^{18}\text{O}_g = ^{14}\text{CO}^{18}\text{O}_{aq}$ $\log K_{^{14}\text{CO}^{18}\text{O}_g}^H = \log K_{\text{CO}_{2g}}^H + \log(\alpha_{\text{CO}_{2aq}-\text{CO}_{2g}}^{^{14}\text{C}}) + \log(\alpha_{\text{CO}_{2aq}-\text{CO}_{2g}}^{^{18}\text{O}}) + \log\left(\frac{\gamma_{^{14}\text{CO}^{18}\text{O}_{aq}} \lambda_{\text{CO}_{2g}}}{\gamma_{\text{CO}_{2aq}} \lambda_{^{14}\text{CO}^{18}\text{O}_g}}\right)_{exp}$
$^{14}\text{C}^{18}\text{O}_{2g}$	$^{14}\text{C}^{18}\text{O}_{2g} = ^{14}\text{C}^{18}\text{O}_{2aq}$ $\log K_{^{14}\text{C}^{18}\text{O}_{2g}}^H = \log K_{\text{CO}_{2g}}^H + \log(\alpha_{\text{CO}_{2aq}-\text{CO}_{2g}}^{^{14}\text{C}}) + 2\log(\alpha_{\text{CO}_{2aq}-\text{CO}_{2g}}^{^{18}\text{O}}) + \log\left(\frac{\gamma_{^{14}\text{C}^{18}\text{O}_{2aq}} \lambda_{\text{CO}_{2g}}}{\gamma_{\text{CO}_{2aq}} \lambda_{^{14}\text{C}^{18}\text{O}_{2g}}}\right)_{exp}$

**CO<sub>2</sub>(aqueous) — HCO<sub>3</sub><sup>-</sup>(aqueous)**

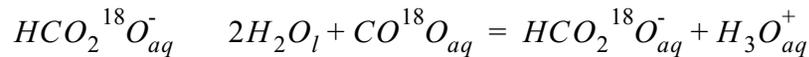


In the bicarbonate equations,

$\log(QQ1)$  = calculated parameter for  $\log K_{\text{HCO}_2^{18}\text{O}_{aq}^-}$ ; see text for numerical procedures.

$\log(QQ2)$  = calculated parameter for  $\log K_{\text{HCO}^{18}\text{O}_{2aq}^-}$ ; see text for numerical procedures.

$\log(QQ3)$  = calculated parameter for  $\log K_{\text{HC}^{18}\text{O}_{3aq}^-}$ ; see text for numerical procedures.



$$\log K_{\text{HCO}_2^{18}\text{O}_{aq}^-} = \log K_{\text{HCO}_{3aq}^-} + \log(1.5) + \log(\alpha_{\text{HCO}_{3aq}^- - \text{CO}_{2aq}}^{^{18}\text{O}}) + \log(QQ1) + \log\left(\frac{\gamma_{\text{HCO}_2^{18}\text{O}_{aq}^-} \gamma_{\text{CO}_{2aq}}}{\gamma_{\text{HCO}_{3aq}^-} \gamma_{\text{CO}^{18}\text{O}_{aq}}}\right)_{exp}$$

**Table 2.** Reactions and equilibrium constants—continued

<b>Species</b>	<b>Reaction and log of the equilibrium constant</b>
$HCO^{18}O_{2aq}^-$	$2H_2O_l + C^{18}O_{2aq} = HCO^{18}O_{2aq}^- + H_3O_{aq}^+$ $\log K_{HCO^{18}O_{2aq}^-} = \log K_{HCO_{3aq}^-} + \log(3) + 2\log\left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O}\right) + \log(QQ2) + \log\left(\frac{\gamma_{HCO^{18}O_{2aq}^-} \gamma_{CO_{2aq}}}{\gamma_{HCO_{3aq}^-} \gamma_{C^{18}O_{2aq}}}\right)_{exp}$
$HC^{18}O_{3aq}^-$	$2H_2O_l + 3CO^{18}O_{aq} = HC^{18}O_{3aq}^- + H_3O_{aq}^+ + 2CO_{2aq}$ $\log K_{HC^{18}O_{3aq}^-} = \log K_{HCO_{3aq}^-} - 3\log(2) + 3\log\left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O}\right) + \log(QQ3) + \log\left(\frac{\gamma_{HC^{18}O_{3aq}^-} \gamma_{CO_{2aq}}^3}{\gamma_{HCO_{3aq}^-} \gamma_{CO^{18}O_{aq}}^3}\right)_{exp}$
$H^{13}CO_{3aq}^-$	$2H_2O_l + {}^{13}CO_{2aq} = H^{13}CO_{3aq}^- + H_3O_{aq}^+$ $\log K_{H^{13}CO_{3aq}^-} = \log K_{HCO_{3aq}^-} + \log\left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{13C}\right) + \log\left(\frac{\gamma_{H^{13}CO_{3aq}^-} \gamma_{CO_{2aq}}}{\gamma_{HCO_{3aq}^-} \gamma_{{}^{13}CO_{2aq}}}\right)_{exp}$
$H^{13}CO_2^{18}O_{aq}^-$	$2H_2O_l + {}^{13}CO^{18}O_{aq} = H^{13}CO_2^{18}O_{aq}^- + H_3O_{aq}^+$ $\log K_{H^{13}CO_2^{18}O_{aq}^-} = \log K_{HCO_{3aq}^-} + \log(1.5) + \log\left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{13C}\right) + \log\left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O}\right) + \log(QQ1) + \log\left(\frac{\gamma_{H^{13}CO_2^{18}O_{aq}^-} \gamma_{CO_{2aq}}}{\gamma_{HCO_{3aq}^-} \gamma_{{}^{13}CO^{18}O_{aq}}}\right)_{exp}$
$H^{13}CO^{18}O_{2aq}^-$	$2H_2O_l + {}^{13}C^{18}O_{2aq} = H^{13}CO^{18}O_{2aq}^- + H_3O_{aq}^+$ $\log K_{H^{13}CO^{18}O_{2aq}^-} = \log K_{HCO_{3aq}^-} + \log(3) + \log\left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{13C}\right) + 2\log\left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O}\right) + \log(QQ2) + \log\left(\frac{\gamma_{H^{13}CO^{18}O_{2aq}^-} \gamma_{CO_{2aq}}}{\gamma_{HCO_{3aq}^-} \gamma_{{}^{13}C^{18}O_{2aq}}}\right)_{exp}$

64 **Table 2.** Reactions and equilibrium constants—continued

<b>Species</b>	<b>Reaction and log of the equilibrium constant</b>
$H^{13}C^{18}O_{3aq}^-$	$2H_2O_l + 3CO^{18}O_{aq} + {}^{13}CO_{2aq} = H^{13}C^{18}O_{3aq}^- + H_3O_{aq}^+ + 3CO_{2aq}$ $\log K_{H^{13}C^{18}O_{3aq}^-} = \log K_{HCO_{3aq}^-} - 3\log(2) + \log\left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{13C}\right) + 3\log\left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O}\right) +$ $\log(QQ3) + \log\left(\frac{\gamma_{H^{13}C^{18}O_{3aq}^-} \gamma_{CO_{2aq}}^4}{\gamma_{HCO_{3aq}^-} \gamma_{CO^{18}O_{aq}}^3 \gamma_{13CO_{2aq}}}\right)_{exp}$
$H^{14}CO_{3aq}^-$	$2H_2O_l + {}^{14}CO_{2aq} = H^{14}CO_{3aq}^- + H_3O_{aq}^+$ $\log K_{H^{14}CO_{3aq}^-} = \log K_{HCO_{3aq}^-} + \log\left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{14C}\right) + \log\left(\frac{\gamma_{H^{14}CO_{3aq}^-} \gamma_{CO_{2aq}}}{\gamma_{HCO_{3aq}^-} \gamma_{14CO_{2aq}}}\right)_{exp}$
$H^{14}CO_2^{18}O_{aq}^-$	$2H_2O_l + {}^{14}CO^{18}O_{aq} = H^{14}CO_2^{18}O_{aq}^- + H_3O_{aq}^+$ $\log K_{H^{14}CO_2^{18}O_{aq}^-} = \log K_{HCO_{3aq}^-} + \log(1.5) + \log\left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{14C}\right) + \log\left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O}\right) +$ $\log(QQ1) + \log\left(\frac{\gamma_{H^{14}CO_2^{18}O_{aq}^-} \gamma_{CO_{2aq}}}{\gamma_{HCO_{3aq}^-} \gamma_{14CO^{18}O_{aq}}}\right)_{exp}$
$H^{14}CO^{18}O_{2aq}^-$	$2H_2O_l + {}^{14}C^{18}O_{2aq} = H^{14}CO^{18}O_{2aq}^- + H_3O_{aq}^+$ $\log K_{H^{14}CO^{18}O_{2aq}^-} = \log K_{HCO_{3aq}^-} + \log(3) + \log\left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{14C}\right) + 2\log\left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O}\right) +$ $\log(QQ2) + \log\left(\frac{\gamma_{H^{14}CO^{18}O_{2aq}^-} \gamma_{CO_{2aq}}}{\gamma_{HCO_{3aq}^-} \gamma_{14C^{18}O_{2aq}}}\right)_{exp}$

**Table 2.** Reactions and equilibrium constants—continued

<b>Species</b>	<b>Reaction and log of the equilibrium constant</b>
$H^{14}C^{18}O_{3aq}^-$	$2H_2O_l + 3CO^{18}O_{aq} + {}^{14}CO_{2aq} = H^{14}C^{18}O_{3aq}^- + H_3O_{aq}^+ + 3CO_{2aq}$ $\log K_{H^{14}C^{18}O_{3aq}^-} = \log K_{HCO_{3aq}^-} - 3\log(2) + \log\left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{14C}\right) + 3\log\left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O}\right) +$ $\log(QQ3) + \log\left(\frac{\gamma_{H^{14}C^{18}O_{3aq}^-} \gamma_{CO_{2aq}}^4}{\gamma_{HCO_{3aq}^-}^3 \gamma_{CO^{18}O_{aq}} \gamma_{CO_{2aq}}^{14C}}\right)_{exp}$
$DCO_{3aq}^-$	$H_2O_l + HDO_{aq} + CO_{2aq} = DCO_{3aq}^- + H_3O_{aq}^+$ $\log K_{DCO_{3aq}^-} = \log K_{HCO_{3aq}^-} - \log(2) + \log\left(\alpha_{HCO_{3aq}^- - H_2O_l}^D\right) + \log\left(\frac{\gamma_{DCO_{3aq}^-}}{\gamma_{HCO_{3aq}^-}}\right)_{exp}$
$DCO_2^{18}O_{aq}^-$	$H_2O_l + HDO_{aq} + CO^{18}O_{aq} = DCO_2^{18}O_{aq}^- + H_3O_{aq}^+$ $\log K_{DCO_2^{18}O_{aq}^-} = \log K_{HCO_{3aq}^-} + \log(0.75) + \log\left(\alpha_{HCO_{3aq}^- - H_2O_l}^D\right) + \log\left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O}\right) +$ $\log(QQ1) + \log\left(\frac{\gamma_{DCO_2^{18}O_{aq}^-} \gamma_{CO_{2aq}}}{\gamma_{HCO_{3aq}^-} \gamma_{CO^{18}O_{aq}}}\right)_{exp}$
$DCO^{18}O_{2aq}^-$	$H_2O_l + HDO_{aq} + C^{18}O_{2aq} = DCO^{18}O_{2aq}^- + H_3O_{aq}^+$ $\log K_{DCO^{18}O_{2aq}^-} = \log K_{HCO_{3aq}^-} + \log(1.5) + \log\left(\alpha_{HCO_{3aq}^- - H_2O_l}^D\right) + 2\log\left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O}\right) +$ $\log(QQ2) + \log\left(\frac{\gamma_{DCO^{18}O_{2aq}^-} \gamma_{CO_{2aq}}}{\gamma_{HCO_{3aq}^-} \gamma_{C^{18}O_{2aq}}}\right)_{exp}$

66 **Table 2.** Reactions and equilibrium constants—continued

<u>Species</u>	<u>Reaction and log of the equilibrium constant</u>
$DC^{18}O_{3aq}^-$	$H_2O_l + HDO_{aq} + 3CO^{18}O_{aq} = DC^{18}O_{3aq}^- + H_3O_{aq}^+ + 2CO_{2aq}$ $\log K_{DC^{18}O_{3aq}^-} = \log K_{HCO_{3aq}^-} - 4\log(2) + \log(\alpha_{HCO_{3aq}^- - H_2O_l}^D) + 3\log(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O}) +$ $\log(QQ3) + \log\left(\frac{\gamma_{DC^{18}O_{3aq}^-} \gamma_{CO_{2aq}}^3}{\gamma_{HCO_{3aq}^-} \gamma_{CO^{18}O_{aq}}^3}\right)_{exp}$
$D^{13}CO_{3aq}^-$	$H_2O_l + HDO_{aq} + {}^{13}CO_{2aq} = D^{13}CO_{3aq}^- + H_3O_{aq}^+$ $\log K_{D^{13}CO_{3aq}^-} = \log K_{HCO_{3aq}^-} - \log(2) + \log(\alpha_{HCO_{3aq}^- - H_2O_l}^D) + \log(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{13C}) + \log\left(\frac{\gamma_{D^{13}CO_{3aq}^-} \gamma_{CO_{2aq}}}{\gamma_{HCO_{3aq}^-} \gamma_{CO_{2aq}}^{13C}}\right)_{exp}$
$D^{13}CO_2^{18}O_{aq}^-$	$H_2O_l + HDO_{aq} + {}^{13}CO^{18}O_{aq} = D^{13}CO_2^{18}O_{aq}^- + H_3O_{aq}^+$ $\log K_{D^{13}CO_2^{18}O_{aq}^-} = \log K_{HCO_{3aq}^-} + \log(0.75) + \log(\alpha_{HCO_{3aq}^- - H_2O_l}^D) + \log(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{13C}) +$ $\log(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O}) + \log(QQ1) + \log\left(\frac{\gamma_{D^{13}CO_2^{18}O_{aq}^-} \gamma_{CO_{2aq}}}{\gamma_{HCO_{3aq}^-} \gamma_{CO^{18}O_{aq}}}\right)_{exp}$
$D^{13}CO^{18}O_{2aq}^-$	$H_2O_l + HDO_{aq} + {}^{13}C^{18}O_{2aq} = D^{13}CO^{18}O_{2aq}^- + H_3O_{aq}^+$ $\log K_{D^{13}CO^{18}O_{2aq}^-} = \log K_{HCO_{3aq}^-} + \log(1.5) + \log(\alpha_{HCO_{3aq}^- - H_2O_l}^D) + \log(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{13C}) +$ $2\log(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O}) + \log(QQ2) + \log\left(\frac{\gamma_{D^{13}CO^{18}O_{2aq}^-} \gamma_{CO_{2aq}}}{\gamma_{HCO_{3aq}^-} \gamma_{CO^{18}O_{2aq}}}\right)_{exp}$

**Table 2.** Reactions and equilibrium constants—continued

<u>Species</u>	<u>Reaction and log of the equilibrium constant</u>
$D^{13}C^{18}O_{3aq}^-$	$H_2O_l + HDO_{aq} + 3CO^{18}O_{aq} + {}^{13}CO_{2aq} = D^{13}C^{18}O_{3aq}^- + H_3O_{aq}^+ + 3CO_{2aq}$ $\log K_{D^{13}C^{18}O_{3aq}^-} = \log K_{HCO_{3aq}^-} - 4\log(2) + \log(\alpha_{HCO_{3aq}^- - H_2O_l}^D) + \log(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{13C}) +$ $3\log(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O}) + \log(QQ3) + \log\left(\frac{\gamma_{D^{13}C^{18}O_{3aq}^-} \gamma_{CO_{2aq}}^4}{\gamma_{HCO_{3aq}^-} \gamma_{CO^{18}O_{aq}}^3 \gamma_{13CO_{2aq}}^{13}}\right)_{exp}$
$D^{14}CO_{3aq}^-$	$H_2O_l + HDO_{aq} + {}^{14}CO_{2aq} = D^{14}CO_{3aq}^- + H_3O_{aq}^+$ $\log K_{D^{14}CO_{3aq}^-} = \log K_{HCO_{3aq}^-} - \log(2) + \log(\alpha_{HCO_{3aq}^- - H_2O_l}^D) + \log(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{14C}) + \log\left(\frac{\gamma_{D^{14}CO_{3aq}^-} \gamma_{CO_{2aq}}}{\gamma_{HCO_{3aq}^-} \gamma_{14CO_{2aq}}}\right)_{exp}$
$D^{14}CO_2^{18}O_{aq}^-$	$H_2O_l + HDO_{aq} + {}^{14}CO^{18}O_{aq} = D^{14}CO_2^{18}O_{aq}^- + H_3O_{aq}^+$ $\log K_{D^{14}CO_2^{18}O_{aq}^-} = \log K_{HCO_{3aq}^-} + \log(0.75) + \log(\alpha_{HCO_{3aq}^- - H_2O_l}^D) + \log(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{14C}) +$ $\log(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O}) + \log(QQ1) + \log\left(\frac{\gamma_{D^{14}CO_2^{18}O_{aq}^-} \gamma_{CO_{2aq}}}{\gamma_{HCO_{3aq}^-} \gamma_{14CO^{18}O_{aq}}}\right)_{exp}$
$D^{14}CO^{18}O_{2aq}^-$	$H_2O_l + HDO_{aq} + {}^{14}C^{18}O_{2aq} = D^{14}CO^{18}O_{2aq}^- + H_3O_{aq}^+$ $\log K_{D^{14}CO^{18}O_{2aq}^-} = \log K_{HCO_{3aq}^-} + \log(1.5) + \log(\alpha_{HCO_{3aq}^- - H_2O_l}^D) + \log(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{14C}) +$ $2\log(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O}) + \log(QQ2) + \log\left(\frac{\gamma_{D^{14}CO^{18}O_{2aq}^-} \gamma_{CO_{2aq}}}{\gamma_{HCO_{3aq}^-} \gamma_{14C^{18}O_{2aq}}}\right)_{exp}$

68 **Table 2.** Reactions and equilibrium constants—continued

<b>Species</b>	<b>Reaction and log of the equilibrium constant</b>
$D^{14}C^{18}O_{3aq}^-$	$H_2O_l + HDO_{aq} + 3CO^{18}O_{aq} + {}^{14}CO_{2aq} = D^{14}C^{18}O_{3aq}^- + H_3O_{aq}^+ + 3CO_{2aq}$ $\log K_{D^{14}C^{18}O_{3aq}^-} = \log K_{HCO_{3aq}^-} - 4\log 2 + \log(\alpha_{HCO_{3aq}^- - H_2O_l}^D) + \log(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{14C}) +$ $3\log(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O}) + \log(QQ3) + \log\left(\frac{\gamma_{D^{14}C^{18}O_{3aq}^-} \gamma_{CO_{2aq}}^4}{\gamma_{HCO_{3aq}^-}^3 \gamma_{CO^{18}O_{aq}} \gamma_{CO_{2aq}}^{14C}}\right)_{exp}$
$TCO_{3aq}^-$	$H_2O_l + HTO_{aq} + CO_{2aq} = TCO_{3aq}^- + H_3O_{aq}^+$ $\log K_{TCO_{3aq}^-} = \log K_{HCO_{3aq}^-} - \log(2) + \log(\alpha_{HCO_{3aq}^- - H_2O_l}^T) + \log\left(\frac{\gamma_{TCO_{3aq}^-}}{\gamma_{HCO_{3aq}^-}}\right)_{exp}$
$TCO_2^{18}O_{aq}^-$	$H_2O_l + HTO_{aq} + CO^{18}O_{aq} = TCO_2^{18}O_{aq}^- + H_3O_{aq}^+$ $\log K_{TCO_2^{18}O_{aq}^-} = \log K_{HCO_{3aq}^-} + \log(0.75) + \log(\alpha_{HCO_{3aq}^- - H_2O_l}^T) + \log(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O}) +$ $\log(QQ1) + \log\left(\frac{\gamma_{TCO_2^{18}O_{aq}^-} \gamma_{CO_{2aq}}}{\gamma_{HCO_{3aq}^-} \gamma_{CO^{18}O_{aq}}}\right)_{exp}$
$T^{13}CO_{3aq}^-$	$H_2O_l + HTO_{aq} + {}^{13}CO_{2aq} = T^{13}CO_{3aq}^- + H_3O_{aq}^+$ $\log K_{T^{13}CO_{3aq}^-} = \log K_{HCO_{3aq}^-} - \log(2) + \log(\alpha_{HCO_{3aq}^- - H_2O_l}^T) + \log(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{13C}) + \log\left(\frac{\gamma_{T^{13}CO_{3aq}^-} \gamma_{CO_{2aq}}}{\gamma_{HCO_{3aq}^-} \gamma_{CO_{2aq}}^{13C}}\right)_{exp}$

**Table 2.** Reactions and equilibrium constants—continued

<u>Species</u>	<u>Reaction and log of the equilibrium constant</u>
	<b>CO<sub>2</sub>(aqueous) — CO<sub>3</sub><sup>-2</sup>(aqueous)</b>
	<b>PHREEQC reference reaction:</b> $3H_2O_l + CO_{2aq} = CO_{3aq}^{-2} + 2H_3O_{aq}^+$ , $K_{CO_{3aq}^{-2}}$
$CO_2^{18}O_{aq}^{-2}$	$3H_2O_l + CO^{18}O_{aq} = CO_2^{18}O_{aq}^{-2} + 2H_3O_{aq}^+$ $\log K_{CO_2^{18}O_{aq}^{-2}} = \log K_{CO_{3aq}^{-2}} + \log(1.5) + \log\left(\alpha_{CO_{3aq}^{-2} - CO_{2aq}}^{18}O\right) + \log\left(\frac{\gamma_{CO_2^{18}O_{aq}^{-2}} \gamma_{CO_{2aq}}}{\gamma_{CO_{3aq}^{-2}} \gamma_{CO^{18}O_{aq}}}\right)_{exp}$
$CO^{18}O_{2aq}^{-2}$	$3H_2O_l + C^{18}O_{2aq} = CO^{18}O_{2aq}^{-2} + 2H_3O_{aq}^+$ $\log K_{CO^{18}O_{2aq}^{-2}} = \log K_{CO_{3aq}^{-2}} + \log(3) + 2\log\left(\alpha_{CO_{3aq}^{-2} - CO_{2aq}}^{18}O\right) + \log\left(\frac{\gamma_{CO^{18}O_{2aq}^{-2}} \gamma_{CO_{2aq}}}{\gamma_{CO_{3aq}^{-2}} \gamma_{C^{18}O_{2aq}}}\right)_{exp}$
$C^{18}O_{3aq}^{-2}$	$3H_2O_l + 3CO^{18}O_{aq} = C^{18}O_{3aq}^{-2} + 2H_3O_{aq}^+ + 2CO_{2aq}$ $\log K_{C^{18}O_{3aq}^{-2}} = \log K_{CO_{3aq}^{-2}} - 3\log(2) + 3\log\left(\alpha_{CO_{3aq}^{-2} - CO_{2aq}}^{18}O\right) + \log\left(\frac{\gamma_{C^{18}O_{3aq}^{-2}} \gamma_{CO_{2aq}}^3}{\gamma_{CO_{3aq}^{-2}} \gamma_{CO^{18}O_{aq}}^3}\right)_{exp}$
$^{13}CO_{3aq}^{-2}$	$3H_2O_l + ^{13}CO_{2aq} = ^{13}CO_{3aq}^{-2} + 2H_3O_{aq}^+$ $\log K_{^{13}CO_{3aq}^{-2}} = \log K_{CO_{3aq}^{-2}} + \log\left(\alpha_{CO_{3aq}^{-2} - CO_{2aq}}^{13}C\right) + \log\left(\frac{\gamma_{^{13}CO_{3aq}^{-2}} \gamma_{CO_{2aq}}}{\gamma_{CO_{3aq}^{-2}} \gamma_{^{13}CO_{2aq}}}\right)_{exp}$
$^{13}CO_2^{18}O_{aq}^{-2}$	$3H_2O_l + ^{13}CO^{18}O_{aq} = ^{13}CO_2^{18}O_{aq}^{-2} + 2H_3O_{aq}^+$ $\log K_{^{13}CO_2^{18}O_{aq}^{-2}} = \log K_{CO_{3aq}^{-2}} + \log(1.5) + \log\left(\alpha_{CO_{3aq}^{-2} - CO_{2aq}}^{13}C\right) + \log\left(\alpha_{CO_{3aq}^{-2} - CO_{2aq}}^{18}O\right) + \log\left(\frac{\gamma_{^{13}CO_2^{18}O_{aq}^{-2}} \gamma_{CO_{2aq}}}{\gamma_{CO_{3aq}^{-2}} \gamma_{^{13}CO^{18}O_{aq}}}\right)_{exp}$

