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## 211. Exchange Equilibrium of Oxygen Isotopes between $\text{BrO}_3^-$ , $\text{ClO}_3^-$ , $\text{IO}_3^-$ and Water

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(5. VII. 72)

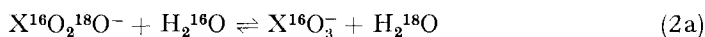
*Summary.* The liquid phase fractionation factors  $\alpha_{\text{H}} = (^{18}\text{O}/^{16}\text{O})_{\text{H}_2\text{O}} / (^{18}\text{O}/^{16}\text{O})_{\text{XO}_3^-}$  and  $\alpha_{\text{D}} = (^{18}\text{O}/^{16}\text{O})_{\text{D}_2\text{O}} / (^{18}\text{O}/^{16}\text{O})_{\text{XO}_3^-}$  (X = Cl, Br, I) were calculated quantum mechanically between 0 and 100°. Experimental values were obtained in the case of  $\text{BrO}_3^-$  at 60° showing good agreement with the calculated results.

In connection with the investigation of the exchange kinetics of oxygen between halogenate ions and water [1] it was of interest to determine the equilibrium fractionation factors

$$\alpha_{\text{H}} = (^{18}\text{O}/^{16}\text{O})_{\text{H}_2\text{O}} / (^{18}\text{O}/^{16}\text{O})_{\text{XO}_3^-} \quad (1a)$$

$$\alpha_{\text{D}} = (^{18}\text{O}/^{16}\text{O})_{\text{D}_2\text{O}} / (^{18}\text{O}/^{16}\text{O})_{\text{XO}_3^-} \quad (1b)$$

of the respective exchange reactions in the liquid phase



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Since these fractionation factors could not be found in the literature they were calculated from the available experimental and theoretical data.

*Calculation of fractionation factors  $\alpha_H$ ,  $\alpha_D$ .* - The quantum mechanics of isotopic exchange reactions according to the formulation of *Bigeleisen & Mayer* [2] leads to the following expressions:

$$\alpha_H = Q_r(\text{H}_2^*\text{O}/\text{H}_2\text{O}) / Q_r(\text{XO}_2^*\text{O}^-/\text{XO}_2^-) \quad (3a)$$

$$\alpha_D = Q_r(\text{D}_2^*\text{O}/\text{D}_2\text{O}) / Q_r(\text{XO}_2^*\text{O}^-/\text{XO}_2^-). \quad (3b)$$

$Q_r$  = reduced partition function<sup>2)</sup> ratio of isotopic molecules.

X = Cl, Br, I and \*O =  $^{18}\text{O}$ .

*Staschewsky* [3] has calculated the gas phase partition function ratios for  $\text{H}_2^*\text{O}/\text{H}_2\text{O}$  and  $\text{D}_2^*\text{O}/\text{D}_2\text{O}$  considering the effects of anharmonicity and vibrational-rotational interactions. The reduced partition function ratios  $Q_r$  for liquid water can be obtained by multiplying these values with the factor  $(18/16)^{3/2}$  and with the appropriate values of the distillation separation factor  $\beta'_H$  and  $\beta'_D$ , respectively, as derived from vapour pressure measurements of *Szapiro & Steckel* [4]. Thus the following relations apply to the  $\text{H}_2\text{O}$ -system (and similarly to the  $\text{D}_2\text{O}$ -system):

$$Q_r(\text{H}_2^*\text{O}/\text{H}_2\text{O})_{\text{liq}} = Q_r(\text{H}_2^*\text{O}/\text{H}_2\text{O})_{\text{vap}} \cdot \beta'_H \quad (4)$$

with

$$\ln \beta'_H = \left[ 1 - \frac{P_{\text{H}_2\text{O}}}{RT} \cdot (V_1 - B_0) \right] \ln (P_{\text{H}_2\text{O}}/P_{\text{H}_2^*\text{O}}) \quad (5)$$

$V_1$  = molar volume of liquid water in  $\text{cm}^3/\text{mole}$

$B_0$  = second virial coefficient of water vapour in  $\text{cm}^3/\text{mole}$

$P_{\text{H}_2\text{O}}, P_{\text{H}_2^*\text{O}}$  = saturation vapour pressures of  $\text{H}_2^{16}\text{O}$  and  $\text{H}_2^{18}\text{O}$  at  $T^\circ\text{K}$

Since the correction term  $P/RT (V_1 - B_0)$  in Eq. (5) amounts to less than 0.016 and differs very little for  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ , only the values for  $\text{H}_2\text{O}$  were used. The calculated values of  $Q_r(\text{H}_2^*\text{O}/\text{H}_2\text{O})_{\text{liq}}$  and  $Q_r(\text{D}_2^*\text{O}/\text{D}_2\text{O})_{\text{liq}}$  are given in Table 1. The values for  $Q_r(\text{H}_2^*\text{O}/\text{H}_2\text{O})_{\text{liq}}$  are in close agreement with the values which *O'Neil & Adami* [5] obtained by measuring the oxygen isotope fractionation factors between  $\text{CO}_2$  and  $\text{H}_2\text{O}_{(\text{liq})}$  and eliminating the calculated partition function ratio  $Q_r(\text{C}^*\text{O}_2/\text{CO}_2)$ . These values are also given in Table 1.

