DETERMINATION OF δ_{18} IN WATER FROM δ_{18} IN EQUILIBRATED CO_2 : INFLUENCE OF CHANGES IN EXPERIMENTAL PARAMETERS ON THE EQUILIBRATION PROCESS

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ABSTRACT The result of an isotopic exchange reaction is expressed in terms of the isotopic abundance ratios, the fractionation factor and the atom number ratio of the reactants. The general formula is applied to the CO_2 - H_2O system and simplified by neglecting terms small in relation to the experimental error. The influence of variations in the experimental parameters on the equilibrium is discussed. It is found that changes in temperature as well as atom number ratio will influence the equilibration process appreciably.

RESUMO O resultado de reação de troca isotópica é expresso em termos das razões de abundância isotópica, do fator de fracionamento e da razão entre os números de átomos dos reagentes. A fórmula geral é aplicada ao sistema CO_2 - H_2O e simplificada desprezando-se termos pequenos comparados com os erros experimentais. A influência de variações nos parâmetros experimentais no equilíbrio é discutida. Demonstra-se que variações de temperatura, bem como da razão entre os números de átomos influenciam apreciavelmente o processo de equilíbrio.

INTRODUCTION The study of fluctuations in the concentration of stable isotopes ^{18}O and D in water by means of mass-spectrometric measurements is an efficient tool in applied fields such as surface and ground-water hydrology and plant physiology (see, for example, Bochin *et al.*, 1972; Santiago *et al.*, 1975; Salati *et al.*, 1974; Gonfiantini *et al.*, 1965; Mook, 1968; Dongmann, 1974; Wagener, 1975). However, water vapor cannot be investigated directly in the mass spectrometer due to the well known memory effect (Drost *et al.*, 1974). In the usual procedure for the deuterium analysis, the water vapor is totally reduced over Uranium (Friedman and Hardcastle, 1970) to form essentially UH_3 and UDH_2 . The hydrides decompose at high temperature and the H_2 -HD-mixture is used for measurement. The Oxygen-18 analysis is done by isotopically equilibrating water with CO_2 , which is then investigated mass-spectrometrically.

The primary purpose of this work is to relate the isotopic composition of equilibrated CO_2 to the relative ^{18}O content of the original water and to discuss the influence of variations in experimental conditions on the results of the equilibration process. However, since isotopic exchange reactions are also employed in equilibration processes of materials other than water, the general formula derived may be of some interest to other investigators in the field of stable isotope physics, as well.

General Formulation Consider an isotopic exchange reaction where the molecules A and B have one common element, existing in two stable isotopic forms 1 and 2.

Let N_{TA} and N_{TB} represent the total number of atoms of the common element in A and B . If N_{1A} , N_{2A} , N_{1B} and N_{2B} designate the number of atoms of isotopes 1 and 2 in A

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and B before the reaction starts and N_{1A}^E , N_{2A}^E , N_{1B}^E and N_{2B}^E the respective numbers after equilibrium has been reached, then

$$N_{1A} + N_{2A} = N_{1A}^E + N_{2A}^E = N_{TA}, \quad (2)$$

$$N_{1B} + N_{2B} = N_{1B}^E + N_{2B}^E = N_{TB}. \quad (3)$$

Eqs. (2) and (3) imply that the chemical nature of the molecules did not change during the reaction.

The isotope abundance ratios R are defined by

$$\begin{aligned} R_{1A} &= \frac{N_{1A}}{N_{2A}}, & R_{1B} &= \frac{N_{1B}}{N_{2B}}; \\ R_{1A}^E &= \frac{N_{1A}^E}{N_{2A}^E}, & R_{1B}^E &= \frac{N_{1B}^E}{N_{2B}^E}. \end{aligned} \quad (4)$$

Eqs. (2)-(4) yield

$$R_{1A}N_{2A} + R_{1B}N_{2B} = R_{1A}^EN_{2A}^E + R_{1B}^EN_{2B}^E. \quad (5)$$

Defining x to represent the ratio of the total number of atoms of the common element in A and B and using Eqs. (2)-(4)

$$\begin{aligned} x &= \frac{N_{TA}}{N_{TB}}, \\ &= \frac{N_{1A} + N_{2A}}{N_{1B} + N_{2B}} = \frac{N_{2A}}{N_{2B}} \left(\frac{1 + R_{1A}}{1 + R_{1B}} \right), \\ &= \frac{N_{2A}^E}{N_{2B}^E} \left(\frac{1 + R_{1A}^E}{1 + R_{1B}^E} \right). \end{aligned} \quad (6)$$