70 **Table 2.** Reactions and equilibrium constants—continued

<b>Species</b>	<b>Reaction and log of the equilibrium constant</b>
$^{13}\text{CO}^{18}\text{O}_{2aq}^{-2}$	$3\text{H}_2\text{O}_l + ^{13}\text{C}^{18}\text{O}_{2aq} = ^{13}\text{CO}^{18}\text{O}_{2aq}^{-2} + 2\text{H}_3\text{O}_{aq}^+$ $\log K_{^{13}\text{CO}^{18}\text{O}_{2aq}^{-2}} = \log K_{\text{CO}_{3aq}^{-2}} + \log(3) + \log\left(\alpha_{\text{CO}_{3aq}^{-2}}^{^{13}\text{C}} - \text{CO}_{2aq}\right) + 2\log\left(\alpha_{\text{CO}_{3aq}^{-2}}^{^{18}\text{O}} - \text{CO}_{2aq}\right) + \log\left(\frac{\gamma_{^{13}\text{CO}^{18}\text{O}_{2aq}^{-2}} \gamma_{\text{CO}_{2aq}}}{\gamma_{\text{CO}_{3aq}^{-2}} \gamma_{^{13}\text{C}^{18}\text{O}_{2aq}}}\right)_{exp}$
$^{13}\text{C}^{18}\text{O}_{3aq}^{-2}$	$3\text{H}_2\text{O}_l + 3\text{CO}^{18}\text{O}_{aq} + ^{13}\text{CO}_{2aq} = ^{13}\text{C}^{18}\text{O}_{3aq}^{-2} + 2\text{H}_3\text{O}_{aq}^+ + 3\text{CO}_{2aq}$ $\log K_{^{13}\text{C}^{18}\text{O}_{3aq}^{-2}} = \log K_{\text{CO}_{3aq}^{-2}} - 3\log(2) + \log\left(\alpha_{\text{CO}_{3aq}^{-2}}^{^{13}\text{C}} - \text{CO}_{2aq}\right) + 3\log\left(\alpha_{\text{CO}_{3aq}^{-2}}^{^{18}\text{O}} - \text{CO}_{2aq}\right) + \log\left(\frac{\gamma_{^{13}\text{C}^{18}\text{O}_{3aq}^{-2}} \gamma_{\text{CO}_{2aq}}^4}{\gamma_{\text{CO}_{3aq}^{-2}} \gamma_{\text{CO}^{18}\text{O}_{aq}}^3 \gamma_{^{13}\text{CO}_{2aq}}}\right)_{exp}$
$^{14}\text{CO}_{3aq}^{-2}$	$3\text{H}_2\text{O}_l + ^{14}\text{CO}_{2aq} = ^{14}\text{CO}_{3aq}^{-2} + 2\text{H}_3\text{O}_{aq}^+$ $\log K_{^{14}\text{CO}_{3aq}^{-2}} = \log K_{\text{CO}_{3aq}^{-2}} + \log\left(\alpha_{\text{CO}_{3aq}^{-2}}^{^{14}\text{C}} - \text{CO}_{2aq}\right) + \log\left(\frac{\gamma_{^{14}\text{CO}_{3aq}^{-2}} \gamma_{\text{CO}_{2aq}}}{\gamma_{\text{CO}_{3aq}^{-2}} \gamma_{^{14}\text{CO}_{2aq}}}\right)_{exp}$
$^{14}\text{CO}_2^{18}\text{O}_{aq}^{-2}$	$3\text{H}_2\text{O}_l + ^{14}\text{CO}^{18}\text{O}_{aq} = ^{14}\text{CO}_2^{18}\text{O}_{aq}^{-2} + 2\text{H}_3\text{O}_{aq}^+$ $\log K_{^{14}\text{CO}_2^{18}\text{O}_{aq}^{-2}} = \log K_{\text{CO}_{3aq}^{-2}} + \log(1.5) + \log\left(\alpha_{\text{CO}_{3aq}^{-2}}^{^{14}\text{C}} - \text{CO}_{2aq}\right) + \log\left(\alpha_{\text{CO}_{3aq}^{-2}}^{^{18}\text{O}} - \text{CO}_{2aq}\right) + \log\left(\frac{\gamma_{^{14}\text{CO}_2^{18}\text{O}_{aq}^{-2}} \gamma_{\text{CO}_{2aq}}}{\gamma_{\text{CO}_{3aq}^{-2}} \gamma_{^{14}\text{CO}^{18}\text{O}_{aq}}}\right)_{exp}$
$^{14}\text{CO}^{18}\text{O}_{2aq}^{-2}$	$3\text{H}_2\text{O}_l + ^{14}\text{C}^{18}\text{O}_{2aq} = ^{14}\text{CO}^{18}\text{O}_{2aq}^{-2} + 2\text{H}_3\text{O}_{aq}^+$ $\log K_{^{14}\text{CO}^{18}\text{O}_{2aq}^{-2}} = \log K_{\text{CO}_{3aq}^{-2}} + \log(3) + \log\left(\alpha_{\text{CO}_{3aq}^{-2}}^{^{14}\text{C}} - \text{CO}_{2aq}\right) + 2\log\left(\alpha_{\text{CO}_{3aq}^{-2}}^{^{18}\text{O}} - \text{CO}_{2aq}\right) + \log\left(\frac{\gamma_{^{14}\text{CO}^{18}\text{O}_{2aq}^{-2}} \gamma_{\text{CO}_{2aq}}}{\gamma_{\text{CO}_{3aq}^{-2}} \gamma_{^{14}\text{C}^{18}\text{O}_{2aq}}}\right)_{exp}$

**Table 2.** Reactions and equilibrium constants—continued

<b>Species</b>	<b>Reaction and log of the equilibrium constant</b>
$^{14}\text{C}^{18}\text{O}_{3aq}^{-2}$	$3\text{H}_2\text{O}_l + 3\text{CO}^{18}\text{O}_{aq} + ^{14}\text{CO}_{2aq} = ^{14}\text{C}^{18}\text{O}_{3aq}^{-2} + 2\text{H}_3\text{O}_{aq}^+ + 3\text{CO}_{2aq}$ $\log K_{^{14}\text{C}^{18}\text{O}_{3aq}^{-2}} = \log K_{\text{CO}_{3aq}^{-2}} - 3\log(2) + \log\left(\alpha_{\text{CO}_{3aq}^{-2} - \text{CO}_{2aq}}^{^{14}\text{C}}\right) + 3\log\left(\alpha_{\text{CO}_{3aq}^{-2} - \text{CO}_{2aq}}^{^{18}\text{O}}\right) +$ $\log\left(\frac{\gamma_{^{14}\text{C}^{18}\text{O}_{3aq}^{-2}} \gamma_{\text{CO}_{2aq}}^4}{\gamma_{\text{CO}_{3aq}^{-2}} \gamma_{\text{CO}^{18}\text{O}_{aq}}^3 \gamma_{^{14}\text{CO}_{2aq}}}\right)_{exp}$
<b>Calcite — CO<sub>2</sub>(aqueous)</b>	
	<b>PHREEQC reference reaction:</b> $\text{CaCO}_{3s} + 2\text{H}_3\text{O}_{aq}^+ = \text{Ca}_{aq}^{+2} + 3\text{H}_2\text{O}_l + \text{CO}_{2aq}$ , $K_{\text{CaCO}_{3s}}$
$\text{CaCO}_2^{18}\text{O}_s$	$\text{CaCO}_2^{18}\text{O}_s + 2\text{H}_3\text{O}_{aq}^+ = \text{Ca}_{aq}^{+2} + 3\text{H}_2\text{O}_l + \text{CO}^{18}\text{O}_{aq}$ $\log K_{\text{CaCO}_2^{18}\text{O}_s} = \log K_{\text{CaCO}_{3s}} - \log(1.5) + \log(\alpha_{\text{CO}_{2aq} - \text{CaCO}_{3s}}^{^{18}\text{O}}) + \log\left(\frac{\lambda_{\text{CaCO}_{3s}} \gamma_{\text{CO}^{18}\text{O}_{aq}}}{\lambda_{\text{CaCO}_2^{18}\text{O}_s} \gamma_{\text{CO}_{2aq}}}\right)_{exp}$
$\text{CaCO}^{18}\text{O}_{2s}$	$\text{CaCO}^{18}\text{O}_{2s} + 2\text{H}_3\text{O}_{aq}^+ = \text{Ca}_{aq}^{+2} + 3\text{H}_2\text{O}_l + \text{C}^{18}\text{O}_{2aq}$ $\log K_{\text{CaCO}^{18}\text{O}_{2s}} = \log K_{\text{CaCO}_{3s}} - \log(3) + 2\log(\alpha_{\text{CO}_{2aq} - \text{CaCO}_{3s}}^{^{18}\text{O}}) + \log\left(\frac{\lambda_{\text{CaCO}_{3s}} \gamma_{\text{C}^{18}\text{O}_{2aq}}}{\lambda_{\text{CaCO}^{18}\text{O}_{2s}} \gamma_{\text{CO}_{2aq}}}\right)_{exp}$
$\text{CaC}^{18}\text{O}_{3s}$	$\text{CaC}^{18}\text{O}_{3s} + 2\text{CO}_{2aq} + 2\text{H}_3\text{O}_{aq}^+ = \text{Ca}_{aq}^{+2} + 3\text{H}_2\text{O}_l + 3\text{CO}^{18}\text{O}_{aq}$ $\log K_{\text{CaC}^{18}\text{O}_{3s}} = \log K_{\text{CaCO}_{3s}} + 3\log(2) + 3\log(\alpha_{\text{CO}_{2aq} - \text{CaCO}_{3s}}^{^{18}\text{O}}) + \log\left(\frac{\lambda_{\text{CaCO}_{3s}} \gamma_{\text{CO}^{18}\text{O}_{aq}}^3}{\lambda_{\text{CaC}^{18}\text{O}_{3s}} \gamma_{\text{CO}_{2aq}}^3}\right)_{exp}$

**Table 2.** Reactions and equilibrium constants—continued

<u>Species</u>	<u>Reaction and log of the equilibrium constant</u>
$Ca^{13}CO_{3s}$	$Ca^{13}CO_{3s} + 2H_3O_{aq}^+ = Ca_{aq}^{+2} + 3H_2O_l + {}^{13}CO_{2aq}$ $\log K_{Ca^{13}CO_{3s}} = \log K_{CaCO_{3s}} + \log(\alpha_{CO_{2aq}}^{13C} - CaCO_{3s}) + \log\left(\frac{\lambda_{CaCO_{3s}} \gamma_{CO_{2aq}}^{13C}}{\lambda_{Ca^{13}CO_{3s}} \gamma_{CO_{2aq}}}\right)_{exp}$
$Ca^{13}CO_2^{18}O_s$	$Ca^{13}CO_2^{18}O_s + 2H_3O_{aq}^+ = Ca_{aq}^{+2} + 3H_2O_l + {}^{13}CO^{18}O_{aq}$ $\log K_{Ca^{13}CO_2^{18}O_s} = \log K_{CaCO_{3s}} - \log(1.5) + \log(\alpha_{CO_{2aq}}^{13C} - CaCO_{3s}) + \log(\alpha_{CO_{2aq}}^{18O} - CaCO_{3s}) +$ $\log\left(\frac{\lambda_{CaCO_{3s}} \gamma_{CO^{18}O_{aq}}^{13C}}{\lambda_{Ca^{13}CO_2^{18}O_s} \gamma_{CO_{2aq}}}\right)_{exp}$
$Ca^{13}CO^{18}O_{2s}$	$Ca^{13}CO^{18}O_{2s} + 2H_3O_{aq}^+ = Ca_{aq}^{+2} + 3H_2O_l + {}^{13}C^{18}O_{2aq}$ $\log K_{Ca^{13}CO^{18}O_{2s}} = \log K_{CaCO_{3s}} - \log(3) + \log(\alpha_{CO_{2aq}}^{13C} - CaCO_{3s}) + 2\log(\alpha_{CO_{2aq}}^{18O} - CaCO_{3s}) +$ $\log\left(\frac{\lambda_{CaCO_{3s}} \gamma_{C^{18}O_{2aq}}^{13C}}{\lambda_{Ca^{13}CO^{18}O_{2s}} \gamma_{CO_{2aq}}}\right)_{exp}$
$Ca^{13}C^{18}O_{3s}$	$Ca^{13}C^{18}O_{3s} + 3CO_{2aq} + 2H_3O_{aq}^+ = Ca_{aq}^{+2} + 3H_2O_l + 3CO^{18}O_{aq} + {}^{13}CO_{2aq}$ $\log K_{Ca^{13}C^{18}O_{3s}} = \log K_{CaCO_{3s}} + 3\log(2) + \log(\alpha_{CO_{2aq}}^{13C} - CaCO_{3s}) + 3\log(\alpha_{CO_{2aq}}^{18O} - CaCO_{3s}) +$ $\log\left(\frac{\lambda_{CaCO_{3s}} \gamma_{CO_{2aq}}^{13C} \gamma_{CO^{18}O_{aq}}^3}{\lambda_{Ca^{13}C^{18}O_{3s}} \gamma_{CO_{2aq}}^4}\right)_{exp}$

**Table 2.** Reactions and equilibrium constants—continued

<b>Species</b>	<b>Reaction and log of the equilibrium constant</b>
$Ca^{14}CO_{3s}$	$Ca^{14}CO_{3s} + 2H_3O_{aq}^+ = Ca^{+2} + 3H_2O_l + {}^{14}CO_{2aq}$ $\log K_{Ca^{14}CO_{3s}} = \log K_{CaCO_{3s}} + \log(\alpha_{CO_{2aq}}^{14C} - CaCO_{3s}) + \log\left(\frac{\lambda_{CaCO_{3s}} \gamma_{CO_{2aq}}^{14C}}{\lambda_{Ca^{14}CO_{3s}} \gamma_{CO_{2aq}}}\right)_{exp}$
$Ca^{14}CO_2^{18}O_s$	$Ca^{14}CO_2^{18}O_s + 2H_3O_{aq}^+ = Ca_{aq}^{+2} + 3H_2O_l + {}^{14}CO^{18}O_{aq}$ $\log K_{Ca^{14}CO_2^{18}O_s} = \log K_{CaCO_{3s}} - \log(1.5) + \log(\alpha_{CO_{2aq}}^{14C} - CaCO_{3s}) + \log(\alpha_{CO_{2aq}}^{18O} - CaCO_{3s}) +$ $\log\left(\frac{\lambda_{CaCO_{3s}} \gamma_{CO^{18}O_{aq}}^{14C}}{\lambda_{Ca^{14}CO_2^{18}O_s} \gamma_{CO_{2aq}}}\right)_{exp}$
$Ca^{14}CO^{18}O_{2s}$	$Ca^{14}CO^{18}O_{2s} + 2H_3O_{aq}^+ = Ca_{aq}^{+2} + 3H_2O_l + {}^{14}C^{18}O_{2aq}$ $\log K_{Ca^{14}CO^{18}O_{2s}} = \log K_{CaCO_{3s}} - \log(3) + \log(\alpha_{CO_{2aq}}^{14C} - CaCO_{3s}) + 2\log(\alpha_{CO_{2aq}}^{18O} - CaCO_{3s}) +$ $\log\left(\frac{\lambda_{CaCO_{3s}} \gamma_{C^{18}O_{2aq}}^{14C}}{\lambda_{Ca^{14}CO^{18}O_{2s}} \gamma_{CO_{2aq}}}\right)_{exp}$
$Ca^{14}C^{18}O_{3s}$	$Ca^{14}C^{18}O_{3s} + 3CO_{2aq} + 2H_3O_{aq}^+ = Ca_{aq}^{+2} + 3H_2O_l + 3CO^{18}O_{aq} + {}^{14}CO_{2aq}$ $\log K_{Ca^{14}C^{18}O_{3s}} = \log K_{CaCO_{3s}} + 3\log(2) + \log(\alpha_{CO_{2aq}}^{14C} - CaCO_{3s}) + 3\log(\alpha_{CO_{2aq}}^{18O} - CaCO_{3s}) +$ $\log\left(\frac{\lambda_{CaCO_{3s}} \gamma_{CO_{2aq}}^{14C} \gamma_{CO^{18}O_{aq}}^3}{\lambda_{Ca^{14}C^{18}O_{3s}} \gamma_{CO_{2aq}}^4}\right)_{exp}$

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

$$10^3 \ln(\alpha) = A_1^\alpha + A_3^\alpha/T_K + A_5^\alpha/T_K^2$$

Fractionation factor	$A_1^\alpha$	$A_3^\alpha$	$A_5^\alpha$	$10^3 \ln(\alpha)$ at T( °C )	Range ( °C )	Source
$\alpha_{H_2O_l-H_2O_g}^D$ 1/	52.612	-76.248x10 <sup>3</sup>	24.844x10 <sup>6</sup>	76.4(25)	0 - 100	Majzoub (1971)
$\alpha_{H_2O_l-H_2O_g}^T$	105.224	-152.496x10 <sup>3</sup>	49.688x10 <sup>6</sup>	152.7(25)	0 - 100	$(\alpha_{H_2O_l-H_2O_g}^D)^2$
$\alpha_{H_2O_l-H_2O_g}^{18O}$ 2/	-2.0667	-0.4156x10 <sup>3</sup>	1.137x10 <sup>6</sup>	9.3(25)	0 - 100	Majzoub (1971)
$\alpha_{OH_{aq}^-H_2O_l}^D$ 3/	-1,435	0.0	0.0	-1435(13.5)	13.5	Heinzinger and Weston (1964a)
$\alpha_{OH_{aq}^-H_2O_l}^T$	-2,870	0.0	0.0	-2870(13.5)	13.5	$(\alpha_{OH_{aq}^-H_2O_l}^D)^2$
$\alpha_{OH_{aq}^-H_2O_l}^{18O}$ 4/	-37.777	0.0	0.0	-37.8(25)	25	Thornton (1962)
$\alpha_{H_3O_{aq}^+H_2O_l}^D$ 5/	40.82	0.0	0.0	40.8(13.5)	13.5	Heinzinger and Weston (1964b)
$\alpha_{H_3O_{aq}^+H_2O_l}^T$	81.64	0.0	0.0	81.6(13.5)	13.5	$(\alpha_{H_3O_{aq}^+H_2O_l}^D)^2$

**Table 3.** Fractionation factors used in the PHREEQC example calculation—continued

Fractionation factor	$A_1^\alpha$	$A_3^\alpha$	$A_5^\alpha$	$10^3 \ln(\alpha)$ at T( °C )	Range ( °C )	Source
$\alpha_{H_3O_{aq}^+-H_2O_l}^{18O}$ 6/	22.86	0.0	0.0	22.9(25)	25	Thornton (1962)
$\alpha_{CO_{2aq}-H_2O_l}^{18O}$ 7/	-21.9285	19.43596x10 <sup>3</sup>	-0.181115x10 <sup>6</sup>	41.2(25)	0 - 100	Bottinga (1968); Friedman and O'Neil (1977); Vogel and others (1970)
$\alpha_{CO_{2aq}-CO_{2g}}^{18O}$ 8/	-1.9585	1.44176x10 <sup>3</sup>	-0.160515x10 <sup>6</sup>	1.07(25)	0 - 60	Vogel and others (1970)
$\alpha_{CO_{2aq}-CO_{2g}}^{13C}$	-0.91	0.0	0.0063x10 <sup>6</sup>	-0.8(25)	0 - 100	Deines and others (1974)
$\alpha_{CO_{2aq}-CO_{2g}}^{14C}$	-1.82	0.0	0.0126x10 <sup>6</sup>	-1.7(25)	0 - 100	$(\alpha_{CO_{2aq}-CO_{2g}}^{13C})^2$
$\alpha_{HCO_{3aq}^- - H_2O_l}^D$	0.0	0.0	0.0	0.0(25)		Assumed
$\alpha_{HCO_{3aq}^- - H_2O_l}^T$	0.0	0.0	0.0	0.0(25)		$(\alpha_{HCO_{3aq}^- - H_2O_l}^D)^2$
$\alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O}$	0.0	0.0	0.0	0.0(25)		Assumed

**Table 3.** Fractionation factors used in the PHREEQC example calculation—continued

Fractionation factor	$A_1^\alpha$	$A_3^\alpha$	$A_5^\alpha$	$10^3 \ln(\alpha)$ at T( °C )	Range ( °C )	Source
$\alpha_{HCO_{3aq}^- - CO_{2aq}}^{13C}$ 9/	-3.63	0.0	$1.0927 \times 10^6$	8.7(25)	0 - 100	Deines and others (1974)
$\alpha_{HCO_{3aq}^- - CO_{2aq}}^{14C}$	-7.26	0.0	$2.1854 \times 10^6$	17.3(25)	0 - 100	$\left( \alpha_{HCO_{3aq}^- - CO_{2aq}}^{13C} \right)^2$
$\alpha_{CO_{3aq}^{2-} - CO_{2aq}}^{18O}$	0.0	0.0	0.0	0.0(25)		Assumed
$\alpha_{CO_{3aq}^{2-} - CO_{2aq}}^{13C}$ 10/	-2.49	0.0	$0.8637 \times 10^6$	7.2(25)	0 - 100	Deines and others (1974)
$\alpha_{CO_{3aq}^{2-} - CO_{2aq}}^{14C}$	-4.98	0.0	$1.7274 \times 10^6$	14.5(25)	0 - 100	$\left( \alpha_{CO_{3aq}^{2-} - CO_{2aq}}^{13C} \right)^2$
$\alpha_{CO_{2aq} - CaCO_{3s}}^{18O}$ 11/	-4.7383	$12.05276 \times 10^3$	$-1.963915 \times 10^6$	13.6(25)	0 - 100	Bottinga (1968); Vogel and others (1970)
$\alpha_{CO_{2aq} - CaCO_{3s}}^{13C}$	2.72	0.0	$-1.1877 \times 10^6$	-10.6(25)	0 - 100	Deines and others (1974)
$\alpha_{CO_{2aq} - CaCO_{3s}}^{14C}$	5.44	0.0	$-2.3754 \times 10^6$	-21.3(25)	0 - 100	$\left( \alpha_{CO_{2aq} - CaCO_{3s}}^{13C} \right)^2$

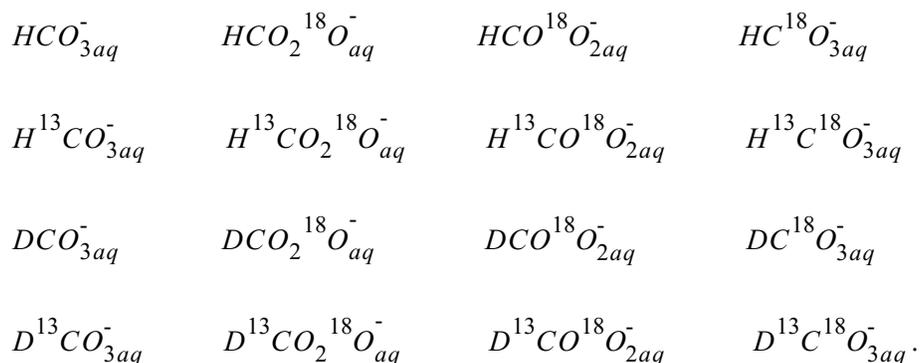
**Table 3.** Fractionation factors used in the PHREEQC example calculation—continued

- 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  $K = 1/4.2$  for the reaction  $HDO + OH^- = OD^- + H_2O$ .
- 4/ Calculated from  $K = 1/1.0385$  for the reaction  $H_2^{18}O + OH^- = {}^{18}OH^- + H_2O$ .
- 5/ Calculated from  $K = 1/0.96$  for the reaction  $HDO + H_3O^+ = H_2DO^+ + H_2O$ .
- 6/ Calculated from  $K = 1/0.9774$  for the reaction  $H_2^{18}O + H_3O^+ = H_3^{18}O^+ + H_2O$ .
- 7/ Calculated from  $\left(\alpha_{CO_{2g}-H_2O_l}^{18O}\right)\left(\alpha_{CO_{2aq}-CO_{2g}}^{18O}\right)$ . Coefficients for  $\alpha_{CO_{2g}-H_2O_l}^{18O}$  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 and others (1970), this table.
- 8/ Calculated from  $\left(\alpha_{CO_{2g}-CO_{2aq}}^{18O}\right)^{-1}$  with coefficients for  $\alpha_{CO_{2g}-CO_{2aq}}^{18O}$  obtained by regression of data from Vogel and others (1970) as presented in Friedman and O’Neil (1977).
- 9/ Calculated from  $\left(\alpha_{HCO_{3aq}^- - CO_{2g}}^{13C}\right) / \left(\alpha_{CO_{2aq} - CO_{2g}}^{13C}\right)$ ; all coefficients are from Deines and others (1974).
- 10/ Calculated from  $\left(\alpha_{CO_{3aq}^{2-} - CO_{2g}}^{13C}\right) / \left(\alpha_{CO_{2aq} - CO_{2g}}^{13C}\right)$ ; all coefficients are from Deines and others (1974).
- 11/ Calculated from  $\left(\alpha_{CO_{2g} - CaCO_{3s}}^{18O}\right)\left(\alpha_{CO_{2aq} - CO_{2g}}^{18O}\right)$ . Coefficients for  $\alpha_{CO_{2g} - CaCO_{3s}}^{18O}$  are from Bottinga (1968) recalculated using the  $CO_2 - H_2O$  fractionation factor of 1.0412 and presented in Friedman and O’Neil (1977); coefficients for  $\alpha_{CO_{2aq} - CO_{2g}}^{18O}$  are from Vogel and others (1970), this table.
- 12/ Calculated from  $\alpha_{CO_{2aq} - CO_{2g}}^{13C} / \alpha_{CaCO_{3s} - CO_{2g}}^{13C}$ ; all coefficients are from Deines and others (1974).

## APPENDIX 1. DERIVATION OF INDIVIDUAL ISOTOPE EQUILIBRIUM CONSTANTS FOR THE BICARBONATE ION

### Isotope Ratios for Bicarbonate

The isotopes that will be considered are H, D, C,  $^{13}\text{C}$ , O, and  $^{18}\text{O}$ . The symmetry numbers of all species are equal to 1. The species are



The intraspecies constants are:

$$K = \frac{n^3_{\text{HCO}_2^{18}\text{O}^-}}{n_{\text{HC}^{18}\text{O}_3^-} n^2_{\text{HCO}_3^-}} \qquad K = \frac{n^3_{\text{HCO}^{18}\text{O}_2^-}}{n^2_{\text{HC}^{18}\text{O}_3^-} n_{\text{HCO}_3^-}} \qquad (\text{A1.1})$$

$$K = \frac{n^3_{\text{H}^{13}\text{CO}_2^{18}\text{O}^-}}{n_{\text{H}^{13}\text{C}^{18}\text{O}_3^-} n^2_{\text{H}^{13}\text{CO}_3^-}} \qquad K = \frac{n^3_{\text{H}^{13}\text{CO}^{18}\text{O}_2^-}}{n^2_{\text{H}^{13}\text{C}^{18}\text{O}_3^-} n_{\text{H}^{13}\text{CO}_3^-}} \qquad (\text{A1.2})$$

$$K = \frac{n^3_{\text{DCO}_2^{18}\text{O}^-}}{n_{\text{DC}^{18}\text{O}_3^-} n^2_{\text{DCO}_3^-}} \qquad K = \frac{n^3_{\text{DCO}^{18}\text{O}_2^-}}{n^2_{\text{DC}^{18}\text{O}_3^-} n_{\text{DCO}_3^-}} \qquad (\text{A1.3})$$

$$K = \frac{n^3_{\text{D}^{13}\text{CO}_2^{18}\text{O}^-}}{n_{\text{D}^{13}\text{C}^{18}\text{O}_3^-} n^2_{\text{D}^{13}\text{CO}_3^-}} \qquad K = \frac{n^3_{\text{D}^{13}\text{CO}^{18}\text{O}_2^-}}{n^2_{\text{D}^{13}\text{C}^{18}\text{O}_3^-} n_{\text{D}^{13}\text{CO}_3^-}} \qquad (\text{A1.4})$$

The following derivations assume that the value of all intraspecies equilibrium constants are equal, but with the value of  $K$  unspecified.