Table 1. *Calculated liquid phase reduced partition function ratios  $Q_r$  of isotopic  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ . In parentheses: values determined by *O'Neil & Adami* [5].*

Temp. ( $^\circ\text{C}$ )	$[Q_r(\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}) - 1] \cdot 10^3$	$[Q_r(\text{D}_2^{18}\text{O}/\text{D}_2^{16}\text{O}) - 1] \cdot 10^3$
0	83.68 (83.43)	101.97
20	75.60 (75.58)	92.61
40	69.04 (68.82)	84.49
60	63.27 (62.81)	77.30
80	58.12 (57.57)	70.88
100	53.56 (52.90)	65.24

<sup>2)</sup> The reduced partition function of a molecule is defined as the ratio of the quantum mechanical and the classical partition functions.

The reduced partition function ratios  $Q_r$  for the isotopic halogenate ions were calculated with a harmonic oscillator rigid rotator approximation. Translational and rotational partition functions in the liquid were neglected since for heavy molecules or ions as  $\text{XO}_3^-$  their contribution to the isotope effect is very small.

Thus,

$$Q_r(\text{XO}_2^*\text{O}^-/\text{XO}_3^-) = \prod_{i=1}^{3n-6} \frac{u_i^* \exp(-u_i^*/2) / [1 - \exp(-u_i^*)]}{u_i \exp(-u_i/2) / [1 - \exp(-u_i)]} \quad (4)$$

with  $u_i = hc \bar{\nu}_i/kT = 1.43880 \bar{\nu}_i/T$ .

The *Wilson* F-G matrix method [6] was used to calculate the vibrational frequencies of  $\text{XO}_3^-$  and  $\text{XO}_2^*\text{O}^-$ . This calculation was performed with the aid of the computer programs of *Schachtschneider* [7], using the geometric parameters and force constants of *Venkateswarlu et al.* [8]. The force constants for  $\text{ClO}_3^-$  had to be recalculated because the  $A_1$  type frequencies obtained with the data of *Venkateswarlu* were about 6–10% higher than the observed frequencies. The calculated frequencies for the anions  $\text{X}^{16}\text{O}_3^-$  and  $\text{X}^{16}\text{O}_2^{18}\text{O}^-$  are given in Table 2.

Table 2. *Vibrational frequencies<sup>a)</sup> of  $\text{X}^{16}\text{O}_3^-$  and  $\text{X}^{16}\text{O}_2^{18}\text{O}^-$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ) in  $\text{cm}^{-1}$*

Ion	Mode of vibr.	X – O str.		O – X – O def.			
		antisym.	sym.	antisym.	sym.		
$\text{Cl}^{16}\text{O}_3^-$		963.9	963.9	939.6	480.5	480.5	620.9
$\text{Cl}^{16}\text{O}_2^{18}\text{O}^-$		963.9	946.5	926.0	474.8	468.9	609.1
$\text{Br}^{16}\text{O}_3^-$		829.1	829.1	801.0	350.4	350.4	442.5
$\text{Br}^{16}\text{O}_2^{18}\text{O}^-$		829.1	815.0	777.0	346.7	341.3	435.8
$\text{I}^{16}\text{O}_3^-$		809.8	809.8	781.0	326.4	326.4	357.4
$\text{I}^{16}\text{O}_2^{18}\text{O}^-$		809.8	795.4	755.2	322.6	317.7	352.2

<sup>a)</sup> for experimental values see Ref. [8].

The calculated values for the liquid-phase reduced partition function ratios  $Q_r$  of all the three  $\text{X}^{16}\text{O}_2^{18}\text{O}^-/\text{X}^{16}\text{O}_3^-$ -pairs in the temperature range of 0–100° are given in Table 3.

Table 3. *Calculated liquid-phase reduced partition function ratios  $Q_r$  of isotopic halogenate ions*

Temp. °C	$Q_r \left( \frac{\text{Cl}^{16}\text{O}_2^{18}\text{O}^-}{\text{Cl}^{16}\text{O}_3^-} \right)$	$Q_r \left( \frac{\text{Br}^{16}\text{O}_2^{18}\text{O}^-}{\text{Br}^{16}\text{O}_3^-} \right)$	$Q_r \left( \frac{\text{I}^{16}\text{O}_2^{18}\text{O}^-}{\text{I}^{16}\text{O}_3^-} \right)$
0	1.08537	1.07440	1.07329
20	1.07563	1.06574	1.06474
40	1.06743	1.05848	1.05758
60	1.06048	1.05235	1.05153
80	1.05454	1.04711	1.04636
100	1.04941	1.04261	1.04192

By introducing the  $Q_r$  values of Table 1 and Table 3 into Eq. (3a) and Eq. (3b) the corresponding fractionation factors  $\alpha_H$  and  $\alpha_D$  as given in Table 4 can be obtained.

