ACTA CHEMICA SCANDINAVICA 26 (1972) 581–584

Sulfur Isotope Effects

II. The Isotopic Exchange Coefficients for the Sulfur Isotopes ^{34}S—^{32}S in the System $SO_{2\ g}$-Aqueous Solutions of SO_2

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The isotopic exchange coefficient for the phase transfer reaction

$$^{34}SO_{2\ g} + {}^{32}SO_{2\ aq} \rightleftharpoons {}^{32}SO_{2\ g} + {}^{34}SO_{2\ aq}$$

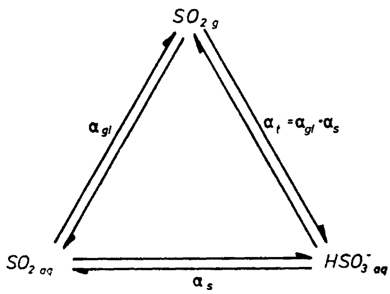
has been measured at 25, 35, and 45°C by means of Rayleigh distillation.

From the results obtained previously for the system $SO_{2\ g} - HSO_3^-{}_{aq}$ the exchange coefficient for the protolytic reaction

$$^{34}SO_{2\ aq} + H^{32}SO_3^-{}_{aq} \rightleftharpoons {}^{32}SO_{2\ aq} + H^{34}SO_3^-{}_{aq}$$

was calculated.

In aqueous solutions of sulfur dioxide with $HSO_3^-{}_{aq}$ concentration < 1 M the concentration of $S_2O_5^{2-}{}_{aq}$ may be neglected [9] and the isotope exchange system may be described as follows:



As seen, the isotopic exchange coefficient for the protolytic step $SO_{2\ aq} \rightleftharpoons H^+{}_{aq} + HSO_3^-{}_{aq}$ is the ratio of the exchange coefficients for the systems $SO_{2\ g} - HSO_3^-{}_{aq}$ and $SO_{2\ g} - SO_{2\ aq}$ and the effective isotopic separation factor between sulfur dioxide and an aqueous solution of sulfur dioxide containing the species $SO_{2\,aq}$ and $HSO_3^-{}_{aq}$ can be written (see I in this series [9])

$$\alpha_0 = \alpha_{gl}[(1 - x_{HSO_3^-}) + \alpha_s\, x_{HSO_3^-}] \tag{1}$$

where $x_{HSO_3^-}$ is the mol fraction $HSO_3^-{}_{aq}$.

In an aqueous solution of sulfur dioxide with a total sulfur concentration ≤ 1 M and pH < 0.3 more than 97 % of the sulfur exists as unprotolyzed species $SO_{2\,aq}$ ($K_1 = 1.72 \times 10^{-2}$ M),[1,2] and the isotope exchange equilibrium for the sulfur isotopes ^{34}S and ^{32}S between gas and solution can be written

$$^{34}SO_{2\,g} + {}^{32}SO_{2\,aq} \rightleftharpoons {}^{32}SO_{2\,g} + {}^{34}SO_{2\,aq} \tag{2}$$

Writing the isotopic ratio in gas and solution as $(^{34}S/^{32}S)_g$ and $(^{34}S/^{32}S)_{aq}$, respectively, the isotopic exchange coefficient for the system is defined as

$$\alpha_{gl} = \frac{(^{34}S/^{32}S)_{aq}}{(^{34}S/^{32}S)_g} \tag{3}$$

The isotopic exchange coefficient α_{gl} includes the isotope effects caused by physical isotope transport between the phases and hydration in the aqueous phase.

The aim of the present work was to measure the isotope effect for the phase transfer reaction [12] and to calculate from these results and results obtained previously for the system $SO_{2\,g} - HSO_3^-{}_{aq}$, the isotopic effect due to the protolytic reaction $SO_{2\,aq} \rightleftharpoons H^+_{aq} + HSO_3^-{}_{aq}$.

Principle. If sulfur dioxide is flushed out of an aqueous solution of sulfur dioxide, containing only the species $SO_{2\,aq}$, sufficiently slowly to maintain isotopic equilibrium in the system at all times, the process may be treated as a modified molecular distillation.

Writing the total amount of sulfur and isotope fraction $(^{34}SO_2/^{32}SO_2)_{aq}$ in solution before and after distillation, respectively, as S_1, x_1 and S_2, x_2, a mass balance for the isotope ^{34}S gives:[9]

$$\alpha_{gl} = \frac{\ln[S_1/S_2] + \ln[(1-x_1)/(1-x_2)]}{\ln[S_1/S_2] - \ln[x_2/x_1]}$$

(The concentrations of ^{33}S and ^{36}S are neglected in this mass balance.)

EXPERIMENTAL

The solutions were prepared by bubbling sulfur dioxide through a 0.5 M aqueous perchloric acid solution until the $SO_{2\,aq}$ concentration was ≈ 1.2 M

The distillations were carried out by slowly flushing out sulfur dioxide by a stream of small nitrogen gas bubbles through 100 ml solution. The distillations were stopped when a few per cent of the initial $SO_{2\,aq}$ concentration was left in solution. During the experiments the solutions and gas were thermostated to $T \pm 0.1$°C.