Eqs. (5) and (6) can be combined to give

$$\frac{N_{2B}}{N_{2B}^E} \left(R_{1B} + xR_{1A} \left(\frac{1 + R_{1B}}{1 + R_{1A}} \right) \right) = R_{1B}^E + xR_{1A}^E \left(\frac{1 + R_{1B}^E}{1 + R_{1A}^E} \right), \quad (7)$$

using Eqs. (3) and (4):

$$\frac{N_{2B}}{N_{2B}^E} = \frac{1 + R_{1B}^E}{1 + R_{1B}}. \quad (8)$$

The isotopic fractionation factor α is defined by

$$\alpha = \frac{R_{1B}^E}{R_{1A}^E}. \quad (9)$$

Substituting Eqs. (8) and (9) into Eq. (7) and solving for R_{1A} yields

$$R_{1A} = \frac{R_{1B}^E \left(\frac{1}{\alpha + R_{1B}^E} + \frac{1}{x(1 + R_{1B}^E)} \right) - \frac{R_{1B}}{x(1 + R_{1B})}}{1 - R_{1B}^E \left(\frac{1}{\alpha + R_{1B}^E} + \frac{1}{x(1 + R_{1B}^E)} \right) + \frac{R_{1B}}{x(1 + R_{1B})}}. \quad (10)$$

Eq. (10) is the general expression for the isotope abundance ratio R_{1A} in A in terms of the ratios R_{1B} and R_{1B}^E in B , the fractionation factor α and the atom number ratio x between A and B . In how far Eq. (10) can be simplified depends on the specific isotope exchange reac-

tion and the values of the experimental parameters such as temperature (through α) and x . In the following, one specific example of special interest will be treated.

EQUILIBRATION OF CO₂ GAS WITH WATER SAMPLES FOR OXYGEN-18 ANALYSIS Consider the isotope equilibration between H₂O and CO₂, the isotopes ¹⁸O and ¹⁶O correspond to 1 and 2 respectively and *A* and *B* to water and CO₂

$$R_{1A} = R_{18}(\text{H}_2\text{O}); \quad R_{1B} = R_{18}(\text{CO}_2); \quad \alpha = \frac{R_{18}^E(\text{CO}_2)}{R_{18}^E(\text{H}_2\text{O})} \quad (11)$$

R's are of the order of 2×10^{-3} , $x \approx 100$ and $\alpha \approx 1.04$ at room temperature. *R*'s relative to 1 (and α) can be neglected and Eq. (10) reduces to

$$R_{18}(\text{H}_2\text{O}) = R_{18}^E(\text{CO}_2) \left(\frac{1}{\alpha} + \frac{1}{x} \right) - \frac{R_{18}(\text{CO}_2)}{x} \quad (12)$$

*R*₁₈(H₂O) of a water sample (*SA*) is usually expressed in terms of the δ value relative to the respective ratio of the standard water (*ST*):

$$\delta_{\text{H}_2\text{O}(\text{ST})}^{\text{H}_2\text{O}(\text{SA})} = \frac{R_{\text{H}_2\text{O}(\text{SA})}}{R_{\text{H}_2\text{O}(\text{ST})}} - 1. \quad (13)$$

Inserting Eq. (12) into Eq. (13) and taking account of the possibility of different experimental conditions (α , x) and (α' , x') when the two equilibration processes are performed, yields

$$\delta_{\text{H}_2\text{O}(\text{SA})}^{\text{H}_2\text{O}(\text{ST})} = \frac{R_{18}^E(\text{CO}_2(\text{SA})) \left(\frac{1}{\alpha} + \frac{1}{x} \right) - \frac{R_{18}(\text{CO}_2(\text{TA}))}{x}}{R_{18}^E(\text{CO}_2(\text{SA})) \left(\frac{1}{\alpha'} + \frac{1}{x'} \right) - \frac{R_{18}(\text{CO}_2(\text{TA}))}{x'}} - 1. \quad (14)$$

Expressing the isotope ratios of the right hand side of Eq. (14) in terms of $\delta^{\text{CO}_2(\text{ST})}$ results in

$$\delta_{\text{H}_2\text{O}(\text{SA})}^{\text{H}_2\text{O}(\text{ST})} = P \delta_{\text{CO}_2(\text{SA})}^{\text{CO}_2(\text{ST})} + Q, \quad (15)$$

where

$$P = \frac{\frac{1}{\alpha} + \frac{1}{x}}{\frac{1}{\alpha'} - \frac{1}{x'} \beta}; \quad (16)$$

$$Q = \frac{\frac{1}{\alpha} - \frac{1}{x} \beta}{\frac{1}{\alpha'} - \frac{1}{x'} \beta} - 1; \quad (17)$$

with Eq. (16), $\delta_{\text{H}_2\text{O}(\text{SA})}^{\text{H}_2\text{O}(\text{ST})}$ can be calculated from the measurable quantities $\delta_{\text{CO}_2(\text{TA})}^{\text{CO}_2(\text{ST})}$ and $\delta_{\text{CO}_2(\text{SA})}^{\text{CO}_2(\text{ST})}$.