Table 4.  $^{18}\text{O}/^{16}\text{O}$ -separation factors  $\alpha_{\text{H}}$  ( $\alpha_{\text{D}}$ ) between liquid  $\text{H}_2\text{O}$  ( $\text{D}_2\text{O}$ ) and halogenate ions

Temp. °C	$\text{ClO}_3^-$		$\text{BrO}_3^-$		$\text{IO}_3^-$	
	$\alpha_{\text{H}}$	$\alpha_{\text{D}}$	$\alpha_{\text{H}}$	$\alpha_{\text{D}}$	$\alpha_{\text{H}}$	$\alpha_{\text{D}}$
0	0.99844	1.01529	1.00862	1.02564	1.00967	1.02671
20	0.99997	1.01579	1.00924	1.02520	1.01019	1.02617
40	1.00150	1.01598	1.00996	1.02456	1.01082	1.02543
60	1.00262	1.01585	1.01036	1.02369	1.01115	1.02448
80	1.00339	1.01549	1.01049	1.02267	1.01121	1.02340
100	1.00395	1.01508	1.01047	1.02167	1.01114	1.02235

*Experimental determination of  $\alpha_{\text{H}}$  and  $\alpha_{\text{D}}$  for  $\text{BrO}_3^-$  at 60°.* – Solutions of  $\text{KBrO}_3$  (0.05M) in 0.1M  $\text{HNO}_3$  ( $\text{DNO}_3$ ) were equilibrated at 60° for 24 hours (about 50 half times for exchange).  $\text{KBrO}_3$ ,  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  of normal  $^{18}\text{O}$  content ( $\sim 0.2\%$ ) were used. Samples of the equilibrated solution were poured into an excess of ice cooled  $\text{AgNO}_3$  solution and the  $\text{AgBrO}_3$  precipitate was centrifuged and washed with water, ethanol and acetone. The  $\text{AgBrO}_3$  was then decomposed by heating in evacuated Pyrex containers to yield oxygen whose  $^{18}\text{O}/^{16}\text{O}$  ratio was compared with that of a standard (tank oxygen) by means of a double-collector isotope-ratio mass spectrometer.

A comparable  $^{18}\text{O}/^{16}\text{O}$  ratio in the water of the equilibrium solution was obtained in the following way: Standard tank oxygen was combined quantitatively with  $\text{H}_2$  (small excess) over a Pd-catalyst leading to water ( $\sim 30$  ml) of exactly the same  $^{18}\text{O}/^{16}\text{O}$  ratio as the standard tank oxygen. The  $^{18}\text{O}/^{16}\text{O}$  ratio in this recombined water and in the solution water were now compared accurately using the  $\text{CO}_2$  exchange technique [9] at 25°. Since the true  $^{18}\text{O}/^{16}\text{O}$  ratios in the standard  $\text{O}_2$  and the recombined water are the same, all discrimination effects by comparing  $^{18}\text{O}/^{16}\text{O}$  ratios in  $\text{H}_2\text{O}$  (as  $\text{CO}_2$ ) and  $\text{O}_2$  can be eliminated, and the fractionation factor  $\alpha_{\text{H}}$  can be calculated easily.

A similar procedure was used in case of  $\text{D}_2\text{O}$  (99.8% D, 0.20%  $^{18}\text{O}$ ) as solvent. Since no special recombination experiment with  $\text{D}_2$  was carried out, the ratio of the fractionation factors of  $^{18}\text{O}/^{16}\text{O}$  between  $\text{CO}_2$  and  $\text{H}_2\text{O}$  ( $\beta_{\text{H}}$ ) and  $\text{CO}_2$  and  $\text{D}_2\text{O}$  ( $\beta_{\text{D}}$ ) at the exchange temperature of 25° had to be introduced. Using the data of *Staschewsky* [10] this ratio becomes

$$\beta_{\text{H}}/\beta_{\text{D}} = 1.0424/1.0259 = 1.0161.$$

All isotope ratios were measured with a relative precision of about  $\pm 0.3\%$ .

From the measurements and Eq. (1) the following separation factors at 60° were secured

$$\alpha_{\text{H}} = 1.010 \pm 0.001 \quad \alpha_{\text{D}} = 1.023 \pm 0.001.$$

These values agree with the calculated values in Table 4 within the limits of error.

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