The concentration of $SO_{2\,aq}$ before and after distillation was determined by iodometry and the isotope ratio $(^{34}S/^{32}S)_{aq}$ determined mass-spectrometrically.[9]

RESULTS

The results obtained are tabulated in Table 1.

Table 1. The isotope exchange coefficient for the sulfur isotopes ^{34}S and ^{32}S in the system $SO_{2\,g} - SO_{2\,aq}$.[a]

	α_{gl} 25°C	α_{gl} 35°C	α_{gl} 45°C
	0.9975	1.00153	1.00057
	0.9980	1.00012	1.00194
	1.0026	1.00220	1.00468
	1.0019	1.00168	1.00447
	0.9996	1.00174	
	0.9997		
$\bar{\alpha}_{gl}$	0.9999 ± 0.0008	1.0015 ± 0.0004	1.0029 ± 0.0010

[a] From Ref. 9.

The exchange coefficients for the protolytic step $SO_{2\,aq} \rightleftharpoons HSO_3{}^-{}_{aq}$ were calculated on the basis of the experimental results and data from part I in this series.[9] They are tabulated in Table 2.

Table 2. The exchange coefficients for the sulfur isotopes ^{34}S and ^{32}S in the system $SO_{2\,g}$ – aqueous solutions of SO_2.

T°C	$SO_{2\,g} - HSO_3{}^-{}_{aq}$[a] α_t	$SO_{2\,g} - SO_{2\,aq}$ α_{gl}	$SO_{2\,aq} - HSO_3{}^-{}_{aq}$ α_s
25	1.0109 ± 0.0007	0.9999 ± 0.0008	1.0110 ± 0.0010
35	1.0110 ± 0.0008	1.0015 ± 0.0004	1.0095 ± 0.0009
45	1.0113 ± 0.0009	1.0029 ± 0.0010	1.0084 ± 0.0013

[a] From Ref. 9.

DISCUSSION

Spectroscopic studies (IR and Raman) show that sulfur dioxide in aqueous solutions ($SO_{2\,aq}$) is only slightly hydrated,[2–4,7] *i.e.* the vibration frequencies found in aqueous solution only slightly deviate from the frequencies found in gaseous and liquid sulfur dioxide.

Thus $(\alpha_{gl} - 1) = \varepsilon_{gl}$ for the aqueous system might be expected to be small and of the same order of magnitude as the ε-value for the system $SO_{2\,g} - SO_{2\,cp}$ (cp relates to condensed phase).

Devyatykh *et al.*[6] have studied experimentally the isotope coefficient for $^{34}S - ^{32}S$ in the system $SO_{2\,g} - SO_{2\,cp}$ and give $\alpha_{gcp} = 1.0018$ at 263 K. Calculations based on statistical theory by Kuznetsova *et al.*[5] give $\alpha_{gcp} = 1.0012$ for the same system. However, as the isotope effect is due partly to the physical transfer of isotopic species across the phase boundary and partly to hydration in the liquid phase the two effects may oppose each other. (For the system

$HCN_g - CN^-_{aq}$ the phase transfer gives a very slight enrichment of the heavy carbon isotope in the gaseous phase.[8]

The temperature effect has been tested with the F-test [13] which from a measure of the ratio of two variances provides critical values which will rarely be exceeded if the variances are both estimates of the same σ^2. The data in Table 1 give a critical value $F = 3.88$ at a 5 % level. The calculated value is slightly higher than the critical value ($F_{calc} = 3.94$). Thus the temperature effect is not within the experimental error at this level, and a slight increase in $\bar{\alpha}_{gl}$ with temperature is found within the temperature range 298 – 318 K.

It is to be emphasized that as the concentration of sulfur dioxide (or hydrogen sulfite and chloride ions in Ref. 9) is not constant during the distillation, a continuous change of the intermolecular interactions may occur. The results obtained should therefore be treated as average values for the concentration range $\approx 0.1 - 1.2$ M.

As seen, the isotope effect due to the protolytic reaction $SO_{2\,aq} \rightleftharpoons HSO_3^-{}_{aq}$, which may involve several steps, is several times greater than the effect due to phase transfer and hydration. The results calculated for the protolytic reaction (Table 2) are in fairly good agreement with the results obtained by Forberg and Westermark [10,11] by anion exchange experiments where no gas phase was involved. However, as the values of α_t are throught to be slightly too low, due to the vapour pressure of the solvent and some entrainment of liquid by the gas stream,[9] so also are the calculated α_s values. As a saturated aqueous solution of sulfur dioxide is approximately 11 % protolyzed [12] the effective separation factor between sulfur dioxide gas and a saturated aqueous solution at 25°C might be calculated from eqn. (1) to be $\alpha_{0\ sat} = 1.0011 \pm 0.0008$.

Acknowledgements. The author wishes to express his appreciation to Professor T. Westermark, Head of this Department, for his kind interest in this research, and to Dr. S. Forberg for valuable discussions. Miss P. Jurik has skillfully assisted in the experimental work. The isotope abundance measurements were performed by the Mass Spectrometric Laboratory, Karolinska Institutet, Stockholm.

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Received May 17, 1971.