These quantities stand for the δ values of tank CO₂ and CO₂ equilibrated with water sample, both with respect to CO₂ equilibrated with standard water. α and x refer to the sample, whereas α' and x' correspond to the standard.

Using literature values (Dongmann, 1973) for the dependence of α on temperature, α can be expressed by the following linear relationship:

$$\alpha(T) = 1.0476 - 2.084 \times 10^{-4} T \quad 5^\circ\text{C} \leq T \leq 40^\circ\text{C} \quad (18)$$

Substituting Eq. (18) into Eqs. (16) and (17) yields

$$P = \frac{\frac{1}{1.0476 - 2.084 \times 10^{-4} T} + \frac{1}{x}}{\frac{1}{1.0476 - 2.084 \times 10^{-4} T'} - \frac{1}{x'} \beta} \quad (19)$$

$$Q = \frac{\frac{1}{1.0476 - 2.084 \times 10^{-4} T} - \frac{1}{x} \beta}{\frac{1}{1.0476 - 2.084 \times 10^{-4} T'} - \frac{1}{x'} \beta} - 1 \quad (20)$$

Eqs. (19) and (20) can be further simplified by neglecting terms small in relation to the experimental error (usually ± 0.0001)

$$P = 1 + \frac{1.0476}{x} - 2.084 \times 10^{-4} \frac{T}{x} + 1.99 \times 10^{-4} (T - T') + \frac{1.0476}{x'} \beta \quad (21)$$

$$Q = 1.99 \times 10^{-4} (T - T') + \beta \left(1.0476 \left(\frac{1}{x'} - \frac{1}{x} \right) - 2.084 \times 10^{-4} \left(\frac{T'}{x'} - \frac{T}{x} \right) \right) \quad (22)$$

In order to evaluate x it is necessary to look at the equilibration process more closely. The samples are prepared by freezing the water of volume V_{H_2O} , removing the residual gas and then adding CO_2 up to a certain pressure P_{CO_2} (Drost *et al.*, 1974). If the CO_2 occupies the volume V_{CO_2} , the O-atom ratio as defined by Eq. (6) is given by

$$x = \frac{1722 \cdot V_{H_2O} \cdot (T + 273)}{V_{CO_2} \cdot P_{CO_2}} \quad (23)$$

where $|P| = \text{Torr}$ and $|T| = ^\circ\text{C}$.

During the equilibration process which usually lasts for about 20 hours, CO_2 dissolves in water. If Eq. (R1) is to describe the reaction between CO_2 in the gas phase and water in the liquid phase only, the O-atom number ratio will increase to a value x^* , since the number density of gaseous CO_2 decreases. From empirical values of solubility (Hildebrand, 1949), including the formation of HCO_3^- ions, making a least square fit to the exponential dependence of solubility on temperature (assuming the Helmholtz free energy to be constant), and applying Henry's law, the solubility S (g/cm^3), within the temperature interval $0^\circ\text{C} - 30^\circ\text{C}$ is given by

$$S(T, P^E) = 3.055 \times 10^{-10} \cdot P^E \cdot \exp\left(\frac{2612.4}{T + 273}\right) \quad (24)$$

where P^E is the pressure at equilibrium in Torr and T the temperature in $^\circ\text{C}$. From Eqs. (23) and (24), x^* may be given the form

$$x^* = x \left(1 + 4.304 \times 10^{-7} \cdot \frac{V_{H_2O}}{V_{CO_2}} \cdot (T + 273) \cdot \exp\left(\frac{2612.4}{T + 273}\right) \right) \quad (25)$$

The effect of solubility on x is quite pronounced as can be seen from the following example: $P = 600 \text{ Torr}$, $T = 27^\circ\text{C}$, $\frac{V_{CO_2}}{V_{H_2O}} = 9$, yield $x = 95.7$ and $x^* = 104$.

Tabs. I and II give an impression of the influence of changes in temperature, T , atom number ratio, x , and isotopic composition of tank CO_2 , β , on the values of P and Q given by Eqs. (19) and (20) for $x' = 100$, $T' = 25^\circ\text{C}$ and for two values of β , $\beta = -0.01$ and -0.015 .