The  $^{18}\text{O}/^{16}\text{O}$  ratio in terms of  $\text{HCO}_2^-$   $^{18}\text{O}_{aq}$

The oxygen-18 isotope ratio is:

$$R_{\text{HCO}_3^-}^{18\text{O}} = \frac{3n_{\text{HC}^{18}\text{O}_3^-} + 2n_{\text{HCO}^{18}\text{O}_2^-} + n_{\text{HCO}_2^{18}\text{O}_a^-} + 3n_{\text{H}^{13}\text{C}^{18}\text{O}_3^-} + 2n_{\text{H}^{13}\text{CO}^{18}\text{O}_2^-} + n_{\text{H}^{13}\text{CO}_2^{18}\text{O}_a^-} + 3n_{\text{DC}^{18}\text{O}_3^-} + 2n_{\text{DCO}^{18}\text{O}_2^-} + n_{\text{DCO}_2^{18}\text{O}_a^-} + 3n_{\text{D}^{13}\text{C}^{18}\text{O}_3^-} + 2n_{\text{D}^{13}\text{CO}^{18}\text{O}_2^-} + n_{\text{D}^{13}\text{CO}_2^{18}\text{O}_a^-}}{3n_{\text{HCO}_3^-} + 2n_{\text{HCO}_2^{18}\text{O}_a^-} + n_{\text{HCO}^{18}\text{O}_2^-} + 3n_{\text{H}^{13}\text{CO}_3^-} + 2n_{\text{H}^{13}\text{CO}_2^{18}\text{O}_a^-} + n_{\text{H}^{13}\text{CO}^{18}\text{O}_2^-} + 3n_{\text{DCO}_3^-} + 2n_{\text{DCO}_2^{18}\text{O}_a^-} + n_{\text{DCO}^{18}\text{O}_2^-} + 3n_{\text{D}^{13}\text{CO}_3^-} + 2n_{\text{D}^{13}\text{CO}_2^{18}\text{O}_a^-} + n_{\text{D}^{13}\text{CO}^{18}\text{O}_2^-}}. \quad (\text{A1.5})$$

Substitute from A1.1 - A1.4 to obtain terms containing one oxygen-18 atom:

$$R_{\text{HCO}_3^-}^{18\text{O}} = \frac{\text{num}(\text{HC}) + \text{num}(\text{H}^{13}\text{C}) + \text{num}(\text{DC}) + \text{num}(\text{D}^{13}\text{C})}{\text{denom}(\text{HC}) + \text{denom}(\text{H}^{13}\text{C}) + \text{denom}(\text{DC}) + \text{denom}(\text{D}^{13}\text{C})}, \text{ where} \quad (\text{A1.6})$$

$$\text{num}(\text{HC}) = 3 \left( \frac{n_{\text{HCO}_2^{18}\text{O}_a^-}^3}{K n_{\text{HCO}_3^-}^2} \right) + 2 \left( K \frac{1}{3} \frac{1}{3} n_{\text{HCO}_3^-} \frac{2}{3} n_{\text{HC}^{18}\text{O}_3^-} \right) + n_{\text{HCO}_2^{18}\text{O}_a^-},$$

$$\text{num}(\text{H}^{13}\text{C}) = 3 \left( \frac{n_{\text{H}^{13}\text{CO}_2^{18}\text{O}_a^-}^3}{K n_{\text{H}^{13}\text{CO}_3^-}^2} \right) + 2 \left( K \frac{1}{3} \frac{1}{3} n_{\text{H}^{13}\text{CO}_3^-} \frac{2}{3} n_{\text{H}^{13}\text{C}^{18}\text{O}_3^-} \right) + n_{\text{H}^{13}\text{CO}_2^{18}\text{O}_a^-},$$

$$\text{num}(\text{DC}) = 3 \left( \frac{n_{\text{DCO}_2^{18}\text{O}_a^-}^3}{K n_{\text{DCO}_3^-}^2} \right) + 2 \left( K \frac{1}{3} \frac{1}{3} n_{\text{DCO}_3^-} \frac{2}{3} n_{\text{DC}^{18}\text{O}_3^-} \right) + n_{\text{DCO}_2^{18}\text{O}_a^-},$$

$$\text{num}(\text{D}^{13}\text{C}) = 3 \left( \frac{n_{\text{D}^{13}\text{CO}_2^{18}\text{O}_a^-}^3}{K n_{\text{D}^{13}\text{CO}_3^-}^2} \right) + 2 \left( K \frac{1}{3} \frac{1}{3} n_{\text{D}^{13}\text{CO}_3^-} \frac{2}{3} n_{\text{D}^{13}\text{C}^{18}\text{O}_3^-} \right) + n_{\text{D}^{13}\text{CO}_2^{18}\text{O}_a^-},$$

$$\text{denom}(\text{HC}) = 3n_{\text{HCO}_3^-} \left\{ 1 + \frac{2}{3} \left( \frac{n_{\text{HCO}_2^{18}\text{O}_a^-}}{n_{\text{HCO}_3^-}} \right) + \frac{1}{3} \left( \frac{K \frac{1}{3} \frac{1}{3} n_{\text{HCO}_3^-} \frac{2}{3} n_{\text{HC}^{18}\text{O}_3^-}}{n_{\text{HCO}_3^-}} \right) \right\},$$

$$\text{denom}(H^{13}C) = 3n_{H^{13}CO_3aq^-} \left\{ 1 + \frac{2}{3} \left( \frac{n_{H^{13}CO_2^{18}O_{aq}^-}}{n_{H^{13}CO_3aq^-}} \right) + \frac{1}{3} \left( \frac{K^{\frac{1}{3}} n^{\frac{1}{3}} n_{H^{13}CO_3aq^-}^{\frac{2}{3}}}{n_{H^{13}CO_3aq^-}} \right) \right\},$$

$$\text{denom}(DC) = 3n_{DCO_3aq^-} \left\{ 1 + \frac{2}{3} \left( \frac{n_{DCO_2^{18}O_{aq}^-}}{n_{DCO_3aq^-}} \right) + \frac{1}{3} \left( \frac{K^{\frac{1}{3}} n^{\frac{1}{3}} n_{DCO_3aq^-}^{\frac{2}{3}}}{n_{DCO_3aq^-}} \right) \right\}, \text{ and}$$

$$\text{denom}(D^{13}C) = 3n_{D^{13}CO_3aq^-} \left\{ 1 + \frac{2}{3} \left( \frac{n_{D^{13}CO_2^{18}O_{aq}^-}}{n_{D^{13}CO_3aq^-}} \right) + \frac{1}{3} \left( \frac{K^{\frac{1}{3}} n^{\frac{1}{3}} n_{D^{13}CO_3aq^-}^{\frac{2}{3}}}{n_{D^{13}CO_3aq^-}} \right) \right\}.$$

Equation A1.6 can be rewritten as

$$R_{HCO_3aq^-}^{18O} = \frac{\left[ 3 \left( \frac{n_{HCO_2^{18}O_{aq}^-}^3}{K n_{HCO_3aq^-}^2} \right) + 2 \left( K^{\frac{1}{3}} n^{\frac{1}{3}} \frac{n_{HCO_2^{18}O_{aq}^-}^2}{K^{\frac{2}{3}} n_{HCO_3aq^-}^{\frac{4}{3}}} \right) + n_{HCO_2^{18}O_{aq}^-} + \sum_{i \neq HC} \text{num}[i] \right]}{\left[ 3n_{HCO_3aq^-} \left\{ 1 + \frac{2}{3} \left( \frac{n_{HCO_2^{18}O_{aq}^-}}{n_{HCO_3aq^-}} \right) + \frac{1}{3} \left( \frac{K^{\frac{1}{3}} n^{\frac{1}{3}} \frac{n_{HCO_2^{18}O_{aq}^-}^2}{K^{\frac{2}{3}} n_{HCO_3aq^-}^{\frac{4}{3}}} \right)}{n_{HCO_3aq^-}} \right\} + \sum_{i \neq HC} \text{denom}[i] \right]}, \quad (\text{A1.7})$$

where  $\sum \text{num}$  sums the analogous numerator [ ] terms for  $H^{13}C$ ,  $DC$ , and  $D^{13}C$ , respectively, and

$\sum \text{denom}$  sums the analogous denominator [ ] terms for  $H^{13}C$ ,  $DC$ , and  $D^{13}C$ , respectively.

Continuing the same notational convention, A1.7 can be written as

$$R_{HCO_3aq}^{18O} = \frac{\left[ 3 \left( \frac{n^3 HCO_2^{18}O_{aq}^-}{Kn^2 HCO_3aq^-} \right) + 2 \left( \frac{n^2 HCO_2^{18}O_{aq}^-}{\frac{1}{3} n HCO_3aq^-} \right) + n_{HCO_2^{18}O_{aq}^-} + \sum_{i \neq HC} num[i] \right]}{\left[ 3n_{HCO_3aq^-} \left\{ 1 + \frac{2}{3} \left( \frac{n_{HCO_2^{18}O_{aq}^-}}{n_{HCO_3aq^-}} \right) + \frac{1}{3} \left( \frac{\frac{n^2 HCO_2^{18}O_{aq}^-}{K^{\frac{1}{3}} n_{HCO_3aq^-}}}{n_{HCO_3aq^-}} \right) \right\} + \sum_{i \neq HC} denom[i] \right]}, \quad (A1.8)$$

$$R_{HCO_3aq}^{18O} = \frac{\left[ 3 \left( \frac{n^3 HCO_2^{18}O_{aq}^-}{Kn^2 HCO_3aq^-} \right) + 2 \left( \frac{n^2 HCO_2^{18}O_{aq}^-}{\frac{1}{3} n HCO_3aq^-} \right) + n_{HCO_2^{18}O_{aq}^-} + \sum_{i \neq HC} num[i] \right]}{\left[ 3n_{HCO_3aq^-} \left\{ 1 + \frac{2}{3} \left( \frac{n_{HCO_2^{18}O_{aq}^-}}{n_{HCO_3aq^-}} \right) + \frac{1}{3} \left( \frac{\frac{n^2 HCO_2^{18}O_{aq}^-}{K^{\frac{1}{3}} n^2 HCO_3aq^-}}{\frac{1}{3} n_{HCO_3aq^-}} \right) \right\} + \sum_{i \neq HC} denom[i] \right]}, \quad (A1.9)$$

$$R_{HCO_3aq}^{18O} = \frac{\left[ n_{HCO_2^{18}O_{aq}^-} + \frac{2}{K^{\frac{1}{3}}} \left( \frac{n^2 HCO_2^{18}O_{aq}^-}{n_{HCO_3aq^-}} \right) + \frac{3}{K} \left( \frac{n^3 HCO_2^{18}O_{aq}^-}{n^2 HCO_3aq^-} \right) + \sum_{i \neq HC} num[i] \right]}{\left[ 3n_{HCO_3aq^-} \left\{ 1 + \frac{2}{3} \left( \frac{n_{HCO_2^{18}O_{aq}^-}}{n_{HCO_3aq^-}} \right) + \frac{1}{3K^{\frac{1}{3}}} \left( \frac{n^2 HCO_2^{18}O_{aq}^-}{n_{HCO_3aq^-}} \right) \right\} + \sum_{i \neq HC} denom[i] \right]}, \quad (A1.10)$$

$$R_{HCO_3^-}^{18O} = \frac{\left[ n_{HCO_2^{18}O^-} \left\{ 1 + \frac{2}{K^{\frac{1}{3}}} \left( \frac{n_{HCO_2^{18}O^-}}{n_{HCO_3^-}} \right) + \frac{3}{K} \left( \frac{n_{HCO_2^{18}O^-}}{n_{HCO_3^-}} \right)^2 \right\} + \sum_{i \neq HC} num[i] \right]}{\left[ 3n_{HCO_3^-} \left\{ 1 + \frac{2}{3} \left( \frac{n_{HCO_2^{18}O^-}}{n_{HCO_3^-}} \right) + \frac{1}{3K^{\frac{1}{3}}} \left( \frac{n_{HCO_2^{18}O^-}}{n_{HCO_3^-}} \right)^2 \right\} + \sum_{i \neq HC} denom[i] \right]}, \text{ and} \quad (A1.11)$$

$$R_{HCO_3^-}^{18O} = \frac{\left[ n_{HCO_2^{18}O^-} \left\{ 1 + \frac{6}{K^{\frac{1}{3}}} \left( \frac{n_{HCO_2^{18}O^-}}{3n_{HCO_3^-}} \right) + \frac{27}{K} \left( \frac{n_{HCO_2^{18}O^-}}{3n_{HCO_3^-}} \right)^2 \right\} + \sum_{i \neq HC} num[i] \right]}{\left[ 3n_{HCO_3^-} \left\{ 1 + 2 \left( \frac{n_{HCO_2^{18}O^-}}{3n_{HCO_3^-}} \right) + \frac{3}{K^{\frac{1}{3}}} \left( \frac{n_{HCO_2^{18}O^-}}{3n_{HCO_3^-}} \right)^2 \right\} + \sum_{i \neq HC} denom[i] \right]}. \quad (A1.12)$$

Writing the complete expression for A1.12 gives

$$R_{HCO_3^-}^{18O} = \frac{\left[ n_{HCO_2^{18}O^-} \left\{ 1 + \frac{6}{K^{\frac{1}{3}}} \left( \frac{n_{HCO_2^{18}O^-}}{3n_{HCO_3^-}} \right) + \frac{27}{K} \left( \frac{n_{HCO_2^{18}O^-}}{3n_{HCO_3^-}} \right)^2 \right\} + \right]}{\left[ 3n_{HCO_3^-} \left\{ 1 + 2 \left( \frac{n_{HCO_2^{18}O^-}}{3n_{HCO_3^-}} \right) + \frac{3}{K^{\frac{1}{3}}} \left( \frac{n_{HCO_2^{18}O^-}}{3n_{HCO_3^-}} \right)^2 \right\} + \right]} \\ \frac{\left[ n_{H^{13}CO_2^{18}O^-} \left\{ 1 + \frac{6}{K^{\frac{1}{3}}} \left( \frac{n_{H^{13}CO_2^{18}O^-}}{3n_{H^{13}CO_3^-}} \right) + \frac{27}{K} \left( \frac{n_{H^{13}CO_2^{18}O^-}}{3n_{H^{13}CO_3^-}} \right)^2 \right\} + \right]}{\left[ 3n_{H^{13}CO_3^-} \left\{ 1 + 2 \left( \frac{n_{H^{13}CO_2^{18}O^-}}{3n_{H^{13}CO_3^-}} \right) + \frac{3}{K^{\frac{1}{3}}} \left( \frac{n_{H^{13}CO_2^{18}O^-}}{3n_{H^{13}CO_3^-}} \right)^2 \right\} + \right]} \\ \frac{\left[ n_{DCO_2^{18}O^-} \left\{ 1 + \frac{6}{K^{\frac{1}{3}}} \left( \frac{n_{DCO_2^{18}O^-}}{3n_{DCO_3^-}} \right) + \frac{27}{K} \left( \frac{n_{DCO_2^{18}O^-}}{3n_{DCO_3^-}} \right)^2 \right\} + \right]}{\left[ 3n_{DCO_3^-} \left\{ 1 + 2 \left( \frac{n_{DCO_2^{18}O^-}}{3n_{DCO_3^-}} \right) + \frac{3}{K^{\frac{1}{3}}} \left( \frac{n_{DCO_2^{18}O^-}}{3n_{DCO_3^-}} \right)^2 \right\} + \right]}$$

$$\frac{n_{D^{13}CO_2^{18}O_{aq}^-} \left\{ 1 + \frac{6}{K^{\frac{1}{3}}} \left( \frac{n_{D^{13}CO_2^{18}O_{aq}^-}}{3n_{D^{13}CO_3aq^-}} \right) + \frac{27}{K} \left( \frac{n_{D^{13}CO_2^{18}O_{aq}^-}}{3n_{D^{13}CO_3aq^-}} \right)^2 \right\}}{3n_{D^{13}CO_3aq^-} \left\{ 1 + 2 \left( \frac{n_{D^{13}CO_2^{18}O_{aq}^-}}{3n_{D^{13}CO_3aq^-}} \right) + \frac{3}{K^{\frac{1}{3}}} \left( \frac{n_{D^{13}CO_2^{18}O_{aq}^-}}{3n_{D^{13}CO_3aq^-}} \right)^2 \right\}}. \quad (A1.13)$$

The four numerator terms in { } brackets are equal and the four denominator terms in { } brackets are equal because the equilibrium constants for the isotope exchange reactions are all equal to 1. Expressing the { } terms as functions of  $H$  and  $C$ , and defining

$$Q1 = \left( \frac{n_{HCO_2^{18}O_{aq}^-}}{3n_{HCO_3aq^-}} \right), \quad (A1.14)$$

gives

$$R_{HCO_3aq^-}^{18O} = \frac{\left( n_{HCO_2^{18}O_{aq}^-} + n_{H^{13}CO_2^{18}O_{aq}^-} + n_{DCO_2^{18}O_{aq}^-} + n_{D^{13}CO_2^{18}O_{aq}^-} \right) \left\{ 1 + \frac{6}{K^{\frac{1}{3}}} (Q1) + \frac{27}{K} (Q1)^2 \right\}}{\left( 3n_{HCO_3aq^-} + 3n_{H^{13}CO_3aq^-} + 3n_{DCO_3aq^-} + 3n_{D^{13}CO_3aq^-} \right) \left\{ 1 + 2(Q1) + \frac{3}{K^{\frac{1}{3}}} (Q1)^2 \right\}}, \quad (A1.15)$$

and

$$R_{HCO_3aq^-}^{18O} = \frac{n_{HCO_2^{18}O_{aq}^-} \left( 1 + \frac{n_{H^{13}CO_2^{18}O_{aq}^-}}{n_{HCO_2^{18}O_{aq}^-}} + \frac{n_{DCO_2^{18}O_{aq}^-}}{n_{HCO_2^{18}O_{aq}^-}} + \frac{n_{D^{13}CO_2^{18}O_{aq}^-}}{n_{HCO_2^{18}O_{aq}^-}} \right) \left\{ 1 + \frac{6}{K^{\frac{1}{3}}} (Q1) + \frac{27}{K} (Q1)^2 \right\}}{3n_{HCO_3aq^-} \left( 1 + \frac{3n_{H^{13}CO_3aq^-}}{3n_{HCO_3aq^-}} + \frac{3n_{DCO_3aq^-}}{3n_{HCO_3aq^-}} + \frac{3n_{D^{13}CO_3aq^-}}{3n_{HCO_3aq^-}} \right) \left\{ 1 + 2(Q1) + \frac{3}{K^{\frac{1}{3}}} (Q1)^2 \right\}}. \quad (A1.16)$$

The terms in ( ) brackets are equal; therefore,

$$R_{HCO_3aq}^{18O} = \left( \frac{n_{HCO_2^{18}O_{aq}^-}}{3n_{HCO_3aq}^-} \right) \frac{\left\{ 1 + \frac{6}{1} (Q1) + \frac{27}{K} (Q1)^2 \right\}}{\left\{ 1 + 2(Q1) + \frac{3}{1} (Q1)^2 \right\}}. \quad (A1.17)$$

Now define

$$qq1 \equiv \frac{\left\{ 1 + \frac{6}{1} (Q1) + \frac{27}{K} (Q1)^2 \right\}}{\left\{ 1 + 2(Q1) + \frac{3}{1} (Q1)^2 \right\}}, \quad (A1.18)$$

which gives

$$R_{HCO_3aq}^{18O} = \left( \frac{n_{HCO_2^{18}O_{aq}^-}}{3n_{HCO_3aq}^-} \right) qq1 = \left( \frac{n_{H^{13}CO_2^{18}O_{aq}^-}}{3n_{H^{13}CO_3aq}^-} \right) qq1 = \left( \frac{n_{DCO_2^{18}O_{aq}^-}}{3n_{DCO_3aq}^-} \right) qq1 = \left( \frac{n_{D^{13}CO_2^{18}O_{aq}^-}}{3n_{D^{13}CO_3aq}^-} \right) qq1. \quad (A1.19)$$

**The  $^{18}O/^{16}O$  ratio in terms of  $HCO^{18}O_{2aq}^-$**

$$R_{HCO_3aq}^{18O} = \frac{\left[ 3n_{HC^{18}O_{3aq}^-} + 2n_{HCO^{18}O_{2aq}^-} + n_{HCO_2^{18}O_{aq}^-} \right] + \sum_{i \neq HC} num[i]}{\left[ 3n_{HCO_3aq}^- + 2n_{HCO_2^{18}O_{aq}^-} + n_{HCO^{18}O_{2aq}^-} \right] + \sum_{i \neq HC} denom[i]}, \quad (A1.20)$$

$$R_{HCO_3aq}^{18O} = \frac{\left[ 3 \left( \frac{n_{HCO^{18}O_{2aq}^-}^{\frac{3}{2}}}{K^{\frac{1}{2}} n_{HCO_3aq}^-^{\frac{1}{2}}} \right) + 2n_{HCO^{18}O_{2aq}^-} + \left( K^{\frac{1}{3}} n_{HCO_3aq}^-^{\frac{2}{3}} n_{HC^{18}O_{3aq}^-}^{\frac{1}{3}} \right) \right] + \sum_{i \neq HC} num[i]}{\left[ 3n_{HCO_3aq}^- + 2 \left( K^{\frac{1}{3}} n_{HCO_3aq}^-^{\frac{2}{3}} n_{HC^{18}O_{3aq}^-}^{\frac{1}{3}} \right) + n_{HCO^{18}O_{2aq}^-} \right] + \sum_{i \neq HC} denom[i]}, \quad (A1.21)$$

$$R_{HCO_3aq}^{18O} = \frac{\left[ 3 \left( \frac{n^{3/2} HCO^{18}O_{2aq}^-}{K^{1/2} n^{1/2} HCO_3aq^-} \right) + 2n_{HCO^{18}O_{2aq}^-} + \left( K^{1/3} n^{2/3} \frac{n^{3/2} HCO^{18}O_{2aq}^-}{K^{1/2} n^{1/2} HCO_3aq^-} \right)^{1/3} \right] + \sum_{i \neq HC} num[i]}{\left[ 3n_{HCO_3aq^-} + 2 \left( K^{1/3} n^{2/3} \frac{n^{3/2} HCO^{18}O_{2aq}^-}{K^{1/2} n^{1/2} HCO_3aq^-} \right)^{1/3} \right] + n_{HCO^{18}O_{2aq}^-} + \sum_{i \neq HC} denom[i]}, \quad (A1.22)$$

$$R_{HCO_3aq}^{18O} = \frac{\left[ 3 \left( \frac{n^{3/2} HCO^{18}O_{2aq}^-}{K^{1/2} n^{1/2} HCO_3aq^-} \right) + 2n_{HCO^{18}O_{2aq}^-} + \left( K^{1/3} n^{2/3} \frac{n^{1/2} HCO^{18}O_{2aq}^-}{K^{1/6} n^{1/6} HCO_3aq^-} \right) \right] + \sum_{i \neq HC} num[i]}{\left[ 3n_{HCO_3aq^-} + 2 \left( K^{1/3} n^{2/3} \frac{n^{1/2} HCO^{18}O_{2aq}^-}{K^{1/6} n^{1/6} HCO_3aq^-} \right) \right] + n_{HCO^{18}O_{2aq}^-} + \sum_{i \neq HC} denom[i]}, \quad (A1.23)$$

$$R_{HCO_3aq}^{18O} = \frac{\left[ \left( K^{1/6} n^{1/2} \frac{n^{1/2} HCO^{18}O_{2aq}^-}{HCO_3aq^-} \right) + 2n_{HCO^{18}O_{2aq}^-} + 3 \left( \frac{n^{3/2} HCO^{18}O_{2aq}^-}{K^{1/2} n^{1/2} HCO_3aq^-} \right) \right] + \sum_{i \neq HC} num[i]}{\left[ 3n_{HCO_3aq^-} + 2 \left( K^{1/6} n^{1/2} \frac{n^{1/2} HCO^{18}O_{2aq}^-}{HCO_3aq^-} \right) + n_{HCO^{18}O_{2aq}^-} \right] + \sum_{i \neq HC} denom[i]}, \quad (A1.24)$$

$$R_{HCO_3aq}^{18O} = \frac{\left[ n^{1/2} HCO^{18}O_{2aq}^- \left\{ \left( K^{1/6} n^{1/2} \frac{n^{1/2} HCO^{18}O_{2aq}^-}{HCO_3aq^-} \right) + 2n^{1/2} HCO^{18}O_{2aq}^- + 3 \left( \frac{n^{3/2} HCO^{18}O_{2aq}^-}{K^{1/2} n^{1/2} HCO_3aq^-} \right) \right\} + \sum_{i \neq HC} num[i]}{\left[ 3^{1/2} n^{1/2} HCO_3aq^- \left\{ 3^{1/2} n^{1/2} HCO_3aq^- + \frac{2}{3^{1/2}} \left( K^{1/6} n^{1/2} \frac{n^{1/2} HCO^{18}O_{2aq}^-}{HCO_3aq^-} \right) + \left( \frac{n^{3/2} HCO^{18}O_{2aq}^-}{3^{1/2} n^{1/2} HCO_3aq^-} \right) \right\} + \sum_{i \neq HC} denom[i]} \right]}, \quad (A1.25)$$

$$R_{HCO_{3aq}^-}^{18O} = \frac{\left[ n_{HCO^{18}O_{2aq}^-}^{\frac{1}{2}} \left\{ \left( K^{\frac{1}{6}} \right) + 2 \left( \frac{n_{HCO^{18}O_{2aq}^-}}{n_{HCO_{3aq}^-}} \right)^{\frac{1}{2}} + \frac{3}{K^{\frac{1}{2}}} \left( \frac{n_{HCO^{18}O_{2aq}^-}}{n_{HCO_{3aq}^-}} \right) \right\} \right] + \sum_{i \neq HC} num[i]}{\left[ 3^{\frac{1}{2}} n_{HCO_{3aq}^-}^{\frac{1}{2}} \left\{ 3^{\frac{1}{2}} + \frac{2K^{\frac{1}{6}}}{3^{\frac{1}{2}}} \left( \frac{n_{HCO^{18}O_{2aq}^-}}{n_{HCO_{3aq}^-}} \right)^{\frac{1}{2}} + \frac{1}{3^{\frac{1}{2}}} \left( \frac{n_{HCO^{18}O_{2aq}^-}}{n_{HCO_{3aq}^-}} \right) \right\} \right] + \sum_{i \neq HC} denom[i]} \quad (A1.26)$$

$$\text{and } R_{HCO_{3aq}^-}^{18O} = \frac{\left[ n_{HCO^{18}O_{2aq}^-}^{\frac{1}{2}} \left\{ \left( K^{\frac{1}{6}} \right) + 2 \left( \frac{n_{HCO^{18}O_{2aq}^-}}{n_{HCO_{3aq}^-}} \right)^{\frac{1}{2}} + \frac{3}{K^{\frac{1}{2}}} \left( \frac{n_{HCO^{18}O_{2aq}^-}}{n_{HCO_{3aq}^-}} \right) \right\} \right] + \sum_{i \neq HC} num[i]}{\left[ 3^{\frac{1}{2}} n_{HCO_{3aq}^-}^{\frac{1}{2}} \left\{ 3^{\frac{1}{2}} + \frac{2K^{\frac{1}{6}}}{3^{\frac{1}{2}}} \left( \frac{n_{HCO^{18}O_{2aq}^-}}{n_{HCO_{3aq}^-}} \right)^{\frac{1}{2}} + \frac{1}{3^{\frac{1}{2}}} \left( \frac{n_{HCO^{18}O_{2aq}^-}}{n_{HCO_{3aq}^-}} \right) \right\} \right] + \sum_{i \neq HC} denom[i]} \quad (A1.27)$$

Analogous to A1.13, A1.15, and A1.16, equation A1.27 reduces to

$$R_{HCO_{3aq}^-}^{18O} = \frac{n_{HCO^{18}O_{2aq}^-}^{\frac{1}{2}} \left\{ \left( K^{\frac{1}{6}} \right) + \frac{6}{3^{\frac{1}{2}}} \left( \frac{n_{HCO^{18}O_{2aq}^-}}{3n_{HCO_{3aq}^-}} \right)^{\frac{1}{2}} + \frac{9}{K^{\frac{1}{2}}} \left( \frac{n_{HCO^{18}O_{2aq}^-}}{3n_{HCO_{3aq}^-}} \right) \right\}}{3^{\frac{1}{2}} n_{HCO_{3aq}^-}^{\frac{1}{2}} \left\{ 3^{\frac{1}{2}} + 2K^{\frac{1}{6}} \left( \frac{n_{HCO^{18}O_{2aq}^-}}{3n_{HCO_{3aq}^-}} \right)^{\frac{1}{2}} + 3 \left( \frac{n_{HCO^{18}O_{2aq}^-}}{3n_{HCO_{3aq}^-}} \right) \right\}} \quad (A1.28)$$

$$\text{Now define } Q2 = \left( \frac{n_{HCO^{18}O_{2aq}^-}}{3n_{HCO_{3aq}^-}} \right)^{\frac{1}{2}}, \text{ and equation A1.28 becomes} \quad (A1.29)$$

$$R_{HCO_{3aq}^-}^{18O} = \left( \frac{n_{HCO^{18}O_{2aq}^-}}{3n_{HCO_{3aq}^-}} \right)^{\frac{1}{2}} \frac{\left\{ K^{\frac{1}{6}} + \frac{6}{3^{\frac{1}{2}}} (Q2) + \frac{9}{K^{\frac{1}{2}}} (Q2)^2 \right\}}{\left\{ 3^{\frac{1}{2}} + 2K^{\frac{1}{6}} (Q2) + 3 (Q2)^2 \right\}} \quad (A1.30)$$

$$\text{Defining } qq2 \equiv \frac{\left\{ K^{\frac{1}{6}} + \frac{6}{3^{\frac{1}{2}}} (Q2) + \frac{9}{K^{\frac{1}{2}}} (Q2)^2 \right\}}{\left\{ 3^{\frac{1}{2}} + 2K^{\frac{1}{6}} (Q2) + 3^{\frac{1}{2}} (Q2)^2 \right\}} \text{ gives} \quad (\text{A1.31})$$

$$\begin{aligned} R_{HCO_3aq}^{18O} &= \left( \frac{n_{HCO_3aq}^{18O} O_{2aq}^-}{3n_{HCO_3aq}^-} \right)^{\frac{1}{2}} qq2 = \left( \frac{n_{H^{13}CO_3aq}^{18O} O_{2aq}^-}{3n_{H^{13}CO_3aq}^-} \right)^{\frac{1}{2}} qq2 \\ &= \left( \frac{n_{DCO_3aq}^{18O} O_{2aq}^-}{3n_{DCO_3aq}^-} \right)^{\frac{1}{2}} qq2 = \left( \frac{n_{D^{13}CO_3aq}^{18O} O_{2aq}^-}{3n_{D^{13}CO_3aq}^-} \right)^{\frac{1}{2}} qq2. \end{aligned} \quad (\text{A1.32})$$

The  $^{18}O/^{16}O$  ratio in terms of  $HC^{18}O_3aq^-$

$$R_{HCO_3aq}^{18O} = \frac{\left[ 3n_{HC^{18}O_3aq}^- + 2n_{HCO_2^{18}O_{aq}^-} + n_{HCO_2^{18}O_{aq}^-} \right] + \sum_{i \neq HC} num[i]}{\left[ 3n_{HCO_3aq}^- + 2n_{HCO_2^{18}O_{aq}^-} + n_{HCO_2^{18}O_{aq}^-} \right] + \sum_{i \neq HC} denom[i]}, \quad (\text{A1.33})$$

$$R_{HCO_3aq}^{18O} = \frac{3n_{HC^{18}O_3aq}^- + 2 \left( K^{\frac{1}{3}} n^{\frac{2}{3}}_{HC^{18}O_3aq} n^{\frac{1}{3}}_{HCO_3aq} \right) + \left( K^{\frac{1}{3}} n^{\frac{1}{3}}_{HC^{18}O_3aq} n^{\frac{2}{3}}_{HCO_3aq} \right) + \sum_{i \neq HC} num[i]}{3n_{HCO_3aq}^- + 2 \left( K^{\frac{1}{3}} n^{\frac{1}{3}}_{HC^{18}O_3aq} n^{\frac{2}{3}}_{HCO_3aq} \right) + \left( K^{\frac{1}{3}} n^{\frac{2}{3}}_{HC^{18}O_3aq} n^{\frac{1}{3}}_{HCO_3aq} \right) + \sum_{i \neq HC} denom[i]}, \quad (\text{A1.34})$$

$$R_{HCO_3aq}^{18O} = \frac{n^{\frac{1}{3}}_{HC^{18}O_3aq} \left\{ 3n^{\frac{2}{3}}_{HC^{18}O_3aq} + 2 \left( K^{\frac{1}{3}} n^{\frac{1}{3}}_{HC^{18}O_3aq} n^{\frac{1}{3}}_{HCO_3aq} \right) + \left( K^{\frac{1}{3}} n^{\frac{2}{3}}_{HCO_3aq} \right) \right\} + \sum_{i \neq HC} num[i]}{n^{\frac{1}{3}}_{HCO_3aq} \left\{ 3n^{\frac{2}{3}}_{HCO_3aq} + 2 \left( K^{\frac{1}{3}} n^{\frac{1}{3}}_{HC^{18}O_3aq} n^{\frac{1}{3}}_{HCO_3aq} \right) + \left( K^{\frac{1}{3}} n^{\frac{2}{3}}_{HC^{18}O_3aq} \right) \right\} + \sum_{i \neq HC} denom[i]}, \text{ or } (\text{A1.35})$$

$$R_{HCO_{3aq}^-}^{18O} = \frac{n_{HC^{18}O_{3aq}^-}^{\frac{1}{3}} n_{HCO_{3aq}^-}^{\frac{2}{3}} \left\{ K_1^{\frac{1}{3}} + 2K^{\frac{1}{3}} \left( \frac{n_{HC^{18}O_{3aq}^-}}{n_{HCO_{3aq}^-}} \right)^{\frac{1}{3}} + 3 \left( \frac{n_{HC^{18}O_{3aq}^-}}{n_{HCO_{3aq}^-}} \right)^{\frac{2}{3}} \right\} + \sum_{i \neq HC} num[i]}{n_{HCO_{3aq}^-}^{\frac{1}{3}} n_{HCO_{3aq}^-}^{\frac{2}{3}} \left\{ 3 + 2K^{\frac{1}{3}} \left( \frac{n_{HC^{18}O_{3aq}^-}}{n_{HCO_{3aq}^-}} \right)^{\frac{1}{3}} + K^{\frac{1}{3}} \left( \frac{n_{HC^{18}O_{3aq}^-}}{n_{HCO_{3aq}^-}} \right)^{\frac{2}{3}} \right\} + \sum_{i \neq HC} denom[i]} \quad (A1.36)$$

Again, analogous to equations A1.13, A1.15, and A1.16, equation A1.36 reduces to

$$R_{HCO_{3aq}^-}^{18O} = \frac{n_{HC^{18}O_{3aq}^-}^{\frac{1}{3}} \left\{ K_1^{\frac{1}{3}} + 2K^{\frac{1}{3}} \left( \frac{n_{HC^{18}O_{3aq}^-}}{n_{HCO_{3aq}^-}} \right)^{\frac{1}{3}} + 3 \left( \frac{n_{HC^{18}O_{3aq}^-}}{n_{HCO_{3aq}^-}} \right)^{\frac{2}{3}} \right\}}{n_{HCO_{3aq}^-}^{\frac{1}{3}} \left\{ 3 + 2K^{\frac{1}{3}} \left( \frac{n_{HC^{18}O_{3aq}^-}}{n_{HCO_{3aq}^-}} \right)^{\frac{1}{3}} + K^{\frac{1}{3}} \left( \frac{n_{HC^{18}O_{3aq}^-}}{n_{HCO_{3aq}^-}} \right)^{\frac{2}{3}} \right\}}, \quad (A1.37)$$

and defining  $Q3 = \left( \frac{n_{HC^{18}O_{3aq}^-}}{n_{HCO_{3aq}^-}} \right)^{\frac{1}{3}}$  yields

$$(A1.38)$$

$$R_{HCO_{3aq}^-}^{18O} = \left( \frac{n_{HC^{18}O_{3aq}^-}}{n_{HCO_{3aq}^-}} \right)^{\frac{1}{3}} \frac{\left\{ K_1^{\frac{1}{3}} + 2K^{\frac{1}{3}}(Q3) + 3(Q3)^2 \right\}}{\left\{ 3 + 2K^{\frac{1}{3}}(Q3) + K^{\frac{1}{3}}(Q3)^2 \right\}}. \quad (A1.39)$$

Defining  $qq3 \equiv \frac{\left\{ K_1^{\frac{1}{3}} + 2K^{\frac{1}{3}}(Q3) + 3(Q3)^2 \right\}}{\left\{ 3 + 2K^{\frac{1}{3}}(Q3) + K^{\frac{1}{3}}(Q3)^2 \right\}}$  gives

$$(A1.40)$$

$$R_{HCO_{3aq}^-}^{18O} = \left( \frac{n_{HC^{18}O_{3aq}^-}}{n_{HCO_{3aq}^-}} \right)^{\frac{1}{3}} qq3 = \left( \frac{n_{H^{13}C^{18}O_{3aq}^-}}{n_{H^{13}CO_{3aq}^-}} \right)^{\frac{1}{3}} qq3$$

$$= \left( \frac{n_{DC^{18}O_{3aq}^-}}{n_{DCO_{3aq}^-}} \right)^{\frac{1}{3}} qq3 = \left( \frac{n_{D^{13}C^{18}O_{3aq}^-}}{n_{D^{13}CO_{3aq}^-}} \right)^{\frac{1}{3}} qq3. \quad (A1.41)$$

## The $^{13}\text{C}/^{12}\text{C}$ isotope ratio

The carbon-13 ratio is

$$R_{\text{HCO}_3^-}^{13\text{C}} = \frac{n_{\text{H}^{13}\text{CO}_3^-} + n_{\text{H}^{13}\text{CO}_2^{18}\text{O}^-} + n_{\text{H}^{13}\text{CO}^{18}\text{O}_2^-} + n_{\text{H}^{13}\text{C}^{18}\text{O}_3^-} +}{n_{\text{HCO}_3^-} + n_{\text{HCO}_2^{18}\text{O}^-} + n_{\text{HCO}^{18}\text{O}_2^-} + n_{\text{HC}^{18}\text{O}_3^-} +} \frac{n_{\text{D}^{13}\text{CO}_3^-} + n_{\text{D}^{13}\text{CO}_2^{18}\text{O}^-} + n_{\text{D}^{13}\text{CO}^{18}\text{O}_2^-} + n_{\text{D}^{13}\text{C}^{18}\text{O}_3^-}}{n_{\text{DCO}_3^-} + n_{\text{DCO}_2^{18}\text{O}^-} + n_{\text{DCO}^{18}\text{O}_2^-} + n_{\text{DC}^{18}\text{O}_3^-}}, \text{ or} \quad (\text{A1.42})$$

$$R_{\text{HCO}_3^-}^{13\text{C}} = \frac{n_{\text{H}^{13}\text{CO}_3^-} \left( 1 + \frac{n_{\text{H}^{13}\text{CO}_2^{18}\text{O}^-}}{n_{\text{H}^{13}\text{CO}_3^-}} + \frac{n_{\text{H}^{13}\text{CO}^{18}\text{O}_2^-}}{n_{\text{H}^{13}\text{CO}_3^-}} + \frac{n_{\text{H}^{13}\text{C}^{18}\text{O}_3^-}}{n_{\text{H}^{13}\text{CO}_3^-}} \right) +}{n_{\text{HCO}_3^-} \left( 1 + \frac{n_{\text{HCO}_2^{18}\text{O}^-}}{n_{\text{HCO}_3^-}} + \frac{n_{\text{HCO}^{18}\text{O}_2^-}}{n_{\text{HCO}_3^-}} + \frac{n_{\text{HC}^{18}\text{O}_3^-}}{n_{\text{HCO}_3^-}} \right) +} \frac{n_{\text{D}^{13}\text{CO}_3^-} \left( 1 + \frac{n_{\text{D}^{13}\text{CO}_2^{18}\text{O}^-}}{n_{\text{D}^{13}\text{CO}_3^-}} + \frac{n_{\text{D}^{13}\text{CO}^{18}\text{O}_2^-}}{n_{\text{D}^{13}\text{CO}_3^-}} + \frac{n_{\text{D}^{13}\text{C}^{18}\text{O}_3^-}}{n_{\text{D}^{13}\text{CO}_3^-}} \right)}{n_{\text{DCO}_3^-} \left( 1 + \frac{n_{\text{DCO}_2^{18}\text{O}^-}}{n_{\text{DCO}_3^-}} + \frac{n_{\text{DCO}^{18}\text{O}_2^-}}{n_{\text{DCO}_3^-}} + \frac{n_{\text{DC}^{18}\text{O}_3^-}}{n_{\text{DCO}_3^-}} \right)}. \quad (\text{A1.43})$$

The terms in brackets are equal; therefore,

$$R_{\text{HCO}_3^-}^{13\text{C}} = \frac{\left( n_{\text{H}^{13}\text{CO}_3^-} + n_{\text{D}^{13}\text{CO}_3^-} \right) \left( 1 + \frac{n_{\text{H}^{13}\text{CO}_2^{18}\text{O}^-}}{n_{\text{H}^{13}\text{CO}_3^-}} + \frac{n_{\text{H}^{13}\text{CO}^{18}\text{O}_2^-}}{n_{\text{H}^{13}\text{CO}_3^-}} + \frac{n_{\text{H}^{13}\text{C}^{18}\text{O}_3^-}}{n_{\text{H}^{13}\text{CO}_3^-}} \right)}{\left( n_{\text{HCO}_3^-} + n_{\text{DCO}_3^-} \right) \left( 1 + \frac{n_{\text{HCO}_2^{18}\text{O}^-}}{n_{\text{HCO}_3^-}} + \frac{n_{\text{HCO}^{18}\text{O}_2^-}}{n_{\text{HCO}_3^-}} + \frac{n_{\text{HC}^{18}\text{O}_3^-}}{n_{\text{HCO}_3^-}} \right)}, \quad (\text{A1.44})$$

$$R_{\text{HCO}_3^-}^{13\text{C}} = \frac{n_{\text{H}^{13}\text{CO}_3^-} \left( 1 + \frac{n_{\text{D}^{13}\text{CO}_3^-}}{n_{\text{H}^{13}\text{CO}_3^-}} \right)}{n_{\text{HCO}_3^-} \left( 1 + \frac{n_{\text{DCO}_3^-}}{n_{\text{HCO}_3^-}} \right)} = \frac{n_{\text{H}^{13}\text{CO}_3^-}}{n_{\text{HCO}_3^-}}, \text{ and} \quad (\text{A1.45})$$

$$\begin{aligned}
R_{HCO_3aq}^{13C} &= \frac{m_{H^{13}CO_3aq}^-}{m_{HCO_3aq}^-} = \frac{n_{H^{13}CO_2^{18}O_{aq}}^-}{n_{HCO_2^{18}O_{aq}}^-} = \frac{n_{H^{13}CO^{18}O_{2aq}}^-}{n_{HCO^{18}O_{2aq}}^-} = \frac{n_{H^{13}C^{18}O_{3aq}}^-}{n_{HC^{18}O_{3aq}}^-} \\
&= \frac{m_{D^{13}CO_3aq}^-}{m_{DCO_3aq}^-} = \frac{n_{D^{13}CO_2^{18}O_{aq}}^-}{n_{DCO_2^{18}O_{aq}}^-} = \frac{n_{D^{13}CO^{18}O_{2aq}}^-}{n_{DCO^{18}O_{2aq}}^-} = \frac{n_{D^{13}C^{18}O_{3aq}}^-}{n_{DC^{18}O_{3aq}}^-} = \frac{n_{T^{13}C^{18}O_{3aq}}^-}{n_{TC^{18}O_{3aq}}^-}.
\end{aligned} \tag{A1.46}$$

### The $^2H/^1H$ isotope ratio

With similar algebra the deuterium isotope ratio is

$$\begin{aligned}
R_{HCO_3aq}^D &= \frac{n_{DCO_3aq}^-}{n_{HCO_3aq}^-} = \frac{n_{DCO_2^{18}O_{aq}}^-}{n_{HCO_2^{18}O_{aq}}^-} = \frac{n_{DCO^{18}O_{2aq}}^-}{n_{HCO^{18}O_{2aq}}^-} = \frac{n_{DC^{18}O_{3aq}}^-}{n_{HC^{18}O_{3aq}}^-} \\
&= \frac{n_{D^{13}CO_3aq}^-}{n_{H^{13}CO_3aq}^-} = \frac{n_{D^{13}CO_2^{18}O_{aq}}^-}{n_{H^{13}CO_2^{18}O_{aq}}^-} = \frac{n_{D^{13}CO^{18}O_{2aq}}^-}{n_{H^{13}CO^{18}O_{2aq}}^-} = \frac{n_{D^{13}C^{18}O_{3aq}}^-}{n_{H^{13}C^{18}O_{3aq}}^-}.
\end{aligned} \tag{A1.47}$$

### Aqueous $CO_2$ —Bicarbonate ion equilibrium

The oxygen-18 isotope ratios are, from equations A1.19, A1.32, and A1.41:

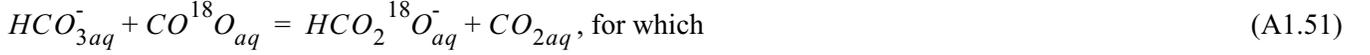
$$R_{HCO_3aq}^{18O} = \left( \frac{n_{HCO_2^{18}O_{aq}}^-}{3n_{HCO_3aq}^-} \right) qq1 \quad R_{HCO_3aq}^{18O} = \left( \frac{n_{HCO_2^{18}O_{aq}}^-}{3n_{HCO_3aq}^-} \right)^{\frac{1}{2}} qq2 \quad R_{HCO_3aq}^{18O} = \left( \frac{n_{HC^{18}O_{3aq}}^-}{n_{HCO_3aq}^-} \right)^{\frac{1}{3}} qq3. \tag{A1.48}$$

### Reaction to $HCO_2^{18}O_{aq}^-$

$$\alpha_{HCO_3aq-CO_{2aq}}^{18O} = \frac{\left( \frac{n_{HCO_2^{18}O_{aq}}^-}{3n_{HCO_3aq}^-} \right) qq1}{\left( \frac{n_{CO^{18}O_{aq}}^-}{2n_{CO_{2aq}}} \right)}, \text{ or} \tag{A1.49}$$

$$\alpha_{HCO_3^- - CO_2}^{18O} = \frac{\left(\frac{n}{3n} \frac{HCO_2^{18}O_{aq}^-}{HCO_3^-}\right) qq1}{\left(\frac{n}{2n} \frac{CO^{18}O_{aq}}{CO_2}\right)} = \frac{1}{\left(\frac{3}{2}\right)} \left(\frac{m}{m} \frac{HCO_2^{18}O_{aq}^-}{HCO_3^-} \frac{m}{m} \frac{CO_2}{CO^{18}O_{aq}}\right) qq1 . \quad (A1.50)$$

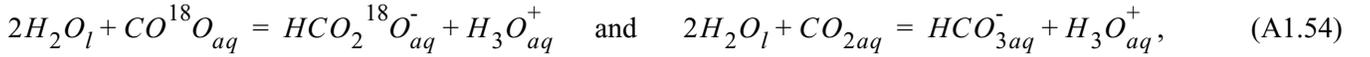
The isotope exchange reaction is



$$K_{HCO_2^{18}O_{aq}^-}^{ex} = \frac{a_{HCO_2^{18}O_{aq}^-} a_{CO_2}}{a_{HCO_3^-} a_{CO^{18}O_{aq}}} = \frac{m_{HCO_2^{18}O_{aq}^-} m_{CO_2} \gamma_{HCO_2^{18}O_{aq}^-} \gamma_{CO_2}}{m_{HCO_3^-} m_{CO^{18}O_{aq}} \gamma_{HCO_3^-} \gamma_{CO^{18}O_{aq}}}, \text{ or} \quad (A1.52)$$

$$K_{HCO_2^{18}O_{aq}^-}^{ex} = \left(\alpha_{HCO_3^- - CO_2}^{18O}\right) \left(\frac{3}{2}\right) \left(\frac{\gamma_{HCO_2^{18}O_{aq}^-} \gamma_{CO_2}}{\gamma_{HCO_3^-} \gamma_{CO^{18}O_{aq}}}\right) \left(\frac{1}{qq1}\right). \quad (A1.53)$$

The PHREEQC species and reference reactions are, respectively,



which, combined with equation A1.52, yield

$$K_{HCO_2^{18}O_{aq}^-}^{ex} = \frac{a_{HCO_2^{18}O_{aq}^-} a_{CO_2}}{a_{CO^{18}O_{aq}} a_{HCO_3^-}} = \left(\frac{a_{HCO_2^{18}O_{aq}^-} a_{H_3O_{aq}^+}}{a_{CO^{18}O_{aq}} a_{H_2O_l}}\right) \left(\frac{a_{CO_2} a_{H_2O_l}^2}{a_{HCO_3^-} a_{H_3O_{aq}^+}}\right) = \frac{K_{HCO_2^{18}O_{aq}^-}}{K_{HCO_3^-}}, \text{ or} \quad (A1.55)$$

$$K_{HCO_2^{18}O_{aq}^-} = K_{HCO_3^-} K_{HCO_2^{18}O_{aq}^-}^{ex}. \quad (A1.56)$$

$$\text{Thus, } K_{HCO_2^{18}O_{aq}^-} = K_{HCO_3^-} \left(\alpha_{HCO_3^- - CO_2}^{18O}\right) \left(\frac{3}{2}\right) \left(\frac{\gamma_{HCO_2^{18}O_{aq}^-} \gamma_{CO_2}}{\gamma_{HCO_3^-} \gamma_{CO^{18}O_{aq}}}\right) \left(\frac{1}{qq1}\right). \quad (A1.57)$$

$$\text{Defining } QQ1 = \frac{1}{qq1}, \quad (A1.58)$$

substituting in equation A1.57, and taking logarithms gives

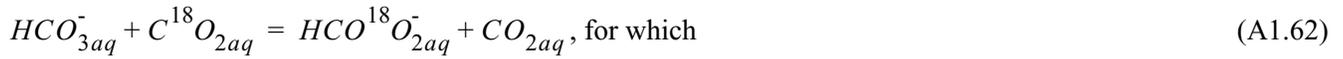
$$\log K_{HCO_2^{18}O_{aq}^-} = \log K_{HCO_3^-} + \log(1.5) + \log\left(\alpha_{HCO_3^- - CO_2}^{18O}\right) + \log(QQ1) + \log\left(\frac{\gamma_{HCO_2^{18}O_{aq}^-} \gamma_{CO_2}}{\gamma_{HCO_3^-} \gamma_{CO^{18}O_{aq}}}\right)_{exp}. \quad (A1.59)$$

Reaction to  $HCO^{18}O_{2aq}^-$

$$R_{HCO_{3aq}^-}^{18O} = \left( \frac{n_{HCO_{2aq}^{18O}^-}}{3n_{HCO_{3aq}^-}} \right)^{\frac{1}{2}} qq2, \text{ or} \quad (A1.60)$$

$$\left( \alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O} \right)^2 = \frac{\left( \frac{n_{HCO_{2aq}^{18O}^-}}{3n_{HCO_{3aq}^-}} \right) (qq2)^2}{\left( \frac{n_{C^{18}O_{2g}}}{n_{CO_{2g}}} \right)} = \left( \frac{1}{3} \right) \left( \frac{m_{HCO_{2aq}^{18O}^-} m_{CO_{2g}}}{m_{HCO_{3aq}^-} m_{C^{18}O_{2g}}} \right) (qq2)^2. \quad (A1.61)$$

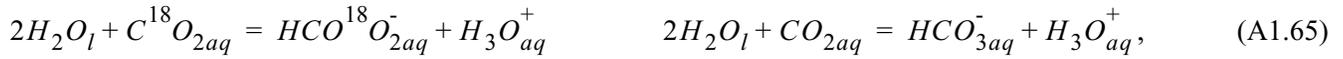
The isotope exchange reaction is



$$K_{HCO_{2aq}^{18O}}^{ex} = \frac{a_{HCO_{2aq}^{18O}^-} a_{CO_{2aq}}}{a_{HCO_{3aq}^-} a_{C^{18}O_{2aq}}} = \frac{m_{HCO_{2aq}^{18O}^-} m_{CO_{2aq}} \gamma_{HCO_{2aq}^{18O}^-} \gamma_{CO_{2aq}}}{m_{HCO_{3aq}^-} m_{C^{18}O_{2aq}} \gamma_{HCO_{3aq}^-} \gamma_{C^{18}O_{2aq}}}, \text{ or} \quad (A1.63)$$

$$K_{HCO_{2aq}^{18O}}^{ex} = \frac{a_{HCO_{2aq}^{18O}^-} a_{CO_{2aq}}}{a_{HCO_{3aq}^-} a_{C^{18}O_{2aq}}} = \left( \alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O} \right)^2 (3) \left( \frac{\gamma_{HCO_{2aq}^{18O}^-} \gamma_{CO_{2aq}}}{\gamma_{HCO_{3aq}^-} \gamma_{C^{18}O_{2aq}}} \right)_{exp} \left( \frac{1}{[qq2]^2} \right). \quad (A1.64)$$