Table I — Values of P and Q for $x' = 100$, $T' = 25^\circ\text{C}$, $\beta = -.01$ using Eqs. (19) and (20)

$T(^{\circ}\text{C}) \backslash X$		80	100	120
22	P	1.0123	1.0097	1.0080
	Q	-0.00057	-0.00060	-0.00062
25	P	1.0129	1.0103	1.0086
	Q	0.00003	0.0	-0.00002
28	P	1.0135	1.0109	1.0092
	Q	0.00063	0.00060	0.00058

Table II — Values of P and Q for $x' = 100$, $T' = 25^\circ\text{C}$, $\beta = -.015$ using Eqs. (19) and (20)

$T(^{\circ}\text{C}) \backslash X$		80	100	120
22	P	1.0123	1.0097	1.0079
	Q	-0.00056	-0.00060	-0.00063
25	P	1.0129	1.0103	1.0085
	Q	0.00004	0.0	-0.00003
28	P	1.0135	1.0109	1.0091
	Q	0.00064	0.00060	0.00058

Discussion and Conclusions 1. Eq. (15) gives the δ value of ^{18}O in a water sample relative to standard water in terms of measurable quantities:

$\delta_{\text{CO}_2(\text{ST})}^{\text{CO}_2(\text{ST})}$, $\delta_{\text{CO}_2(\text{TA})}^{\text{CO}_2(\text{ST})}$; T , T' ; x and x' . The expression is very general as it includes explicitly the influence of variations in the experimental parameters.

It should be pointed out that Eq. (5) of Craig (Craig, 1957) relates the measured ^{18}O enrichment of CO_2 equilibrated with the water sample (whose ^{18}O concentration has been slightly changed by the added CO_2) to the ^{18}O enrichment of CO_2 in equilibrium

with the original water sample. This equation can be derived from Eq. (12) of the present work by expressing the results in terms of δ 's and recognizing that δ in Craig's work is given by

$$\delta = (1 + \delta_{\text{H}_2\text{O}(SA)}^{\text{H}_2\text{O}(ST)})\alpha - 1.$$

2. The isotopic composition of CO_2 (for example, commercial CO_2) may not be identical in the two equilibration processes. Tabs. I and II show that the effect of such changes ($\beta = -0.01$ to $\beta = -0.015$) on $\delta_{\text{H}_2\text{O}(SA)}^{\text{H}_2\text{O}(ST)}$ is less than the analytical error (± 0.0001). Hence such effects may be neglected.

3. The atomic number ratio may change due to volume differences in the vessels employed for equilibration, dissolution of a fraction of CO_2 in water, existence of water vapor and errors in the determination of P_{CO_2} , V_{CO_2} and $V_{\text{H}_2\text{O}}$, which quantities are used in calculating x [Eq. (23)]. Tabs. I and II demonstrate that, for constant T , the changes in Q are negligible but those in P are important. Consequently, variations in x should be considered in the determination of $\delta_{\text{H}_2\text{O}(SA)}^{\text{H}_2\text{O}(ST)}$.

4. Fluctuations in temperature influence both P and Q strongly. It is imperative therefore that the temperature is the same in both equilibration processes. Furthermore, since the room temperature will usually be different from the temperature of the equilibration bath, CO_2 gas should be separated from the water immediately after removing the equilibration vessel from the bath. This is usually done by freezing the water (containing dissolved CO_2) in a dry-ice-alcohol bath. This process, even though very fast, may influence the isotopic equilibrium reached in the temperature bath because both α (due to its dependence on the temperature) and x (due to the increase in solubility of CO_2 in water) may change noticeably. It might be of practical importance, therefore, to study the shift in isotopic equilibrium as a function of temperature difference and freezing-out time. It should be pointed out that the method of sample preparation varies somewhat from one laboratory to the other. Consequently, it is necessary to apply distinct corrections in each specific case. Thus, for example, some of the laboratories do not follow the usual procedure discussed above, but draw a sample from the water vapour- CO_2 mixture in order to minimize the effect of temperature on equilibrium. Other laboratories make use of two standards so that some corrections do not apply.

5. The value of α given in the literature (Dongmann, 1973) and used in the above calculations is supposed to correspond to reaction (R1) only (Craig, 1957). However, the measured α is the effective isotopic fractionation factor which is the net result of a number of exchange processes occurring in the CO_2 -water system:

where (G), (L), (D), (V) designate gas, liquid, dissolved and vapour respectively. Since the influence of the above reactions on the equilibration process would be a function of the solubility of CO_2 in water and therefore on x , the effective α will not only depend on temperature but also on the volume ratio $V_{\text{H}_2\text{O}}/V_{\text{CO}_2}$ with which the equilibration process was performed.

Acknowledgements One of the authors (H. L. A.) would like to thank the Brazilian Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for partial financial assistance.

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