The PHREEQC species and reference reactions are, respectively,



which, combined with equation A1.63, yield

$$K_{HCO_{2aq}^{18O}}^{ex} = \frac{a_{HCO_{2aq}^{18O}^-} a_{CO_{2aq}}}{a_{C^{18}O_{2aq}} a_{HCO_{3aq}^-}} = \left( \frac{a_{HCO_{2aq}^{18O}^-} a_{H_3O_{aq}^+}}{a_{C^{18}O_{2aq}} a_{H_2O_l}^2} \right) \left( \frac{a_{CO_{2aq}} a_{H_2O_l}^2}{a_{HCO_{3aq}^-} a_{H_3O_{aq}^+}} \right) = \frac{K_{HCO_{2aq}^{18O}}}{K_{HCO_{3aq}^-}}, \text{ or} \quad (A1.66)$$

$$K_{HCO_{2aq}^{18O}} = K_{HCO_{3aq}^-} K_{HCO_{2aq}^{18O}}^{ex}.$$

$$\text{Thus, } K_{HCO_{2aq}^{18O}} = K_{HCO_{3aq}^-} \left( \alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O} \right)^2 (3) \left( \frac{\gamma_{HCO_{2aq}^{18O}^-} \gamma_{CO_{2aq}}}{\gamma_{HCO_{3aq}^-} \gamma_{C^{18}O_{2aq}}} \right)_{exp} \left( \frac{1}{[qq2]^2} \right). \quad (A1.67)$$

$$\text{Defining } QQ2 = \frac{1}{[qq2]^2}, \quad (A1.68)$$

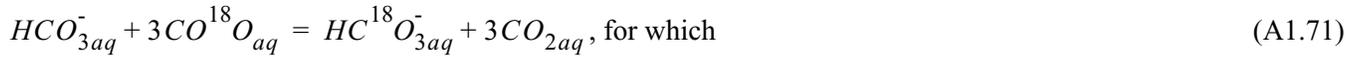
substituting in equation A1.67, and taking logarithms gives

$$\log K_{HCO^{18}O_{2aq}^-} = \log K_{HCO_{3aq}^-} + \log(3) + 2\log\left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O}\right) + \log(QQ2) + \log\left(\frac{\gamma_{HCO^{18}O_{2aq}^-} \gamma_{CO_{2aq}}}{\gamma_{HCO_{3aq}^-} \gamma_{C^{18}O_{2aq}}}\right)_{exp}. \quad (A1.69)$$

**Reaction to  $HC^{18}O_{3aq}^-$**

$$\left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O}\right)^3 = \frac{\left(\frac{n_{HC^{18}O_{3aq}^-}}{n_{HCO_{3aq}^-}}\right) qq3}{\left(\frac{n_{CO^{18}O_{aq}}}{2n_{CO_{2aq}}}\right)^3} = \frac{m_{HC^{18}O_{3aq}^-} m_{CO_{2aq}}^3}{\left(\frac{1}{2}\right)^3 m_{HCO_{3aq}^-} m_{CO^{18}O_{aq}}^3} (qq3)^3. \quad (A1.70)$$

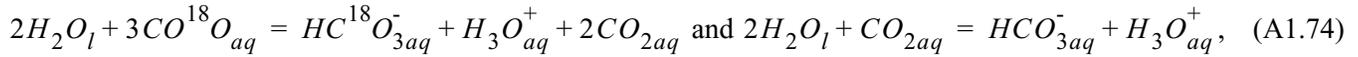
The isotope exchange reaction is



$$K_{HC^{18}O_{3aq}^-}^{ex} = \frac{a_{HC^{18}O_{3aq}^-} a_{CO_{2aq}}^3}{a_{HCO_{3aq}^-} a_{CO^{18}O_{aq}}^3} = \frac{m_{HC^{18}O_{3aq}^-} m_{CO_{2aq}}^3 \gamma_{HC^{18}O_{3aq}^-} \gamma_{CO_{2aq}}^3}{m_{HCO_{3aq}^-} m_{CO^{18}O_{aq}}^3 \gamma_{HCO_{3aq}^-} \gamma_{CO^{18}O_{aq}}^3}, \text{ or} \quad (A1.72)$$

$$K_{HC^{18}O_{3aq}^-}^{ex} = \left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O}\right)^3 \left(\frac{1}{2}\right)^3 \left(\frac{\gamma_{HC^{18}O_{3aq}^-} \gamma_{CO_{2aq}}^3}{\gamma_{HCO_{3aq}^-} \gamma_{CO^{18}O_{aq}}^3}\right)_{exp} \left(\frac{1}{[qq3]^3}\right). \quad (A1.73)$$

The PHREEQC species and reference reactions are, respectively,



which, combined with equation A1.72, yield

$$K_{HC^{18}O_{3aq}^-}^{ex} = \frac{a_{HC^{18}O_{3aq}^-} a_{CO_{2aq}}^3}{a_{HCO_{3aq}^-} a_{CO^{18}O_{aq}}^3} = \left(\frac{a_{HC^{18}O_{3aq}^-} a_{CO_{2aq}}^2 a_{H_3O_{aq}^+}}{a_{CO^{18}O_{aq}}^3 a_{H_2O_l}^2}\right) \left(\frac{a_{CO_{2aq}} a_{H_2O_l}^2}{a_{HCO_{3aq}^-} a_{H_3O_{aq}^+}}\right) = \frac{K_{HC^{18}O_{3aq}^-}}{K_{HCO_{3aq}^-}}, \text{ or} \quad (A1.75)$$

$$K_{HC^{18}O_{3aq}^-} = K_{HCO_{3aq}^-} K_{HC^{18}O_{3aq}^-}^{ex}. \quad (A1.76)$$

$$\text{Thus, } K_{HC^{18}O_{3aq}^-} = K_{HCO_{3aq}^-} \left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O}\right)^3 \left(\frac{1}{2}\right)^3 \left(\frac{\gamma_{HC^{18}O_{3aq}^-} \gamma_{CO_{2aq}}^3}{\gamma_{HCO_{3aq}^-} \gamma_{CO^{18}O_{aq}}^3}\right)_{exp} \left(\frac{1}{[qq3]^3}\right). \quad (A1.77)$$

$$\text{Defining } QQ3 = \left( \frac{1}{[qq3]^3} \right), \quad (\text{A1.78})$$

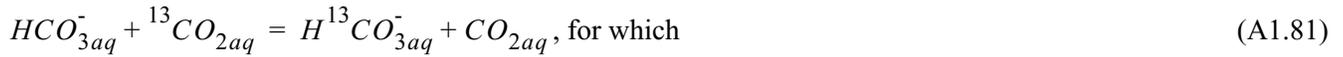
substituting in equation A1.77, and taking logarithms gives

$$\begin{aligned} \log K_{HC^{18}O_{3aq}^-} &= \log K_{HCO_{3aq}^-} - 3\log(2) + 3\log\left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O}\right) + \\ &\log(QQ3) + \log\left(\frac{\gamma_{HC^{18}O_{3aq}^-} \gamma_{CO_{2aq}}^3}{\gamma_{HCO_{3aq}^-} \gamma_{CO^{18}O_{aq}}^3}\right)_{exp}. \end{aligned} \quad (\text{A1.79})$$

**Reaction to  $H^{13}CO_{3aq}^-$**

$$\left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{13C}\right) = \frac{\left(\frac{n_{H^{13}CO_{3aq}^-}}{n_{HCO_{3aq}^-}}\right)}{\left(\frac{n_{13CO_{2aq}}}{n_{CO_{2aq}}}\right)} = \frac{m_{H^{13}CO_{3aq}^-} m_{CO_{2aq}}}{m_{HCO_{3aq}^-} m_{13CO_{2aq}}}. \quad (\text{A1.80})$$

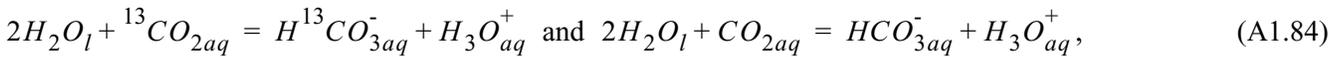
The isotope exchange reaction is



$$K_{H^{13}CO_{3aq}^-}^{ex} = \frac{a_{H^{13}CO_{3aq}^-} a_{CO_{2aq}}}{a_{HCO_{3aq}^-} a_{13CO_{2aq}}} = \frac{m_{H^{13}CO_{3aq}^-} m_{CO_{2aq}} \gamma_{H^{13}CO_{3aq}^-} \gamma_{CO_{2aq}}}{m_{HCO_{3aq}^-} m_{13CO_{2aq}} \gamma_{HCO_{3aq}^-} \gamma_{13CO_{2aq}}}, \text{ or} \quad (\text{A1.82})$$

$$K_{H^{13}CO_{3aq}^-}^{ex} = \frac{a_{H^{13}CO_{3aq}^-} a_{CO_{2aq}}}{a_{HCO_{3aq}^-} a_{13CO_{2aq}}} = \left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O}\right) \left(\frac{\gamma_{H^{13}CO_{3aq}^-} \gamma_{CO_{2aq}}}{\gamma_{HCO_{3aq}^-} \gamma_{13CO_{2aq}}}\right)_{exp}. \quad (\text{A1.83})$$

The PHREEQC species and reference reactions are, respectively,



which, combined with equation A1.82, yield

$$K_{H^{13}CO_{3aq}^-}^{ex} = \frac{a_{H^{13}CO_{3aq}^-} a_{CO_{2aq}}}{a_{HCO_{3aq}^-} a_{13CO_{2aq}}} = \left(\frac{a_{H^{13}CO_{3aq}^-} a_{H_3O_{aq}^+}}{a_{13CO_{2aq}} a_{H_2O_l}^2}\right) \left(\frac{a_{CO_{2aq}} a_{H_2O_l}^2}{a_{HCO_{3aq}^-} a_{H_3O_{aq}^+}}\right) = \frac{K_{H^{13}CO_{3aq}^-}}{K_{HCO_{3aq}^-}}. \quad (\text{A1.85})$$

$$\text{Thus, } K_{H^{13}CO_3^-} = K_{HCO_3^-} K_{H^{13}CO_3^-}^{ex} = K_{HCO_3^-} \left( \alpha_{HCO_3^- - CO_2aq}^{13C} \right) \left( \frac{\gamma_{H^{13}CO_3^-} \gamma_{CO_2aq}}{\gamma_{HCO_3^-} \gamma_{^{13}CO_2aq}} \right)_{exp}. \quad (A1.86)$$

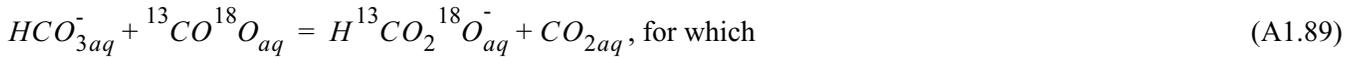
Taking logarithms gives

$$\log K_{H^{13}CO_3^-} = \log K_{HCO_3^-} + \log \left( \alpha_{HCO_3^- - CO_2aq}^{13C} \right) + \log \left( \frac{\gamma_{H^{13}CO_3^-} \gamma_{CO_2aq}}{\gamma_{HCO_3^-} \gamma_{^{13}CO_2aq}} \right)_{exp}. \quad (A1.87)$$

**Reaction to  $H^{13}CO_2^{18}O_{aq}^-$**

$$\begin{aligned} \left( \alpha_{HCO_3^- - CO_2aq}^{18O} \right) \left( \alpha_{HCO_3^- - CO_2aq}^{13C} \right) &= \frac{\left( \frac{n_{H^{13}CO_2^{18}O_{aq}^-}}{3n_{H^{13}CO_3^-}} \right) (qq1) \left( \frac{n_{H^{13}CO_3^-}}{n_{HCO_3^-}} \right)}{\left( \frac{n_{^{13}CO^{18}O_{aq}}}{2n_{^{13}CO_2aq}} \right) \left( \frac{n_{^{13}CO_2aq}}{n_{CO_2aq}} \right)} \\ &= \frac{m_{H^{13}CO_2^{18}O_{aq}^-} m_{CO_2aq}}{\left( \frac{3}{2} \right) m_{HCO_3^-} m_{^{13}CO^{18}O_{aq}}} (qq1). \end{aligned} \quad (A1.88)$$

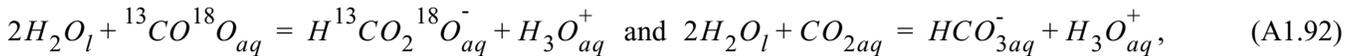
The isotope exchange reaction is



$$K_{H^{13}CO_2^{18}O_{aq}^-}^{ex} = \frac{a_{H^{13}CO_2^{18}O_{aq}^-} a_{CO_2aq}}{a_{HCO_3^-} a_{^{13}CO^{18}O_{aq}}} = \frac{m_{H^{13}CO_2^{18}O_{aq}^-} m_{CO_2aq}}{m_{HCO_3^-} m_{^{13}CO^{18}O_{aq}}} \frac{\gamma_{H^{13}CO_2^{18}O_{aq}^-} \gamma_{CO_2aq}}{\gamma_{HCO_3^-} \gamma_{^{13}CO^{18}O_{aq}}}, \text{ or} \quad (A1.90)$$

$$K_{H^{13}CO_2^{18}O_{aq}^-}^{ex} = \left( \frac{3}{2} \right) \left( \alpha_{HCO_3^- - CO_2aq}^{13C} \right) \left( \alpha_{HCO_3^- - CO_2aq}^{18O} \right) \left( \frac{\gamma_{H^{13}CO_2^{18}O_{aq}^-} \gamma_{CO_2aq}}{\gamma_{HCO_3^-} \gamma_{^{13}CO^{18}O_{aq}}} \right)_{exp} \left( \frac{1}{qq1} \right). \quad (A1.91)$$

The PHREEQC species and reference reactions are, respectively,



which, combined with equation A1.90, yield

$$K_{H^{13}CO_2^{18}O_{aq}^-}^{ex} = \frac{a_{H^{13}CO_2^{18}O_{aq}^-} a_{CO_2aq}}{a_{HCO_3^-} a_{^{13}CO^{18}O_{aq}}}$$

$$= \left( \frac{a_{H^{13}CO_2^{18}O_{aq}^-} a_{H_3O_{aq}^+}}{a_{^{13}CO^{18}O_{aq}^-} a_{H_2O_l}^2} \right) \left( \frac{a_{CO_{2aq}} a_{H_2O_l}^2}{a_{HCO_{3aq}^-} a_{H_3O_{aq}^+}} \right) = \frac{K_{H^{13}CO_2^{18}O_{aq}^-}}{K_{HCO_{3aq}^-}}. \quad (A1.93)$$

$$\text{Thus, } K_{H^{13}CO_2^{18}O_{aq}^-} = K_{HCO_{3aq}^-} \left( \frac{3}{2} \right) \left( \alpha_{HCO_{3aq}^- - CO_{2aq}}^{^{13}C} \right) \left( \alpha_{HCO_{3aq}^- - CO_{2aq}}^{^{18}O} \right) \times \left( \frac{\gamma_{H^{13}CO_2^{18}O_{aq}^-} \gamma_{CO_{2aq}}}{\gamma_{HCO_{3aq}^-} \gamma_{^{13}CO^{18}O_{aq}^-}} \right)_{exp} \left( \frac{1}{qq1} \right). \quad (A1.94)$$

$$\text{Defining } QQ1 = \left( \frac{1}{qq1} \right), \quad (A1.95)$$

substituting in equation A1.94, and taking logarithms gives

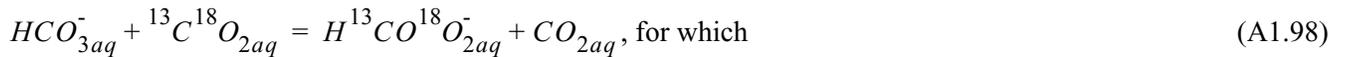
$$\log K_{H^{13}CO_2^{18}O_{aq}^-} = \log K_{HCO_{3aq}^-} + \log(1.5) + \log \left( \alpha_{HCO_{3aq}^- - CO_{2aq}}^{^{13}C} \right) + \log \left( \alpha_{HCO_{3aq}^- - CO_{2aq}}^{^{18}O} \right) + \log \left( \frac{\gamma_{H^{13}CO_2^{18}O_{aq}^-} \gamma_{CO_{2aq}}}{\gamma_{HCO_{3aq}^-} \gamma_{^{13}CO^{18}O_{aq}^-}} \right)_{exp} + \log(QQ1). \quad (A1.96)$$

**Reaction to  $H^{13}CO^{18}O_{2aq}^-$**

$$\left( \alpha_{HCO_{3aq}^- - CO_{2aq}}^{^{18}O} \right)^2 \left( \alpha_{HCO_{3aq}^- - CO_{2aq}}^{^{13}C} \right) = \frac{\left( \frac{n_{H^{13}CO^{18}O_{2aq}^-}}{3n_{H^{13}CO_{3aq}^-}} \right) ([qq2]^2) \left( \frac{n_{H^{13}CO_{3aq}^-}}{n_{HCO_{3aq}^-}} \right)}{\left( \frac{n_{^{13}C^{18}O_{2aq}}}{n_{^{13}CO_{2aq}}} \right) \left( \frac{n_{^{13}CO_{2aq}}}{n_{CO_{2aq}}} \right)}$$

$$= \frac{\left( \frac{1}{3} \right)^m m_{H^{13}CO^{18}O_{2aq}^-} m_{CO_{2aq}}}{m_{HCO_{3aq}^-} m_{^{13}C^{18}O_{2aq}}} ([qq2]^2). \quad (A1.97)$$

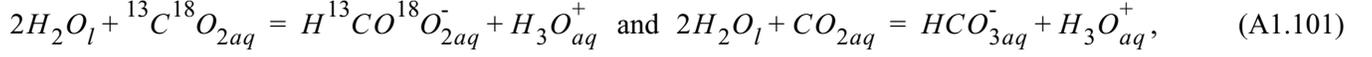
The isotope exchange reaction is



$$K_{H^{13}CO^{18}O_{2aq}^-}^{ex} = \frac{a_{H^{13}CO^{18}O_{2aq}^-} a_{CO_{2aq}}}{a_{HCO_{3aq}^-} a_{^{13}C^{18}O_{2aq}}} = \frac{m_{H^{13}CO^{18}O_{2aq}^-} m_{CO_{2aq}}}{m_{HCO_{3aq}^-} m_{^{13}C^{18}O_{2aq}}} \frac{\gamma_{H^{13}CO^{18}O_{2aq}^-} \gamma_{CO_{2aq}}}{\gamma_{HCO_{3aq}^-} \gamma_{^{13}C^{18}O_{2aq}}}, \text{ or} \quad (A1.99)$$

$$K_{H^{13}CO^{18}O_{2aq}^-}^{ex} = (3) \left( \alpha_{HCO_{3aq}^- - CO_{2aq}}^{13C} \right) \left( \alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O} \right)^2 \left( \frac{\gamma_{H^{13}CO^{18}O_{2aq}^-} \gamma_{CO_{2aq}}}{\gamma_{HCO_{3aq}^-} \gamma_{^{13}C^{18}O_{2aq}}} \right)_{exp} \left( \frac{1}{[qq2]^2} \right). \quad (A1.100)$$

The PHREEQC species and reference reactions are, respectively,



which, combined with equation A1.99, yield

$$\begin{aligned} K_{H^{13}CO^{18}O_{2aq}^-}^{ex} &= \frac{a_{H^{13}CO^{18}O_{2aq}^-} a_{CO_{2aq}}}{a_{HCO_{3aq}^-} a_{^{13}C^{18}O_{2aq}}} \\ &= \left( \frac{a_{H^{13}CO^{18}O_{2aq}^-} a_{H_3O_{aq}^+}}{a_{^{13}C^{18}O_{2aq}} a_{H_2O_l}^2} \right) \left( \frac{a_{CO_{2aq}} a_{H_2O_l}^2}{a_{HCO_{3aq}^-} a_{H_3O_{aq}^+}} \right) = \frac{K_{H^{13}CO^{18}O_{2aq}^-}}{K_{HCO_{3aq}^-}}. \end{aligned} \quad (A1.102)$$

$$\begin{aligned} \text{Thus, } K_{H^{13}CO^{18}O_{2aq}^-} &= K_{HCO_{3aq}^-} (3) \left( \alpha_{HCO_{3aq}^- - CO_{2aq}}^{13C} \right) \left( \alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O} \right)^2 \times \\ &\quad \left( \frac{\gamma_{H^{13}CO^{18}O_{2aq}^-} \gamma_{CO_{2aq}}}{\gamma_{HCO_{3aq}^-} \gamma_{^{13}C^{18}O_{2aq}}} \right)_{exp} \left( \frac{1}{[qq2]^2} \right). \end{aligned} \quad (A1.103)$$

$$\text{Defining } QQ2 = \left( \frac{1}{[qq2]^2} \right), \quad (A1.104)$$

substituting in equation A1.103, and taking logarithms gives

$$\begin{aligned} \log K_{H^{13}CO^{18}O_{2aq}^-} &= \log K_{HCO_{3aq}^-} + \log(3) + \log \left( \alpha_{HCO_{3aq}^- - CO_{2aq}}^{13C} \right) + \\ &\quad 2 \log \left( \alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O} \right) + \log \left( \frac{\gamma_{H^{13}CO^{18}O_{2aq}^-} \gamma_{CO_{2aq}}}{\gamma_{HCO_{3aq}^-} \gamma_{^{13}C^{18}O_{2aq}}} \right)_{exp} + \log(QQ2). \end{aligned} \quad (A1.105)$$

**Reaction to  $H^{13}C^{18}O_{3aq}^-$**

$$\left( \alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O} \right)^3 \left( \alpha_{HCO_{3aq}^- - CO_{2aq}}^{13C} \right) = \frac{\left( \frac{n_{H^{13}C^{18}O_{3aq}^-}}{n_{H^{13}CO_{3aq}^-}} \right) ([qq3]^3) \left( \frac{n_{H^{13}CO_{3aq}^-}}{n_{HCO_{3aq}^-}} \right)}{\left( \frac{n_{CO^{18}O_{aq}}}{2n_{CO_{2aq}}} \right)^3 \left( \frac{n_{^{13}CO_{2aq}}}{n_{CO_{2aq}}} \right)}$$

$$= \frac{\left(\frac{m_{H^{13}C^{18}O_{3aq}^-}}{m_{HCO_{3aq}^-}}\right)}{\left(\frac{1}{2}\right)^3 \left(\frac{m_{CO^{18}O_{aq}}}{m_{CO_{2aq}}}\right)^3 \left(\frac{m_{^{13}CO_{2aq}}}{m_{CO_{2aq}}}\right)} ([qq3]^3) = \frac{1}{\left(\frac{1}{2}\right)^3} \left(\frac{m_{H^{13}C^{18}O_{3aq}^-}}{m_{HCO_{3aq}^-}}\right) \left(\frac{m_{CO_{2aq}}^4}{m_{CO^{18}O_{aq}}^3 m_{^{13}CO_{2aq}}}\right)^3 ([qq3]^3). \quad (A1.106)$$

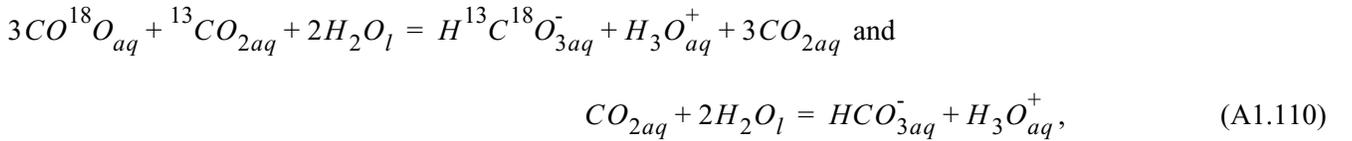
The isotope exchange reaction is



$$K_{H^{13}C^{18}O_{3aq}^-}^{ex} = \frac{a_{H^{13}C^{18}O_{3aq}^-} a_{CO_{2aq}}^4}{a_{HCO_{3aq}^-}^3 a_{CO^{18}O_{aq}} a_{^{13}CO_{2aq}}} = \frac{\gamma_{H^{13}C^{18}O_{3aq}^-} \gamma_{CO_{2aq}}^4}{\gamma_{HCO_{3aq}^-}^3 \gamma_{CO^{18}O_{aq}} \gamma_{^{13}CO_{2aq}}} \frac{m_{H^{13}C^{18}O_{3aq}^-} m_{CO_{2aq}}^4}{m_{HCO_{3aq}^-}^3 m_{CO^{18}O_{aq}} m_{^{13}CO_{2aq}}}, \text{ or} \quad (A1.108)$$

$$K_{H^{13}C^{18}O_{3aq}^-}^{ex} = \left(\frac{1}{2}\right)^3 \left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{^{18}O}\right)^3 \left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{^{13}C}\right) \times \left(\frac{\gamma_{H^{13}C^{18}O_{3aq}^-} \gamma_{CO_{2aq}}^4}{\gamma_{HCO_{3aq}^-}^3 \gamma_{CO^{18}O_{aq}} \gamma_{^{13}CO_{2aq}}}\right)_{exp} \left(\frac{1}{[qq3]^3}\right). \quad (A1.109)$$

The PHREEQC species and reference reactions are, respectively,



which, combined with equation A1.108, yield

$$K_{H^{13}C^{18}O_{3aq}^-}^{ex} = \left(\frac{a_{H^{13}C^{18}O_{3aq}^-} a_{CO_{2aq}}^3 a_{H_3O_{aq}^+}}{a_{CO^{18}O_{aq}}^3 a_{^{13}CO_{2aq}} a_{H_2O_l}^2}\right) \left(\frac{a_{CO_{2aq}} a_{H_2O_l}^2}{a_{HCO_{3aq}^-} a_{H_3O_{aq}^+}}\right) = \frac{K_{H^{13}C^{18}O_{3aq}^-}}{K_{HCO_{3aq}^-}}. \quad (A1.111)$$

$$\text{Thus, } K_{H^{13}C^{18}O_{3aq}^-} = K_{HCO_{3aq}^-} \left(\frac{1}{2}\right)^3 \left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{^{18}O}\right)^3 \left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{^{13}C}\right) \times \left(\frac{\gamma_{H^{13}C^{18}O_{3aq}^-} \gamma_{CO_{2aq}}^4}{\gamma_{HCO_{3aq}^-}^3 \gamma_{CO^{18}O_{aq}} \gamma_{^{13}CO_{2aq}}}\right)_{exp} \left(\frac{1}{[qq3]^3}\right). \quad (A1.112)$$

$$\text{Defining } QQ3 = \left( \frac{1}{[qq3]^3} \right), \quad (\text{A1.113})$$

substituting in equation A1.112, and taking logarithms gives

$$\begin{aligned} \log K_{H^{13}C^{18}O_{3aq}^-} &= \log K_{HCO_{3aq}^-} - 3\log 2 + \log \left( \alpha_{HCO_{3aq}^- - CO_{2aq}}^{13C} \right) + \\ &3\log \left( \alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O} \right) + \log \left( \frac{\gamma_{H^{13}C^{18}O_{3aq}^-} \gamma_{CO_{2aq}}^4}{\gamma_{HCO_{3aq}^-}^3 \gamma_{CO^{18}O_{aq}}^3 \gamma_{CO_{2aq}}^{13}} \right)_{exp} + \log(QQ3). \end{aligned} \quad (\text{A1.114})$$

### Reaction to $DCO_{3aq}^-$

$$\left( \alpha_{HCO_{3aq}^- - H_2O_l}^D \right) = \frac{\left( \frac{n_{DCO_{3aq}^-}}{n_{HCO_{3aq}^-}} \right)}{\left( \frac{n_{HDO_{aq}}}{2n_{H_2O_l}} \right)} = \frac{m_{DCO_{3aq}^-}}{\left( \frac{1}{2} \right) \left( \frac{m_{HDO_{aq}}}{55.5} \right) m_{HCO_{3aq}^-}}. \quad (\text{A1.115})$$

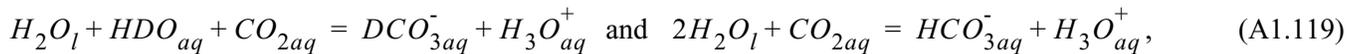
The isotope exchange reaction is



$$K_{DCO_{3aq}^-}^{ex} = \frac{a_{DCO_{3aq}^-} a_{H_2O_l}}{a_{HDO_{aq}} a_{HCO_{3aq}^-}} = \frac{\gamma_{DCO_{3aq}^-} a_{H_2O_l} m_{DCO_{3aq}^-}}{\left( \frac{a_{H_2O_l}}{55.5} \right) \gamma_{HCO_{3aq}^-} m_{HDO_{aq}} m_{HCO_{3aq}^-}} = \frac{\gamma_{DCO_{3aq}^-} m_{DCO_{3aq}^-}}{\gamma_{HCO_{3aq}^-} \left( \frac{m_{HDO_{aq}}}{55.5} \right) m_{HCO_{3aq}^-}}, \quad (\text{A1.117})$$

$$\text{or } K_{DCO_{3aq}^-}^{ex} = \left( \frac{\gamma_{DCO_{3aq}^-}}{\gamma_{HCO_{3aq}^-}} \right)_{exp} \left( \frac{1}{2} \right) \left( \alpha_{HCO_{3aq}^- - H_2O_l}^D \right). \quad (\text{A1.118})$$

The PHREEQC species and reference reactions are, respectively,



which, combined with equation A1.117, yield

$$K_{DCO_{3aq}^-}^{ex} = \frac{a_{DCO_{3aq}^-} a_{H_2O_l}}{a_{HDO_{aq}} a_{HCO_{3aq}^-}} = \left( \frac{a_{DCO_{3aq}^-} a_{H_3O_{aq}^+}}{a_{HDO_{aq}} a_{H_2O_l} a_{CO_{2aq}}} \right) \left( \frac{a_{H_2O_l} a_{H_2O_l} a_{CO_{2aq}}}{a_{HCO_{3aq}^-} a_{H_3O_{aq}^+}} \right) = \frac{K_{DCO_{3aq}^-}}{K_{HCO_{3aq}^-}}. \quad (\text{A1.120})$$

$$\text{Thus, } K_{DCO_3aq}^- = K_{HCO_3aq}^- K_{DCO_3aq}^{ex} = K_{HCO_3aq}^- \left(\frac{1}{2}\right) \left(\alpha_{HCO_3aq}^D - H_2O_l\right) \left(\frac{\gamma_{DCO_3aq}^-}{\gamma_{HCO_3aq}^-}\right)_{exp}. \quad (\text{A1.121})$$

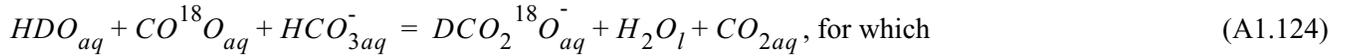
Taking logarithms gives

$$\log K_{DCO_3aq}^- = \log K_{HCO_3aq}^- - \log(2) + \log\left(\alpha_{HCO_3aq}^D - H_2O_l\right) + \log\left(\frac{\gamma_{DCO_3aq}^-}{\gamma_{HCO_3aq}^-}\right)_{exp}. \quad (\text{A1.122})$$

**Reaction to  $DCO_2^{18}O_{aq}^-$**

$$\begin{aligned} \left(\alpha_{HCO_3aq}^D - H_2O_l\right) \left(\alpha_{HCO_3aq}^{18O} - CO_{2aq}\right) &= \frac{\left(\frac{n_{DCO_2^{18}O_{aq}^-}}{n_{HCO_2^{18}O_{aq}^-}}\right) \left(\frac{n_{HCO_2^{18}O_{aq}^-}}{3n_{HCO_3aq}^-}\right) (qq1)}{\left(\frac{n_{HDO_{aq}}}{2n_{H_2O_l}}\right) \left(\frac{n_{CO^{18}O_{aq}}}{2n_{CO_{2aq}}}\right)} \\ &= \frac{m_{DCO_2^{18}O_{aq}^-} m_{CO_{2aq}}}{\left(\frac{3}{4}\right) m_{HCO_3aq}^- \left(\frac{m_{HDO_{aq}}}{55.5}\right) m_{CO^{18}O_{aq}}} (qq1). \end{aligned} \quad (\text{A1.123})$$

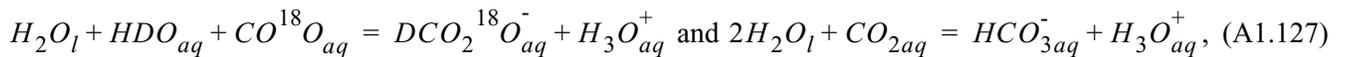
The isotope exchange reaction is



$$\begin{aligned} K_{DCO_2^{18}O_{aq}^-}^{ex} &= \frac{a_{DCO_2^{18}O_{aq}^-} a_{H_2O_l} a_{CO_{2aq}}}{a_{CO^{18}O_{aq}} a_{HDO_{aq}} a_{HCO_3aq}^-} = \frac{\gamma_{DCO_2^{18}O_{aq}^-} a_{H_2O_l} \gamma_{CO_{2aq}}}{\gamma_{CO^{18}O_{aq}} \left(\frac{a_{H_2O_l}}{55.5}\right) \gamma_{HCO_3aq}^-} \frac{m_{DCO_2^{18}O_{aq}^-} m_{CO_{2aq}}}{m_{CO^{18}O_{aq}} m_{HDO_{aq}} m_{HCO_3aq}^-} \\ &= \frac{\gamma_{DCO_2^{18}O_{aq}^-} \gamma_{CO_{2aq}}}{\gamma_{CO^{18}O_{aq}} \gamma_{HCO_3aq}^-} \frac{m_{DCO_2^{18}O_{aq}^-} m_{CO_{2aq}}}{m_{CO^{18}O_{aq}} \left(\frac{m_{HDO_{aq}}}{55.5}\right) m_{HCO_3aq}^-}, \text{ or} \end{aligned} \quad (\text{A1.125})$$

$$K_{DCO_2^{18}O_{aq}^-}^{ex} = \left(\frac{3}{4}\right) \left(\alpha_{HCO_3aq}^D - H_2O_l\right) \left(\alpha_{HCO_3aq}^{18O} - CO_{2aq}\right) \left(\frac{\gamma_{DCO_2^{18}O_{aq}^-} \gamma_{CO_{2aq}}}{\gamma_{CO^{18}O_{aq}} \gamma_{HCO_3aq}^-}\right)_{exp} \left(\frac{1}{qq1}\right). \quad (\text{A1.126})$$

The PHREEQC species and reference reactions are



which, combined with equation A1.125, yield

$$K_{DCO_2^{18}O_{aq}^-}^{ex} = \left( \frac{a_{DCO_2^{18}O_{aq}^-} a_{H_3O_{aq}^+}}{a_{HDO_{aq}} a_{CO^{18}O_{aq}}} \right) \left( \frac{a_{CO_{2aq}} a_{H_2O_l} a_{H_2O_l}}{a_{HCO_{3aq}^-} a_{H_3O_{aq}^+}} \right) = \frac{K_{DCO_2^{18}O_{aq}^-}}{K_{HCO_{3aq}^-}}. \quad (A1.128)$$

Thus,

$$K_{DCO_2^{18}O_{aq}^-} = K_{HCO_{3aq}^-} \left( \frac{3}{4} \right) \left( \alpha_{HCO_{3aq}^- - H_2O_l}^D \right) \left( \alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O} \right) \left( \frac{\gamma_{DCO_2^{18}O_{aq}^-} \gamma_{CO_{2aq}}}{\gamma_{CO^{18}O_{aq}} \gamma_{HCO_{3aq}^-}} \right)_{exp} \left( \frac{1}{qq1} \right). \quad (A1.129)$$

$$\text{Defining } QQ1 = \left( \frac{1}{qq1} \right), \quad (A1.130)$$

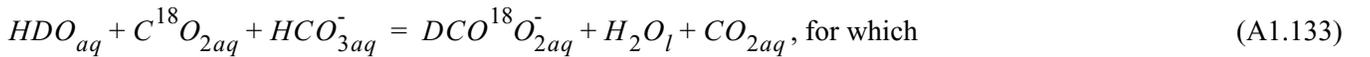
substituting in equation A1.129, and taking logarithms gives

$$\begin{aligned} \log K_{DCO_2^{18}O_{aq}^-} &= \log K_{HCO_{3aq}^-} + \log(0.75) + \log \left( \alpha_{HCO_{3aq}^- - H_2O_l}^D \right) + \\ &\log \left( \alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O} \right) + \log \left( \frac{\gamma_{DCO_2^{18}O_{aq}^-} \gamma_{CO_{2aq}}}{\gamma_{CO^{18}O_{aq}} \gamma_{HCO_{3aq}^-}} \right)_{exp} + \log(QQ1). \end{aligned} \quad (A1.131)$$

### Reaction to $DCO^{18}O_{2aq}^-$

$$\begin{aligned} \left( \alpha_{HCO_{3aq}^- - H_2O_l}^D \right) \left( \alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O} \right)^2 &= \frac{\left( \frac{n_{DCO^{18}O_{2aq}^-}}{n_{HCO^{18}O_{2aq}^-}} \right) \left( \frac{n_{HCO^{18}O_{2aq}^-}}{3n_{HCO_{3aq}^-}} \right) ([qq2]^2)}{\left( \frac{n_{HDO_{aq}}}{2n_{H_2O_l}} \right) \left( \frac{n_{C^{18}O_{2aq}}}{n_{CO_{2aq}}} \right)} \\ &= \frac{m_{DCO^{18}O_{2aq}^-} m_{CO_{2aq}}}{\left( \frac{3}{2} \right) m_{HCO_{3aq}^-} \left( \frac{m_{HDO_{aq}}}{55.5} \right) m_{C^{18}O_{2aq}}} ([qq2]^2). \end{aligned} \quad (A1.132)$$

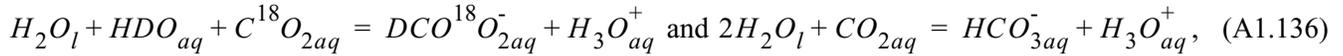
The isotope exchange reaction is



$$K_{DCO^{18}O_{2aq}^-}^{ex} = \frac{a_{DCO^{18}O_{2aq}^-} a_{H_2O_l} a_{CO_{2aq}}}{a_{C^{18}O_{2aq}} a_{HDO_{aq}} a_{HCO_{3aq}^-}} = \frac{\gamma_{DCO^{18}O_{2aq}^-} a_{H_2O_l} \gamma_{CO_{2aq}}}{\gamma_{C^{18}O_{2aq}} \left( \frac{a_{H_2O_l}}{55.5} \right) \gamma_{HCO_{3aq}^-}} \frac{m_{DCO^{18}O_{2aq}^-} m_{CO_{2aq}}}{m_{C^{18}O_{2aq}} m_{HDO_{aq}} m_{HCO_{3aq}^-}}, \text{ or} \quad (A1.134)$$

$$\begin{aligned}
K_{DCO^{18}O_{2aq}}^{ex} &= \frac{\gamma_{DCO^{18}O_{2aq}} \gamma_{CO_{2aq}} m_{DCO^{18}O_{2aq}} m_{CO_{2aq}}}{\gamma_{C^{18}O_{2aq}} \gamma_{HCO_{3aq}^-} m_{C^{18}O_{2aq}} \left(\frac{m_{HDO_{aq}}}{55.5}\right) m_{HCO_{3aq}^-}} \\
&= \left(\frac{3}{2}\right) \left(\alpha_{HCO_{3aq}^- - H_2O_l}^D\right) \left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O}\right)^2 \left(\frac{\gamma_{DCO^{18}O_{2aq}} \gamma_{CO_{2aq}}}{\gamma_{C^{18}O_{2aq}} \gamma_{HCO_{3aq}^-}}\right)_{exp} \left(\frac{1}{[qq2]^2}\right). \tag{A1.135}
\end{aligned}$$

The PHREEQC species and reference reactions are, respectively,



which, combined with equation A1.134, yield

$$K_{DCO^{18}O_{2aq}}^{ex} = \left(\frac{a_{DCO^{18}O_{2aq}^-} a_{H_3O_{aq}^+}}{a_{HDO_{aq}} a_{C^{18}O_{2aq}} a_{H_2O_l}}\right) \left(\frac{a_{CO_{2aq}} a_{H_2O_l} a_{H_2O_l}}{a_{HCO_{3aq}^-} a_{H_3O_{aq}^+}}\right) = \frac{K_{DCO^{18}O_{2aq}^-}}{K_{HCO_{3aq}^-}}. \tag{A1.137}$$

$$\begin{aligned}
\text{Thus, } K_{DCO^{18}O_{2aq}} &= K_{HCO_{3aq}^-} \left(\frac{3}{2}\right) \left(\alpha_{HCO_{3aq}^- - H_2O_l}^D\right) \left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O}\right)^2 \times \\
&\quad \left(\frac{\gamma_{DCO^{18}O_{2aq}} \gamma_{CO_{2aq}}}{\gamma_{C^{18}O_{2aq}} \gamma_{HCO_{3aq}^-}}\right)_{exp} \left(\frac{1}{[qq2]^2}\right). \tag{A1.138}
\end{aligned}$$

$$\text{Defining } QQ2 = \left(\frac{1}{[qq2]^2}\right), \tag{A1.139}$$

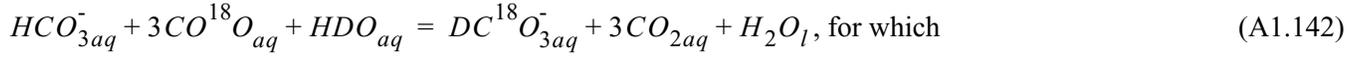
substituting in equation A1.138, and taking logarithms gives

$$\begin{aligned}
\log K_{DCO^{18}O_{2aq}} &= \log K_{HCO_{3aq}^-} + \log(1.5) + \log\left(\alpha_{HCO_{3aq}^- - H_2O_l}^D\right) + \\
&\quad 2\log\left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O}\right) + \log\left(\frac{\gamma_{DCO^{18}O_{2aq}} \gamma_{CO_{2aq}}}{\gamma_{C^{18}O_{2aq}} \gamma_{HCO_{3aq}^-}}\right)_{exp} + \log(QQ2). \tag{A1.140}
\end{aligned}$$

Reaction to  $DC^{18}O_{3aq}^-$

$$\begin{aligned} \left(\alpha_{HCO_{3aq}^- - H_2O_l}^D\right) \left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O}\right)^3 &= \frac{\left(\frac{n_{DC^{18}O_{3aq}^-}}{n_{HC^{18}O_{3aq}^-}}\right) \left(\frac{n_{HC^{18}O_{3aq}^-}}{n_{HCO_{3aq}^-}}\right) ([qq3]^3)}{\left(\frac{n_{HDO_{aq}}}{2n_{H_2O_l}}\right) \left(\frac{n_{CO^{18}O_{aq}}}{2n_{CO_{2aq}}}\right)^3} \\ &= \frac{1}{\left(\frac{1}{2}\right)^4} \frac{1}{\left(\frac{m_{HDO_{aq}}}{55.5}\right)} \left(\frac{m_{DC^{18}O_{3aq}^-}}{m_{HCO_{3aq}^-}}\right) \left(\frac{m_{CO_{2aq}}^3}{m_{CO^{18}O_{aq}}^3}\right)^3 ([qq3]^3). \end{aligned} \quad (A1.141)$$

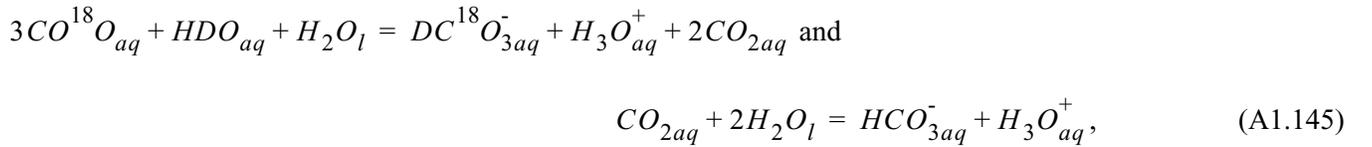
The isotope exchange reaction is



$$\begin{aligned} K_{DC^{18}O_{3aq}^-}^{ex} &= \frac{a_{DC^{18}O_{3aq}^-} a_{CO_{2aq}}^3 a_{H_2O_l}}{a_{HCO_{3aq}^-} a_{CO^{18}O_{aq}}^3 a_{HDO_{aq}}} \\ &= \frac{\gamma_{DC^{18}O_{3aq}^-} \gamma_{CO_{2aq}}^3 a_{H_2O_l} m_{DC^{18}O_{3aq}^-} m_{CO_{2aq}}^3}{\gamma_{HCO_{3aq}^-} \gamma_{CO^{18}O_{aq}}^3 \left(\frac{a_{H_2O_l}}{55.5}\right) m_{HCO_{3aq}^-} m_{CO^{18}O_{aq}}^3 m_{HDO_{aq}}}, \text{ or} \end{aligned} \quad (A1.143)$$

$$K_{DC^{18}O_{3aq}^-}^{ex} = \left(\frac{1}{2}\right)^4 \left(\alpha_{HCO_{3aq}^- - H_2O_l}^D\right) \left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O}\right)^3 \left(\frac{\gamma_{DC^{18}O_{3aq}^-} \gamma_{CO_{2aq}}^3}{\gamma_{HCO_{3aq}^-} \gamma_{CO^{18}O_{aq}}^3}\right)_{exp} \left(\frac{1}{[qq3]^3}\right). \quad (A1.144)$$

The PHREEQC species and reference reactions are



which, combined with equation A1.143, yield

$$K_{DC^{18}O_{3aq}^-}^{ex} = \left(\frac{a_{DC^{18}O_{3aq}^-} a_{CO_{2aq}}^2 a_{H_3O_{aq}^+}}{a_{CO^{18}O_{aq}}^3 a_{HDO_{aq}} a_{H_2O_l}}\right) \left(\frac{a_{CO_{2aq}} a_{H_2O_l} a_{H_2O_l}}{a_{HCO_{3aq}^-} a_{H_3O_{aq}^+}}\right) = \frac{K_{DC^{18}O_{3aq}^-}}{K_{HCO_{3aq}^-}}. \quad (A1.146)$$

Thus,

$$K_{DC^{18}O_{3aq}^-} = K_{HCO_{3aq}^-} \left(\frac{1}{2}\right)^4 \left(\alpha_{HCO_{3aq}^- - H_2O_l}^D\right) \left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O}\right) \left(\frac{\gamma_{DC^{18}O_{3aq}^-} \gamma_{CO_{2aq}}^3}{\gamma_{HCO_{3aq}^-} \gamma_{CO^{18}O_{aq}}^3}\right)_{exp} \left(\frac{1}{[qq3]^3}\right). \quad (A1.147)$$

$$\text{Defining } QQ3 = \left(\frac{1}{[qq3]^3}\right), \quad (A1.148)$$

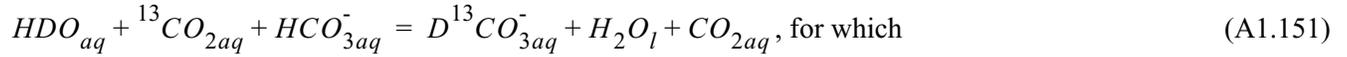
substituting in equation A1.147, and taking logarithms gives

$$\begin{aligned} \log K_{DC^{18}O_{3aq}^-} &= \log K_{HCO_{3aq}^-} - 4\log 2 + \log\left(\alpha_{HCO_{3aq}^- - H_2O_l}^D\right) + \\ &3\log\left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O}\right) + \log\left(\frac{\gamma_{DC^{18}O_{3aq}^-} \gamma_{CO_{2aq}}^3}{\gamma_{HCO_{3aq}^-} \gamma_{CO^{18}O_{aq}}^3}\right)_{exp} + \log(QQ3). \end{aligned} \quad (A1.149)$$

### Reaction to $D^{13}CO_{3aq}^-$

$$\left(\alpha_{HCO_{3aq}^- - H_2O_l}^D\right) \left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{13C}\right) = \frac{\left(\frac{n_{D^{13}CO_{3aq}^-}}{n_{H^{13}CO_{3aq}^-}}\right) \left(\frac{n_{H^{13}CO_{3aq}^-}}{n_{HCO_{3aq}^-}}\right)}{\left(\frac{n_{HDO_{aq}}}{2n_{H_2O_l}}\right) \left(\frac{n_{^{13}CO_{2aq}}}{n_{CO_{2aq}}}\right)} = \frac{m_{D^{13}CO_{3aq}^-} m_{CO_{2aq}}}{\left(\frac{1}{2}\right) \left(\frac{m_{HDO_{aq}}}{55.5}\right) m_{^{13}CO_{2aq}} m_{HCO_{3aq}^-}} \quad (A1.150)$$

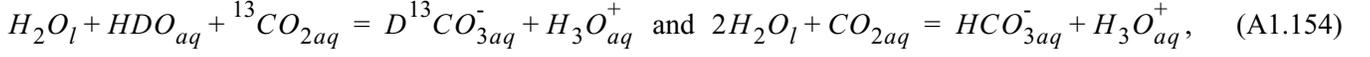
The isotope exchange reaction is



$$K_{D^{13}CO_{3aq}^-}^{ex} = \frac{a_{D^{13}CO_{3aq}^-} a_{H_2O_l} a_{CO_{2aq}}}{a_{^{13}CO_{2aq}} a_{HDO_{aq}} a_{HCO_{3aq}^-}} = \frac{\gamma_{D^{13}CO_{3aq}^-} a_{H_2O_l} \gamma_{CO_{2aq}}}{\gamma_{^{13}CO_{2aq}} \left(\frac{a_{H_2O_l}}{55.5}\right) \gamma_{HCO_{3aq}^-}} \frac{m_{D^{13}CO_{3aq}^-} m_{CO_{2aq}}}{m_{^{13}CO_{2aq}} m_{HDO_{aq}} m_{HCO_{3aq}^-}}, \text{ or} \quad (A1.152)$$

$$\begin{aligned} K_{D^{13}CO_{3aq}^-}^{ex} &= \frac{\gamma_{D^{13}CO_{3aq}^-} \gamma_{CO_{2aq}}}{\gamma_{^{13}CO_{2aq}} \gamma_{HCO_{3aq}^-} m_{^{13}CO_{2aq}} \left(\frac{m_{HDO_{aq}}}{55.5}\right) m_{HCO_{3aq}^-}} \\ &= \left(\frac{1}{2}\right) \left(\alpha_{HCO_{3aq}^- - H_2O_l}^D\right) \left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{13C}\right) \left(\frac{\gamma_{D^{13}CO_{3aq}^-} \gamma_{CO_{2aq}}}{\gamma_{^{13}CO_{2aq}} \gamma_{HCO_{3aq}^-}}\right)_{exp}. \end{aligned} \quad (A1.153)$$

The PHREEQC species and reference reactions are, respectively,



which, combined with equation A1.152, yield

$$K_{D^{13}CO_{3aq}^-}^{ex} = \left( \frac{a_{D^{13}CO_{3aq}^-}}{a_{HDO_{aq}}} \frac{a_{H_3O_{aq}^+}}{a_{H_2O_l}} \right) \left( \frac{a_{CO_{2aq}} a_{H_2O_l} a_{H_2O_l}}{a_{HCO_{3aq}^-} a_{H_3O_{aq}^+}} \right) = \frac{K_{D^{13}CO_{3aq}^-}}{K_{HCO_{3aq}^-}}. \quad (A1.155)$$

$$\text{Thus, } K_{D^{13}CO_{3aq}^-} = K_{HCO_{3aq}^-} \left( \frac{1}{2} \right) \left( \alpha_{HCO_{3aq}^- - H_2O_l}^D \right) \left( \alpha_{HCO_{3aq}^- - CO_{2aq}}^{13C} \right) \left( \frac{\gamma_{D^{13}CO_{3aq}^-} \gamma_{CO_{2aq}}}{\gamma_{13CO_{2aq}} \gamma_{HCO_{3aq}^-}} \right)_{exp}. \quad (A1.156)$$

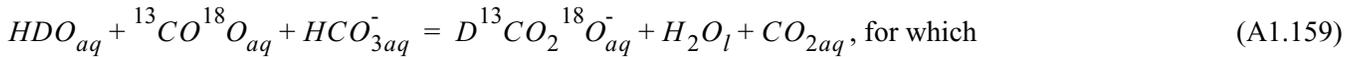
Taking logarithms gives

$$\begin{aligned} \log K_{D^{13}CO_{3aq}^-} &= \log K_{HCO_{3aq}^-} - \log(2) + \log \left( \alpha_{HCO_{3aq}^- - H_2O_l}^D \right) + \\ &\quad \log \left( \alpha_{HCO_{3aq}^- - CO_{2aq}}^{13C} \right) + \log \left( \frac{\gamma_{D^{13}CO_{3aq}^-} \gamma_{CO_{2aq}}}{\gamma_{13CO_{2aq}} \gamma_{HCO_{3aq}^-}} \right)_{exp}. \end{aligned} \quad (A1.157)$$

### Reaction to $D^{13}CO_2^{18}O_{aq}^-$

$$\begin{aligned} &\left( \alpha_{HCO_{3aq}^- - H_2O_l}^D \right) \left( \alpha_{HCO_{3aq}^- - CO_{2aq}}^{13C} \right) \left( \alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O} \right) \\ &= \frac{\left( \frac{n_{D^{13}CO_2^{18}O_{aq}^-}}{n_{H^{13}CO_2^{18}O_{aq}^-}} \right) \left( \frac{n_{H^{13}CO_2^{18}O_{aq}^-}}{n_{HCO_2^{18}O_{aq}^-}} \right) \left( \frac{n_{HCO_2^{18}O_{aq}^-}}{3n_{HCO_{3aq}^-}} \right) (qq1)}{\left( \frac{n_{HDO_{aq}}}{2n_{H_2O_l}} \right) \left( \frac{n_{13CO^{18}O_{aq}}}{n_{CO^{18}O_{aq}}} \right) \left( \frac{n_{CO^{18}O_{aq}}}{2n_{CO_{2aq}}} \right)} = \frac{m_{D^{13}CO_2^{18}O_{aq}^-} m_{CO_{2aq}}}{\left( \frac{3}{4} \right) m_{HCO_{3aq}^-} \left( \frac{m_{HDO_{aq}}}{55.5} \right) m_{13CO^{18}O_{aq}}} (qq1). \end{aligned} \quad (A1.158)$$

The isotope exchange reaction is

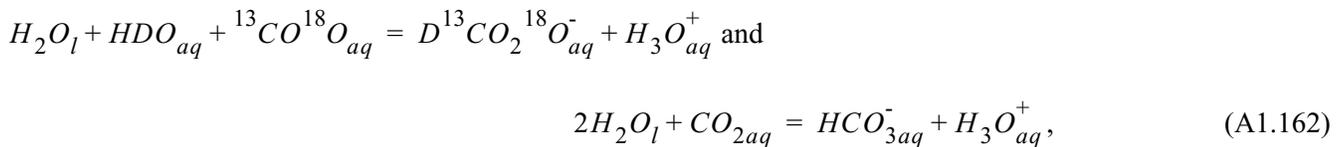


$$\begin{aligned} K_{D^{13}CO_2^{18}O_{aq}^-}^{ex} &= \frac{a_{D^{13}CO_2^{18}O_{aq}^-} a_{H_2O_l} a_{CO_{2aq}}}{a_{HDO_{aq}} a_{13CO^{18}O_{aq}} a_{HCO_{3aq}^-}} \\ &= \frac{\gamma_{D^{13}CO_2^{18}O_{aq}^-} a_{H_2O_l} \gamma_{CO_{2aq}} m_{D^{13}CO_2^{18}O_{aq}^-} m_{CO_{2aq}}}{\left( \frac{a_{H_2O_l}}{55.5} \right) \gamma_{13CO^{18}O_{aq}} \gamma_{HCO_{3aq}^-} m_{HDO_{aq}} m_{13CO^{18}O_{aq}} m_{HCO_{3aq}^-}} \end{aligned}$$

$$= \left( \frac{\gamma_{D^{13}CO_2^{18}O_{aq}^-} \gamma_{CO_{2aq}}}{\gamma_{^{13}CO^{18}O_{aq}^-} \gamma_{HCO_{3aq}^-}} \right) \frac{m_{D^{13}CO_2^{18}O_{aq}^-} m_{CO_{2aq}}}{\exp\left(\frac{m_{HDO_{aq}}}{55.5}\right) m_{^{13}CO^{18}O_{aq}^-} m_{HCO_{3aq}^-}}, \text{ or} \quad (\text{A1.160})$$

$$K_{D^{13}CO_2^{18}O_{aq}^-}^{ex} = \left(\frac{3}{4}\right) \left(\alpha_{HCO_{3aq}^- - H_2O_l}^D\right) \left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{^{13}C}\right) \left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{^{18}O}\right) \times \left( \frac{\gamma_{D^{13}CO_2^{18}O_{aq}^-} \gamma_{CO_{2aq}}}{\gamma_{^{13}CO^{18}O_{aq}^-} \gamma_{HCO_{3aq}^-}} \right) \exp\left(\frac{1}{qq1}\right). \quad (\text{A1.161})$$

The PHREEQC species and reference reactions are, respectively,



which, combined with equation A1.160, yield

$$K_{D^{13}CO_2^{18}O_{aq}^-}^{ex} = \frac{a_{D^{13}CO_2^{18}O_{aq}^-} a_{H_2O_l} a_{CO_{2aq}}}{a_{HDO_{aq}} a_{^{13}CO^{18}O_{aq}^-} a_{HCO_{3aq}^-}} = \left( \frac{a_{D^{13}CO_2^{18}O_{aq}^-} a_{H_3O_{aq}^+}}{a_{HDO_{aq}} a_{^{13}CO^{18}O_{aq}^-} a_{H_2O_l}} \right) \left( \frac{a_{H_2O_l} a_{CO_{2aq}} a_{H_2O_l}}{a_{HCO_{3aq}^-} a_{H_3O_{aq}^+}} \right), \quad (\text{A1.163})$$

$$\text{or } K_{D^{13}CO_2^{18}O_{aq}^-}^{ex} = \frac{K_{D^{13}CO_2^{18}O_{aq}^-}}{K_{HCO_{3aq}^-}}. \quad (\text{A1.164})$$

$$\begin{aligned} \text{Thus, } K_{D^{13}CO_2^{18}O_{aq}^-} &= K_{HCO_{3aq}^-} K_{D^{13}CO_2^{18}O_{aq}^-}^{ex} \\ &= K_{HCO_{3aq}^-} \left(\frac{3}{4}\right) \left(\alpha_{HCO_{3aq}^- - H_2O_l}^D\right) \left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{^{13}C}\right) \left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{^{18}O}\right) \times \\ &\quad \left( \frac{\gamma_{D^{13}CO_2^{18}O_{aq}^-} \gamma_{CO_{2aq}}}{\gamma_{^{13}CO^{18}O_{aq}^-} \gamma_{HCO_{3aq}^-}} \right) \exp\left(\frac{1}{qq1}\right). \end{aligned} \quad (\text{A1.165})$$

$$\text{Defining } QQ1 = \left(\frac{1}{qq1}\right), \quad (\text{A1.166})$$

substituting in equation A1.165, and taking logarithms gives

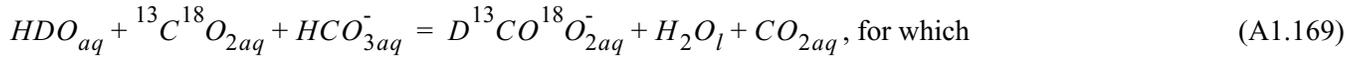
$$\log K_{D^{13}CO_2^{18}O_{aq}^-} = \log K_{HCO_{3aq}^-} + \log(0.75) + \log\left(\alpha_{HCO_{3aq}^- - H_2O_l}^D\right) +$$

$$\log\left(\alpha_{HCO_3^- - CO_2aq}^{13C}\right) + \log\left(\alpha_{HCO_3^- - CO_2aq}^{18O}\right) + \log\left(\frac{\gamma_{D^{13}CO_2^{18}O_{aq}^-} \gamma_{CO_2aq}}{\gamma_{^{13}CO^{18}O_{aq}^-} \gamma_{HCO_3^-}}\right)_{exp} + \log(QQ1). \quad (A1.167)$$

**Reaction to  $D^{13}CO^{18}O_{2aq}^-$**

$$\begin{aligned} & \left(\alpha_{HCO_3^- - H_2O_l}^D\right) \left(\alpha_{HCO_3^- - CO_2aq}^{13C}\right) \left(\alpha_{HCO_3^- - CO_2aq}^{18O}\right)^2 \\ &= \frac{\left(\frac{n_{D^{13}CO^{18}O_{2aq}^-}}{n_{H^{13}CO^{18}O_{2aq}^-}}\right) \left(\frac{n_{H^{13}CO^{18}O_{2aq}^-}}{n_{HCO^{18}O_{2aq}^-}}\right) \left(\frac{n_{HCO^{18}O_{2aq}^-}}{3n_{HCO_3^-}}\right) ([qq2]^2)}{\left(\frac{n_{HDO_{aq}}}{2n_{H_2O_l}}\right) \left(\frac{n_{^{13}C^{18}O_{2aq}}}{n_{C^{18}O_{2aq}}}\right) \left(\frac{n_{C^{18}O_{2aq}}}{n_{CO_2aq}}\right)} \\ &= \frac{m_{D^{13}CO^{18}O_{2aq}^-} m_{CO_2aq}}{\left(\frac{3}{2}\right) m_{HCO_3^-} \left(\frac{m_{HDO_{aq}}}{55.5}\right) m_{^{13}C^{18}O_{2aq}}} ([qq2]^2). \end{aligned} \quad (A1.168)$$

The isotope exchange reaction is

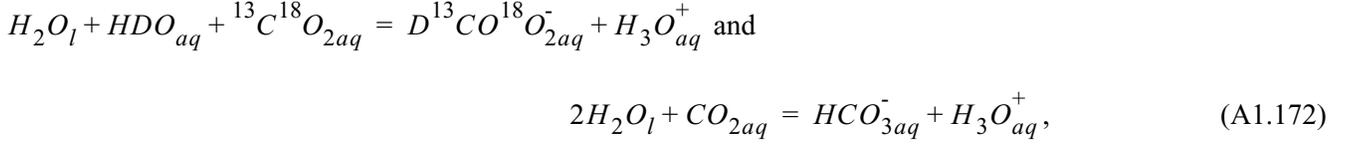


$$\begin{aligned} K_{D^{13}CO^{18}O_{2aq}^-}^{ex} &= \frac{a_{D^{13}CO^{18}O_{2aq}^-} a_{H_2O_l} a_{CO_2aq}}{a_{HDO_{aq}} a_{^{13}C^{18}O_{2aq}} a_{HCO_3^-}} \\ &= \frac{\gamma_{D^{13}CO^{18}O_{2aq}^-} a_{H_2O_l} \gamma_{CO_2aq} m_{D^{13}CO^{18}O_{2aq}^-} m_{CO_2aq}}{\left(\frac{a_{H_2O_l}}{55.5}\right) \gamma_{^{13}C^{18}O_{2aq}} \gamma_{HCO_3^-} m_{HDO_{aq}} m_{^{13}C^{18}O_{2aq}} m_{HCO_3^-}}, \\ &= \left(\frac{\gamma_{D^{13}CO^{18}O_{2aq}^-} \gamma_{CO_2aq}}{\gamma_{^{13}C^{18}O_{2aq}} \gamma_{HCO_3^-}}\right)_{exp} \frac{m_{D^{13}CO^{18}O_{2aq}^-} m_{CO_2aq}}{\left(\frac{m_{HDO_{aq}}}{55.5}\right) m_{^{13}C^{18}O_{2aq}} m_{HCO_3^-}}, \text{ or} \end{aligned} \quad (A1.170)$$

$$K_{D^{13}CO^{18}O_{2aq}^-}^{ex} = \left(\frac{3}{2}\right) \left(\alpha_{HCO_3^- - H_2O_l}^D\right) \left(\alpha_{HCO_3^- - CO_2aq}^{13C}\right) \left(\alpha_{HCO_3^- - CO_2aq}^{18O}\right)^2 \times$$

$$\left( \frac{\gamma_{D^{13}CO^{18}O_{2aq}^-} \gamma_{CO_{2aq}}}{\gamma_{^{13}C^{18}O_{2aq}} \gamma_{HCO_{3aq}^-}} \right)_{exp} \left( \frac{1}{[qq2]^2} \right). \quad (A1.171)$$

The PHREEQC species and reference reactions are, respectively,



which, combined with equation A1.170, yield

$$K_{D^{13}CO^{18}O_{2aq}^-}^{ex} = \frac{a_{D^{13}CO^{18}O_{2aq}^-} a_{H_2O_l} a_{CO_{2aq}}}{a_{HDO_{aq}} a_{^{13}C^{18}O_{2aq}} a_{HCO_{3aq}^-}}$$

$$\left( \frac{a_{D^{13}CO^{18}O_{2aq}^-} a_{H_3O_{aq}^+}}{a_{HDO_{aq}} a_{^{13}C^{18}O_{2aq}} a_{H_2O_l}} \right) \left( \frac{a_{H_2O_l} a_{CO_{2aq}} a_{H_2O_l}}{a_{HCO_{3aq}^-} a_{H_3O_{aq}^+}} \right) = \frac{K_{D^{13}CO^{18}O_{2aq}^-}}{K_{HCO_{3aq}^-}}. \quad (A1.173)$$

$$\text{Thus, } K_{D^{13}CO^{18}O_{2aq}^-} = K_{HCO_{3aq}^-} \left( \frac{3}{2} \right) \left( \alpha_{HCO_{3aq}^- - H_2O_l}^D \right) \left( \alpha_{HCO_{3aq}^- - CO_{2aq}}^{^{13}C} \right) \left( \alpha_{HCO_{3aq}^- - CO_{2aq}}^{^{18}O} \right)^2 \times$$

$$\left( \frac{\gamma_{D^{13}CO^{18}O_{2aq}^-} \gamma_{CO_{2aq}}}{\gamma_{^{13}C^{18}O_{2aq}} \gamma_{HCO_{3aq}^-}} \right)_{exp} \left( \frac{1}{[qq2]^2} \right). \quad (A1.174)$$

$$\text{Defining } QQ2 = \left( \frac{1}{[qq2]^2} \right), \quad (A1.175)$$

substituting in equation A1.174, and taking logarithms gives

$$\log K_{D^{13}CO^{18}O_{2aq}^-} = \log K_{HCO_{3aq}^-} + \log(1.5) + \log \left( \alpha_{HCO_{3aq}^- - H_2O_l}^D \right) + \log \left( \alpha_{HCO_{3aq}^- - CO_{2aq}}^{^{13}C} \right) +$$

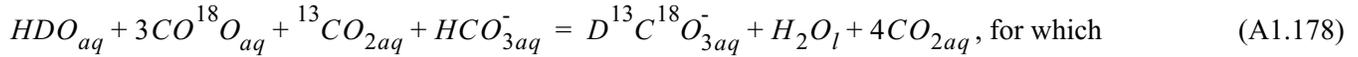
$$2 \log \left( \alpha_{HCO_{3aq}^- - CO_{2aq}}^{^{18}O} \right) + \log \left( \frac{\gamma_{D^{13}CO^{18}O_{2aq}^-} \gamma_{CO_{2aq}}}{\gamma_{^{13}C^{18}O_{2aq}} \gamma_{HCO_{3aq}^-}} \right)_{exp} + \log(QQ2). \quad (A1.176)$$

**Reaction to  $D^{13}C^{18}O_{3aq}^-$**

$$\left( \alpha_{HCO_{3aq}^- - H_2O_l}^D \right) \left( \alpha_{HCO_{3aq}^- - CO_{2aq}}^{^{13}C} \right) \left( \alpha_{HCO_{3aq}^- - CO_{2aq}}^{^{18}O} \right)^3 =$$

$$\begin{aligned}
& \frac{\left(\frac{n_{D^{13}C^{18}O_{3aq}^-}}{n_{H^{13}C^{18}O_{3aq}^-}}\right)\left(\frac{n_{H^{13}CO_{3aq}^-}}{n_{HCO_{3aq}^-}}\right)\left(\frac{n_{H^{13}C^{18}O_{3aq}^-}}{n_{H^{13}CO_{3aq}^-}}\right)([qq3]^3)}{\left(\frac{n_{HDO_{aq}}}{2n_{H_2O_l}}\right)\left(\frac{n_{^{13}CO_{2aq}}}{n_{CO_{2aq}}}\right)\left(\frac{n_{CO^{18}O_{aq}}}{2n_{CO_{2aq}}}\right)^3} \\
&= \frac{\left(\frac{m_{D^{13}C^{18}O_{3aq}^-}}{m_{HCO_{3aq}^-}}\right)([qq3]^3)}{\left(\frac{1}{2}\right)^4\left(\frac{m_{HDO_{aq}}}{55.5}\right)\left(\frac{m_{^{13}CO_{2aq}}}{m_{CO_{2aq}}}\right)\left(\frac{m_{CO^{18}O_{aq}}}{m_{CO_{2aq}}}\right)^3} \\
&= \frac{m_{D^{13}C^{18}O_{3aq}^-} m_{CO_{2aq}}^4 ([qq3]^3)}{\left(\frac{1}{2}\right)^4 m_{HCO_{3aq}^-} \left(\frac{m_{HDO_{aq}}}{55.5}\right) m_{^{13}CO_{2aq}}^3 m_{CO^{18}O_{aq}}^3}. \tag{A1.177}
\end{aligned}$$

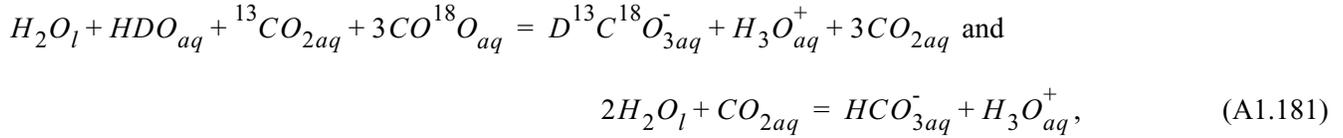
The isotope exchange reaction is



$$\begin{aligned}
K_{D^{13}C^{18}O_{3aq}^-}^{ex} &= \frac{a_{D^{13}C^{18}O_{3aq}^-} a_{H_2O_l}^4 a_{CO_{2aq}}}{a_{HDO_{aq}} a_{CO^{18}O_{aq}}^3 a_{^{13}CO_{2aq}} a_{HCO_{3aq}^-}} \\
&= \frac{\gamma_{D^{13}C^{18}O_{3aq}^-} a_{H_2O_l}^4 \gamma_{CO_{2aq}}^4}{\left(\frac{a_{H_2O_l}}{55.5}\right)^3 \gamma_{CO^{18}O_{aq}}^3 \gamma_{^{13}CO_{2aq}} \gamma_{HCO_{3aq}^-}} \frac{m_{D^{13}C^{18}O_{3aq}^-}^4 m_{CO_{2aq}}^4}{m_{HDO_{aq}} m_{CO^{18}O_{aq}}^3 m_{^{13}CO_{2aq}} m_{HCO_{3aq}^-}} \\
&= \left(\frac{\gamma_{D^{13}C^{18}O_{3aq}^-} \gamma_{CO_{2aq}}^4}{\gamma_{CO^{18}O_{aq}}^3 \gamma_{^{13}CO_{2aq}} \gamma_{HCO_{3aq}^-}}\right) \frac{m_{D^{13}C^{18}O_{3aq}^-}^4 m_{CO_{2aq}}^4}{\exp\left(\frac{m_{HDO_{aq}}}{55.5}\right) m_{CO^{18}O_{aq}}^3 m_{^{13}CO_{2aq}} m_{HCO_{3aq}^-}}, \text{ or} \tag{A1.179}
\end{aligned}$$

$$\begin{aligned}
K_{D^{13}C^{18}O_{3aq}^-}^{ex} &= \left(\frac{\gamma_{D^{13}C^{18}O_{3aq}^-} \gamma_{CO_{2aq}}^4}{\gamma_{CO^{18}O_{aq}}^3 \gamma_{^{13}CO_{2aq}} \gamma_{HCO_{3aq}^-}}\right)_{exp} \times \\
&\quad \left(\frac{1}{2}\right)^4 \left(\alpha_{HCO_{3aq}^-}^D - H_2O_l\right) \left(\alpha_{HCO_{3aq}^-}^{^{13}C} - CO_{2aq}\right) \left(\alpha_{HCO_{3aq}^-}^{^{18}O} - CO_{2aq}\right)^3 \left(\frac{1}{[qq3]^3}\right). \tag{A1.180}
\end{aligned}$$

The PHREEQC species and reference reactions are, respectively,



which, combined with equation A1.179, yield

$$K_{D^{13}C^{18}O_{3aq}^-}^{ex} = \frac{a_{D^{13}C^{18}O_{3aq}^-} a_{H_2O_l}^4 a_{CO_{2aq}}}{a_{HDO_{aq}} a_{CO^{18}O_{aq}}^3 a_{{}^{13}CO_{2aq}} a_{HCO_{3aq}^-}}$$

$$= \left( \frac{a_{D^{13}C^{18}O_{3aq}^-} a_{CO_{2aq}}^3 a_{H_3O_{aq}^+}}{a_{HDO_{aq}} a_{{}^{13}CO_{2aq}} a_{CO^{18}O_{aq}}^3 a_{H_2O_l}} \right) \left( \frac{a_{H_2O_l} a_{CO_{2aq}} a_{H_2O_l}}{a_{HCO_{3aq}^-} a_{H_3O_{aq}^+}} \right) = \frac{K_{D^{13}C^{18}O_{3aq}^-}}{K_{HCO_{3aq}^-}}. \quad (A1.182)$$

$$\text{Thusl, } K_{D^{13}C^{18}O_{3aq}^-} = K_{HCO_{3aq}^-} K_{D^{13}C^{18}O_{3aq}^-}^{ex} = K_{HCO_{3aq}^-} \left(\frac{1}{2}\right)^4 \left(\alpha_{HCO_{3aq}^- - H_2O_l}^D\right) \left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{13C}\right) \times$$

$$\left(\alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O}\right)^3 \left( \frac{\gamma_{D^{13}C^{18}O_{3aq}^-} \gamma_{CO_{2aq}}^4}{\gamma_{CO^{18}O_{aq}}^3 \gamma_{{}^{13}CO_{2aq}} \gamma_{HCO_{3aq}^-}} \right)_{exp} \left( \frac{1}{[qq3]^3} \right). \quad (A1.183)$$

$$\text{Defining } QQ3 = \left( \frac{1}{[qq3]^3} \right), \quad (A1.184)$$

substituting in equation A1.183, and taking logarithms gives

$$\log K_{D^{13}C^{18}O_{3aq}^-} = \log K_{HCO_{3aq}^-} - 4\log 2 + \log \left( \alpha_{HCO_{3aq}^- - H_2O_l}^D \right) + \log \left( \alpha_{HCO_{3aq}^- - CO_{2aq}}^{13C} \right) +$$

$$3\log \left( \alpha_{HCO_{3aq}^- - CO_{2aq}}^{18O} \right) + \log \left( \frac{\gamma_{D^{13}C^{18}O_{3aq}^-} \gamma_{CO_{2aq}}^4}{\gamma_{CO^{18}O_{aq}}^3 \gamma_{{}^{13}CO_{2aq}} \gamma_{HCO_{3aq}^-}} \right)_{exp} + \log(QQ3). \quad (A1.185)$$

## APPENDIX 2. ISOTOPIC DATA INPUT FOR PHREEQC

Isotopes are treated as separate chemical components in PHREEQC; thus, in most respects minor isotopes are treated as elements, with separate mole-balance equations for each element. To facilitate definitions of minor isotopes, the definition of an element name has been expanded such that any alphanumeric string may be used as an element name if it is enclosed in square brackets; for example, [18O] is a legitimate element or isotope name. In the PHREEQC database, *iso.dat*, the major isotope of an element has been named with the chemical formula of the element (for example, “C” represents carbon-12). Deuterium has been named “D” and tritium “T”. Other minor isotopes have been named with the atomic number followed by the chemical symbol for the element, with the number and symbol enclosed in square brackets (for example, [13C] represents carbon-13).

Several new functions have been added to the Basic interpreter that can be used in Basic programs defined in the **CALCULATE\_VALUES**, **RATES**, **USER\_PRINT**, and **USER\_PUNCH** data blocks. These new Basic functions are described in Table A2.1.

**Table A2.1.**--Special Basic statements and functions for PHREEQC related to isotopes

Special PHREEQC statement or function	Explanation
CALC_VALUE(“R(13C)_CO2(aq)”)	Result of executing named Basic program that has been defined in <b>CALCULATE_VALUES</b> data block.
LK_NAMED(“Log_K_HCO3-”)	Log10 of K for an expression evaluated at the current temperature as defined in the <b>NAMED_EXPRESSION</b> data block.
LK_PHASE(“Calcite”)	Log10 of K for a phase at current temperature as defined in <b>PHASES</b> data block.
LK_SPECIES(“Log_K_HCO3-”)	Log10 of K for a species at current temperature as defined in <b>SOLUTION_SPECIES</b> , <b>EXCHANGE_SPECIES</b> , or <b>SURFACE_SPECIES</b> data block.
SUM_GAS(“{H,D,T}2[18O]”, “[18O]”)	Sum of element in gases with specified template. This example sums the moles of oxygen-18 in all isotopic forms of water containing oxygen-18 in the <b>GAS_PHASE</b> .
SUM_SPECIES(“*{H,D,T}C{O,[18O]}3*”, “C”)	Sum of element in aqueous, exchange, and surface species with specified template. This example sums the carbon-12 in all isotopic forms of bicarbonate containing carbon-12.
SUM_S_S(“Calcite”, “[18O]”)	Sum of element in a specified solid solution. This example sums the oxygen-18 in all isotopic forms defined in the solid solution “calcite.”

Five new keyword data blocks have been added to PHREEQC to implement the approach to isotope calculations that is described in this report: **CALCULATE\_VALUES**, **ISOTOPES**, **ISOTOPE\_ALPHAS**, **ISOTOPE\_RATIOS**, and **NAMED\_EXPRESSION**. The input formats for these data blocks are presented in the same format and with the same conventions that are described by Parkhurst and Appelo (1999). In addition, new identifiers are presented for the following data blocks: **PHASES**, **PRINT**, **SELECTED\_OUTPUT**, and **SOLUTION\_SPECIES**. Descriptions presented here include only the new identifiers for the data blocks and

sufficient additional information to put the descriptions in context. **EXCHANGE\_SPECIES** and **SURFACE\_SPECIES** have the new identifier **-add\_logk**, which is described in detail in the description of the **PHASES** and **SOLUTION\_SPECIES** data blocks. The new data blocks and data blocks with new identifiers are described here in alphabetical order.

## CALCULATE\_VALUES

This keyword data block is used to define Basic programs for the calculation of quantities that can be printed to the output file or used in other Basic programs for PHREEQC. The primary use of the data block is to define the calculation of arbitrary isotope ratios and isotope fractionation values. Normally, this data block is included in the database file and only additions and modifications are included in the input file.

### Example data block

```
Line 0: CALCULATE_VALUES
Line 1a:   R(13C)_CO2(aq)
Line 2a:   -start
Basic:  10 ratio = -9999.999
Basic:  20 if (TOT("[13C]") <= 0) THEN GOTO 100
Basic:  30 total_13C = SUM_SPECIES("[13C]{O,[18O]}2", "[13C]")
Basic:  40 total_12C = SUM_SPECIES("C{O,[18O]}2", "C")
Basic:  50 ratio = total_13C/total_12C
Basic:  100 SAVE ratio
Line 3a:   -end
Line 1b:   R(18O)_CO2(aq)
Line 2b:   -start
Basic:  10 ratio = -9999.999
Basic:  20 if (TOT("[18O]") <= 0) THEN GOTO 100
Basic:  30 if (TOT("C") <= 0) THEN GOTO 100
Basic:  40 total_180 = SUM_SPECIES("{C,[13C],[14C]}{O,[18O]}2", "[18O]")
Basic:  50 total_160 = SUM_SPECIES("{C,[13C],[14C]}{O,[18O]}2", "O")
Basic:  60 ratio = total_180/total_160
Basic:  100 SAVE ratio
Line 3b:   -end
```

### Explanation

Line 0: **CALCULATE\_VALUES**

**CALCULATE\_VALUES** is the keyword for the data block. No other data are input on the keyword line.

Line 1: *name of program*

*name of program*--Alphanumeric character string that identifies the following Basic program, no spaces are allowed.

Line 2: **-start**

**-start**--Identifier marks the beginning of a Basic program.

Basic: *numbered Basic statement*

*numbered Basic statement*--A valid Basic language statement that must be numbered. The statements are evaluated in numerical order. The last statement must be "**SAVE expression**", where the value

of *expression* is the numeric result of evaluating the program. New functions that are available through the Basic interpreter are listed in table A2.1.

Line 3: **-end**

**-end**--Identifier marks the end of a Basic program. Note the hyphen is required to avoid a conflict with the keyword **END**.

#### Notes

A Basic interpreter (David Gillespie, Synaptics, Inc., San Jose, Calif., written commun., 1997) distributed with the Linux operating system (Free Software Foundation, Inc.) is embedded in PHREEQC. The Basic interpreter is used for defining general rate expressions for kinetic reactions (**RATES** data block) and for generating results for printing to the output (**USER\_PRINT**) and selected-output file (**USER\_PUNCH**). A Basic program is needed for each isotopic ratio (**ISOTOPE\_RATIOS**) and isotope fractionation value (**ISOTOPE\_ALPHAS**) that are to be printed to the output file. Each program must stand alone with its own set of variables and numbered statement lines. No data are passed between Basic programs, and there is no conflict using the same variable names or line numbers in separate programs.

#### Example problems

The keyword **CALCULATE\_VALUES** is used in the *iso.dat* database.

#### Related keywords

**ISOTOPE\_ALPHAS**, **ISOTOPE\_RATIOS**, **RATES**, **USER\_PRINT**, and **USER\_PUNCH**.

## ISOTOPES

This keyword data block is used to define the names, units, and absolute ratio of the standard for individual minor isotopes. By convention in PHREEQC, the major isotope of an element is given the element name and is defined in **SOLUTION\_MASTER\_SPECIES**, all other isotopes are defined in the **ISOTOPES** and **SOLUTION\_MASTER\_SPECIES** data block. Normally, this data block is included in the database file and only additions and modifications are included in the input file.

### Example data block

```
Line 0:  ISOTOPES
Line 1a: H
Line 2a:  -isotope D      permil 155.76e-6      #VSMOW
Line 2b:  -isotope T      TU      1e-18      #1 THO in 10^18 H2O
Line 1b: C
Line 2c:  -isotope [13C] permil 0.0111802      #VPDB
Line 2d:  -isotope [14C] pmc      1.175887709e-12 #13.56 dpm
```

### Explanation

#### Line 0: ISOTOPES

**ISOTOPES** is the keyword for the data block. No other data are input on the keyword line.

#### Line 1: *element name*

*element name*--Name of an element for which minor isotopes are to be defined. *Element name* must be an element defined in a **SOLUTION\_MASTER\_SPECIES** data block. *Element name* represents the major isotope of the element, H represents  $^1\text{H}$  and C represents  $^{12}\text{C}$  in this example.

#### Line 2: **-isotope** *isotope\_name units standard*

Information for a minor isotope of *element name* is defined. Optionally, **isotope** or **-i[isotope]**.

*isotope\_name*--Name of a minor isotope of the element. For most minor isotopes, the convention for naming in PHREEQC databases is the isotope number preceding the element name and enclosed with square brackets; for example, [13C] and [14C]. The square brackets are necessary when a number is to be included in an isotope name. The isotope name must also be defined in a **SOLUTION\_MASTER\_SPECIES** data block.

*units*--Reporting units for the isotope analysis. Units that can be used are limited to percent, permil, tritium units (TU), and picocuries per liter (pCi/L), which is treated as equivalent to picocuries per kilogram water.

*standard*--Absolute measure of isotopic abundance in the standard. For percent and permil, it is the absolute ratio of the minor isotope to the major isotope in the reference standard. The comments following the “#” in line 2 indicate the reference standard but are not required input.

## Notes

One major isotope must be defined for an element in a **SOLUTION\_MASTER\_SPECIES** data block, and all minor isotopes are defined in both an **ISOTOPES** and a **SOLUTION\_MASTER\_SPECIES** data block. Once the names of the element and isotopes have been defined in these data blocks, definitions for both major and minor isotopes are made in the **SOLUTION\_SPECIES**, **EXCHANGE\_SPECIES**, **SURFACE\_SPECIES**, and **PHASES** data blocks.

Isotopic composition of a solution is defined in the **SOLUTION** data block by including the isotope name in the same way that other elements and element redox states are defined; however, minor isotope composition is interpreted to be in the units defined by the *units* field for the specified isotope in the **ISOTOPES** data block. It is not possible to specify concentrations of minor isotopes in other concentration units. To determine the number of moles of the minor isotope in a solution, the solution is first speciated assuming the total element concentration (for example, the total for element C or H) includes all minor isotopes; the minor isotope definitions are ignored during this part of the calculation. After the initial solution calculation, the total concentration of the element is partitioned among the major and minor isotopes of the element in accordance with the defined minor isotope compositions. After the partitioning, all isotopes are considered to be separate components, and the total concentration of the element corresponds to the concentration of the major isotope.

## Example problems

The keyword **ISOTOPES** is used in the *iso.dat* database.

## Related keywords

**EXCHANGE\_SPECIES**, **PHASES**, **SOLUTION**, **SOLUTION\_MASTER\_SPECIES**, **SOLUTION\_SPECIES**, and **SURFACE\_SPECIES**.

## ISOTOPE\_ALPHAS

This keyword data block is used to print a data block in the output file that compares calculated isotopic ratios to experimental isotopic ratios, from which the equilibrium constants of the isotope model were derived.

Fractionation values (alphas) are ratios of isotopic ratios that describe the amount of isotopic fractionation between phases and between aqueous species. Normally, this data block is included in the database file and only additions and modifications are included in the input file.

### Example data block

```
Line 0:  ISOTOPE_ALPHAS
Line 1a: Alpha_18O_CO2(aq)/CO2(g)      Log_alpha_18O_CO2(aq)/CO2(g)
Line 1b: Alpha_13C_CO2(aq)/CO2(g)      Log_alpha_13C_CO2(aq)/CO2(g)
Line 1c: Alpha_18O_CO2(aq)/H2O(l)      Log_alpha_18O_CO2(aq)/H2O(l)
Line 1d: Alpha_D_H2O(l)/H2O(g)         Log_alpha_D_H2O(l)/H2O(g)
```

### Explanation

Line 0: **ISOTOPE\_ALPHAS**

**ISOTOPE\_ALPHAS** is the keyword for the data block. No other data are input on the keyword line.

Line 1: *named\_value* [*named\_expression*]

Definition of the an isotope ratio to be printed to the “Isotope Alphas” section of the output file.

*named\_value*--Name of a Basic program defined in a **CALCULATE\_VALUES** data block; the name is also used to identify the results in the “Isotope Alphas” section of the output file. The Basic program defines the calculation of an isotope ratio based on the current distribution of species; for example, in the *iso.dat* database, the **CALCULATE\_VALUES** Basic program

Alpha\_18O\_CO2(aq)/CO2(g), defines the ratio  $\alpha_{CO_{2(aq)} - CO_{2(g)}} = \frac{\left( \frac{{}^{18}O}{{}^{16}O} \right)_{nCO_{2(aq)}}}{\left( \frac{{}^{18}O}{{}^{16}O} \right)_{nCO_{2(g)}}}$ . The

literal string, *named\_value*, will be printed, replacing underscores with spaces, in an output section headed “Isotope Alphas” in the output file. The string will be followed by the result calculated by the **CALCULATE\_VALUES** program and 1000 times the natural log of the result.

*named\_expression*--The name of an expression defined in a **NAMED\_EXPRESSION** keyword data block. The expression is used to calculate the experimental isotopic ratio from which thermodynamic equilibrium constants were derived, expressed as  $1000\ln(\alpha)$ . The expression will be evaluated at the temperature specified for the current simulation. If *named\_expression* is not entered, no value will be printed for  $1000\ln(\alpha)$  in the output file.

### Notes

The **ISOTOPE\_ALPHAS** data block is used to generate additional information in the output file related to fractionation among phases and species. The output data block will be printed if at least one minor isotope is present in the chemical system. In most cases,  $1000\ln(\alpha)$  in the column headed by the current temperature will be the same as the value headed by "Solution", which is calculated by the **CALCULATE\_VALUES** Basic program.

These two values will be the same whenever  $\alpha = K^{\frac{1}{n}}$ . For the current database, only oxygen-18 in bicarbonate does not meet this condition and the two values may differ.

**Table A2.2.**—Example of results generated by an **ISOTOPE\_ALPHAS** data block.

Isotope Ratio	Solution alpha	1000ln(Alpha)	
		Solution	25.0 C
Alpha 18O CO2(aq)/CO2(g)	0.99893	-1.0715	-1.0715
Alpha 13C CO2(aq)/CO2(g)	0.99916	-0.83913	-0.83913
Alpha 18O CO2(aq)/H2O(l)	1.041	40.151	40.151
Alpha D H2O(l)/H2O(g)	1.0793	76.356	76.356

### Example problems

The keyword **ISOTOPE\_ALPHAS** data block is used in the *iso.dat* database.

### Related keywords

**CALCULATE\_VALUES** and **NAMED\_EXPRESSION**.

## ISOTOPE\_RATIOS

This keyword data block is used to print a data block to the output file of (1) the absolute ratio of minor isotope to major isotope for each minor isotope and (2) the ratio converted to standard measurement units. Normally, this data block is included in the database file and only additions and modifications are included in the input file.

### Example data block

```
Line 0:  ISOTOPE_RATIOS
Line 1a:  R(13C)_Calcite      [13C]
Line 1b:  R(18O)_Calcite     [18O]
Line 1c:  R(13C)_CO2(g)     [13C]
Line 1d:  R(18O)_CO2(g)     [18O]
```

### Explanation

#### Line 0: ISOTOPE\_RATIOS

**ISOTOPE\_RATIOS** is the keyword for the data block. No other data are input on the keyword line.

#### Line 1: *named\_value isotope\_name*

Definition of an isotope ratio to be printed to the “Isotope Ratios” section of the output file.

*named\_value*--Name of a Basic program defined in a **CALCULATE\_VALUES** data block; the name also is used to identify the results in the “Isotope Ratios” section of the output file. The Basic program defines the calculation of an isotope ratio; for example, in the *iso.dat* database, the **CALCULATE\_VALUES** Basic program R(13C)\_CO2(g), defines the ratio

$$R_{CO_{2(g)}} = \frac{n_{^{18}O}^{CO_{2(g)}}}{n_{^{16}O}^{CO_{2(g)}}}. \text{ The literal string, } \textit{named\_value}, \text{ will be printed, replacing underscores with}$$

spaces, in an output section headed “Isotope Ratios” in the output file. The string will be followed by the result calculated by the **CALCULATE\_VALUES** program.

*isotope\_name*--The name of the isotope for which the ratio is calculated. This name is used to determine how to convert the absolute isotope ratio to conventional units relative to a standard for the specified isotope. Minor isotope names and units are defined in the **ISOTOPES** data block.

### Notes

The **ISOTOPE\_RATIOS** data block is used to print to the output file isotope values in standard units and as absolute ratios of minor to major isotopes. The output data block will be printed if at least one minor isotope is present in the chemical system. The ratio of minor to major isotope must be defined by a **CALCULATE\_VALUES**

Basic program. These ratios are the basis for calculation of fractionation values (**ISOTOPE\_ALPHAS**), which are ratios of two isotope ratios.

**Table A2.3.**—Example of results generated by an **ISOTOPE\_RATIOS** data block.

-----Isotope Ratios-----		
Isotope Ratio	Ratio	Standard units
R(13C) Calcite	1.12049e-02	2.2111 permil
R(18O) Calcite	2.04774e-03	21.217 permil
R(13C) CO2(g)	1.10956e-02	-7.5644 permil
R(18O) CO2(g)	2.08958e-03	42.08 permil

#### Example problems

The keyword **ISOTOPE\_RATIOS** data block is used in the *iso.dat* database.

#### Related keywords

**CALCULATE\_VALUES**, **ISOTOPES**, and **ISOTOPE\_ALPHAS**.

## NAMED\_EXPRESSION

This data block was implemented to facilitate isotopic calculations. It allows analytical expressions that are functions of temperature to be defined and referenced by name. The purpose is to separate fractionation factors from log Ks, so that the fractionation factor or its temperature dependence can be easily modified. A named expression can be added to the log K for a species or phase by the **-add\_logk** identifier in **SOLUTION\_SPECIES**, **EXCHANGE\_SPECIES**, **SURFACE\_SPECIES**, or **PHASES** data blocks. Normally, this data block is included in the database file and only additions and modifications are included in the input file.

### Example data block

```
Line 0:  NAMED_EXPRESSION
Line 1a:  Log_alpha_D_H2O(l)/H2O(g)
Line 2a:   ln_alpha1000  52.612  0.0  -76.248e3  0.0  24.844e6
Line 1b:  Log_KH_H2O(g) H2O(g) = H2O(l)
Line 3b:   log_k          1.51
Line 4b:   delta_h        -44.03  kJ
Line 1c:  Log_KH_CO2(g) CO2(g) = CO2(aq)
Line 3c:   log_k          -1.468
Line 4c:   delta_h        -4.776 kcal
Line 5c:   a_e            108.3865  0.01985076  -6919.53  -40.451  669365.0
```

### Explanation

#### Line 0: NAMED\_EXPRESSION

Keyword for the data block. No other data are input on the keyword line. Optionally, **NAMED\_ANALYTICAL\_EXPRESSION** or **NAMED\_ANALYTICAL\_EXPRESSIONS**.

#### Line 1: Name of expression

*Name of expression*--A name to identify the expression. The value of the expression can be combined with other log K expressions with the identifier **-add\_logk name of expression** in **SOLUTION\_SPECIES**, **EXCHANGE\_SPECIES**, **SURFACE\_SPECIES**, and **PHASES** data blocks.

#### Line 2: ln\_alpha1000 $A_1, A_2, A_3, A_4, A_5$

**ln\_alpha1000**--Identifier to define expression for  $1000\ln(\alpha)$ , which is a form frequently used in the literature for fractionation factors. Optionally, **ln\_alpha1000** or **-ln[\_alpha1000]**.

$A_1, A_2, A_3, A_4, A_5$ --Five values defining  $1000\ln(\alpha)$  as a function of temperature in the expression

$$1000\ln\alpha = A_1 + A_2T + \frac{A_3}{T} + A_4\log_{10}T + \frac{A_5}{T^2}, \text{ where } T \text{ is in Kelvin.}$$

#### Line 3: log\_k log K

**log\_k**--Identifier for log K at 25°C. Optionally, **-log\_k**, **logk**, **-l[og\_k]**, or **-l[ogk]**.

*log K*--Log K at 25°C of an equilibrium constant or fractionation factor. Default is 0.0.

Line 4: **delta\_h** *enthalpy*, [*units*]

**delta\_h**--Identifier for enthalpy of reaction at 25°C. Optionally, **-delta\_h**, **deltah**, **-d[elta\_h]**, or **-d[eltah]**.

*enthalpy*--Enthalpy of reaction at 25°C for the reaction. Default is 0.0.

*units*--Default units are kilojoules per mole. Units may be calories, kilocalories, joules, or kilojoules per mole. Only the energy unit is needed (per mole is assumed) and abbreviations of these units are acceptable. Explicit definition of units for all enthalpy values is recommended. The enthalpy of reaction is used in the van't Hoff equation to determine the temperature dependence of the equilibrium constant. Internally, all enthalpy calculations are performed with the units of kilojoules per mole.

Line 5: **-analytical\_expression**  $A_1, A_2, A_3, A_4, A_5$

**-analytical\_expression**--Identifier for coefficients for an analytical expression for the temperature dependence of  $\log K$ . Optionally, **analytical\_expression**, **a\_e**, **ae**, **-a[analytical\_expression]**, **-a[\_e]**, **-a[e]**.

$A_1, A_2, A_3, A_4, A_5$ --Five values defining  $\log K$  as a function of temperature in the expression

$$\log_{10}K = A_1 + A_2T + \frac{A_3}{T} + A_4\log_{10}T + \frac{A_5}{T^2}, \text{ where } T \text{ is in Kelvin.}$$

#### Notes

Line 1 must be entered first in the definition of a named expression. Additional sets of lines (lines 1-5 as needed) may be added to define all of the named expressions. The value of the expression is constant if only *log\_k* is defined. If *delta\_h* is also defined, the value of the expression is evaluated with the van't Hoff expression. If **-analytical\_expression** is defined, it takes precedence over the *log\_k* and *delta\_h* definitions.

The named expressions are used primarily to define the equilibrium constants for reactions involving isotopes. In the derivations presented in this report, the equilibrium constants for isotopic species are calculated by summing a series of logarithmic terms including a base equilibrium constant corresponding to the analogous species composed of major isotopes, a symmetry derived constant, and one or more fractionation factors. To avoid manual recalculation of the sum of these terms for each of many species when different fractionation factors are desired, the definitions of equilibrium constants can be specified to be a sum of one or more named expressions. By defining separate named expressions for each fractionation factor, it is possible to include this named expression in the definition of all equilibrium constants that depend on the fractionation factor. By redefining a single named expression for the fractionation factor, all  $\log K$ s that depend on the fractionation factor will be calculated with the redefined value. It is also useful to define some base equilibrium constants as named expressions so that a single expression can be used as the base  $\log K$  for all analogous isotopic species. A named expression can be added to an equilibrium constant for a species or phase with the **-add\_logk** *named expression*

identifier in the **SOLUTION\_SPECIES**, **EXCHANGE\_SPECIES**, **SURFACE\_SPECIES**, and **PHASES** data blocks. The value of a named expression can be retrieved in Basic programs with the function `LK_NAMED("name of expression")`. The **ISOTOPE\_ALPHAS** data block allows a named expression to be specified to compare the calculated solution fractionation value to an analytical expression for the fractionation value.

#### **Example problems**

The keyword **NAMED\_EXPRESSION** is used in the *iso.dat* database.

#### **Related keywords**

**ISOTOPE\_ALPHAS**, **SOLUTION\_SPECIES**, **EXCHANGE\_SPECIES**, **SURFACE\_SPECIES**, and **PHASES**.

## PHASES

New options **-add\_logk** and **-add\_constant** have been added to allow named expressions and constant values to be summed in the calculation of log K values. The option may also be used in **EXCHANGE\_SPECIES**, **SOLUTION\_SPECIES**, and **SURFACE\_SPECIES** data blocks.

### Example data block

```
Line 0:  PHASES
Line 1:  Ca[14C][18O]3
Line 2:  Ca[14C][18O]3+3CO2+2H3O+=Ca+2+3H2O+3CO[18O]+[14C]O2
Line 3:  -add_constant 0.903089986991          # 3*log10(2)
Line 4a: -add_logk      Log_K_calcite          1.0
Line 4b: -add_logk      Log_alpha_14C_CO2(aq)/Calcite 1.0
Line 4c: -add_logk      Log_alpha_18O_CO2(aq)/Calcite 3.0
```

### Explanation

Line 0: **PHASES**

Keyword for the data block. No other data are input on the keyword line.

Line 1: *Phase name*

*phase name*--Alphanumeric name of phase, no spaces are allowed.

Line 2: *Dissolution reaction*

Dissolution reaction for phase to aqueous species. Any aqueous species, including e<sup>-</sup>, may be used in the dissolution reaction. The chemical formula for the defined phase must be the first chemical formula on the left-hand side of the equation. The dissolution reaction must precede any identifiers related to the phase. The stoichiometric coefficient for the phase in the chemical reaction must be 1.0.

Line 3: **-add\_constant** *constant*

**-add\_constant**--Identifier for adding a constant to the log *K* expression. Optionally, **add\_constant** or **-add\_c[onstant]**.

*constant*--The constant is added, along with other **-add\_logk** and **-add\_constant** expressions, to calculate log *K* for the reaction.

Line 4: **-add\_logk** *named\_expression* [*coefficient*]

**-add\_logk**--An expression defined in a **NAMED\_EXPRESSION** data block is evaluated and added to the log *K* for the reaction. Optionally, **add\_logk**, **add\_log\_k**, **-ad[d\_log\_k]**, or **-ad[d\_logk]**.

*named\_expression*--Name of the expression defined in a **NAMED\_EXPRESSION** data block.

*coefficient*--Multiply the result of evaluating the named expression by *coefficient* before adding to the log *K* for the reaction. Default 1.

### Notes

Multiple **-add\_constant** and **-add\_logk** identifiers may be used for a single reaction; however, only one **log\_k** identifier is allowed. The log K for a reaction is the sum of the values calculated for **log\_k** (default 0), the constants defined by **-add\_constant** identifiers, and the values of all the named expressions defined by **-add\_logk** identifiers.

## PRINT

Three new identifiers have been added to this keyword data block to control blocks of output written to the output file that are related to isotopes.

### Example data block

```
Line 0:  PRINT
Line 1:  -initial_isotopes      true
Line 2:  -isotope_alphas       true
Line 3:  -isotope_ratios       true
Line 4:  -censor_species        1e-8
```

### Explanation

Line 0: **PRINT**

Keyword for the data block. No other data are input on the keyword line.

Line 1: **-initial\_isotopes** [(*True* or *False*)]

**-initial\_isotopes**--Prints molalities of minor isotopes for initial solution calculations if value is **true**; excludes print if value is **false**. Default is **true**. Optionally, **initial\_isotopes** or **ini[tial\_isotopes]**.

Line 2: **-isotope\_alphas** [(*True* or *False*)]

**-isotope\_alphas**--Prints ratios of isotope ratios as defined by the **ISOTOPE\_ALPHAS** data block if value is **true**; excludes print if value is **false**. Default is **true**. Optionally, **isotope\_alphas** or **-isotope\_a[lphas]**.

Line 3: **-isotopes\_ratios** [(*True* or *False*)]

**-isotope\_ratios**--Prints isotope ratios in standard units as defined by the **ISOTOPE\_RATIOS** data block if value is **true**; excludes print if value is **false**. Default is **true**. Optionally, **isotope\_ratios** or **-isotope\_r[atios]**.

Line 4: **-censor\_species** [*relative\_minimum*]

**-censor\_species**--Limits printing in the “Distribution of species” section of the output file. Aqueous species with small concentrations relative to the total concentration of an element or element redox state are not printed. This print-control option is not affected by **-reset**. Optionally, **censor\_species** or **-c[ensor\_species]**.

*relative\_minimum*--If an aqueous species molality is less than *relative\_minimum* times the total concentration of the element or redox state being printed, then the species data are not printed for that element or redox state. Default 0.0, all aqueous species are printed.

## SELECTED\_OUTPUT

Two new options have been added to control printing of isotopic data and results of Basic programs defined with the **CALCULATE\_VALUES** data block.

### Example data block

```
Line 0: SELECTED_OUTPUT
Line 1:   -isotopes           R(D)      R(13C)
Line 2:   -calculate_values R(D)  R(13C)_CO2(aq) Alpha_D_HCO3-/H2O(1)
```

### Explanation

Line 0: **SELECTED\_OUTPUT**

**SELECTED\_OUTPUT** is the keyword for the data block. No additional data are input on this line. Optionally, **SELECTED\_OUT**, **SELECT\_OUTPUT**, or **SELECT\_OUT**.

Line 1: **-isotopes** *list of isotope\_ratios*

**-isotopes**--Identifier allows definition of a list of isotope-ratio names for which the conventional isotope ratios (units will be permil, pmc, TU, or others) will be written to the selected-output file. Optionally, **-is[otopes]**. Note the hyphen is required to avoid a conflict with the keyword **ISOTOPES**.

*list of isotope\_ratios*--List of isotope-ratio names that have been defined in an **ISOTOPE\_RATIOS** data block. The list may continue on subsequent line(s). After each calculation, the specified isotope ratio, converted to standard units as defined by the **ISOTOPES** data block, will be written to the selected-output file. The heading for the column in the selected-output file will be the isotope-ratio name prepended with "I\_". If the isotope-ratio name is not found or the isotope is not present in the calculation, the value will be printed as -9999.999.

Line 2: **-calculate\_values** *list of calculate-value names*

**-calculate\_values**--Identifier allows definition of a list of names of Basic programs for which the calculated values will be written to the selected-output file. Optionally, **-ca[alculate\_values]**. Note the hyphen is required to avoid a conflict with the keyword **CALCULATE\_VALUES**.

*list of calculate-value names*--List of names of Basic programs that have been defined in a **CALCULATE\_VALUES** data block. The list may continue on subsequent line(s). After each calculation, the value calculated by the Basic program will be written to the selected-output file. The heading for the column in the selected-output file will be the program name prepended with "V\_". If the name is not found in the list of definitions or the value can not be calculated, the value will be printed as -9999.999.

## SOLUTION\_SPECIES

New identifiers **-add\_logk** and **-add\_constant** have been added to allow named expressions and constant values to be summed in the calculation of log K values. The option may also be used in **EXCHANGE\_SPECIES**, **PHASES**, and **SURFACE\_SPECIES** data blocks. The identifier **-activity\_water** has been added to allow isotopic variants of water to have a special activity coefficient.

### Example data block

```
Line 0: SOLUTION_SPECIES
Line 1a: H2O + HDO = OD- + H3O+
Line 2a: -add_constant -0.301029995663 #-Log10(2)
Line 3a: -add_logk Log_K_water 1.0
Line 3b: -add_logk Log_alpha_D_OH-/H2O(1) 1.0
Line 1a: D2O = D2O
Line 4: -activity_water
```

### Explanation

#### Line 0: SOLUTION\_SPECIES

Keyword for the data block. No other data are input on the keyword line.

#### Line 1: Association reaction

Association reaction for aqueous species. The defined species must be the first species to the right of the equal sign. The association reaction must precede any identifiers related to the aqueous species. The association reaction is an identity reaction for each primary master species.

#### Line 2: -add\_constant constant

**-add\_constant**--Identifier for adding a constant to the log *K* expression. Optionally, **add\_constant** or **-add\_c[onstant]**.

*constant*--The constant is added, along with other **-add\_logk** and **-add\_constant** expressions, to calculate log *K* for the reaction.

#### Line 3: -add\_logk named\_expression [coefficient]

**-add\_logk**--An expression defined in a **NAMED\_EXPRESSION** data block is evaluated and added to the log *K* for the reaction. Optionally, **add\_logk**, **add\_log\_k**, **-ad[d\_log\_k]**, or **-ad[d\_logk]**. *named\_expression*--Name of the expression defined in a **NAMED\_EXPRESSION** data block.

*coefficient*--Multiply the result of evaluating the named expression by *coefficient* before adding to the log *K* for the reaction. Default 1.

#### Line 4: -activity\_water

**-activity\_water**--the defined species is an isotopic variant of water and will have an activity coefficient

equal to  $\frac{a_{H_2O}}{55.5}$ , which effectively causes the activity of the species to be equal to its mole fraction. Optionally, **activity\_water**, or **-ac[tivity\_water]**.

### Notes

Multiple **-add\_constant** and **-add\_logk** identifiers may be used for a single reaction; however, only one **log\_k** identifier is allowed. The log K for a reaction is the sum of the values calculated for **log\_k** (default 0), the constants defined by **-add\_constant** identifiers, and the values of all the named expressions defined by **-add\_logk** identifiers. The identifier **-activity\_water** identifier should only be used on isotopic variants of water, such as HDO, D<sub>2</sub>O, H<sub>2</sub><sup>18</sup>O, and others.