

Sulfur Isotope Effects

III. Enrichment of ^{34}S by Chemical Exchange Between $\text{SO}_2\text{ g}$ and Aqueous Solutions of SO_2

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The isotope fractionation factors for the sulfur isotopes $^{34}\text{S} - ^{32}\text{S}$ between sulfur dioxide and aqueous solutions of sulfur dioxide with different fractions of the species $\text{SO}_2\text{ aq}$, $\text{HSO}_3^-\text{ aq}$ and $\text{S}_2\text{O}_5^{2-}\text{ aq}$ were measured at 25, 35, and 45°C.

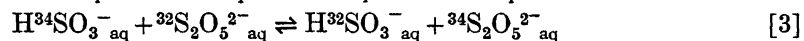
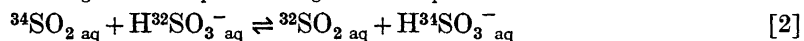
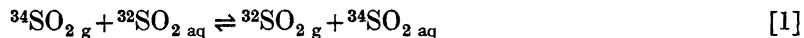
The isotope effect for the sulfur isotopes $^{34}\text{S} - ^{32}\text{S}$ in the exchange system $\text{SO}_2\text{ g} - \text{HSO}_3^-\text{ aq}$ in which the heavy isotope concentrates in the solution has been shown to be mainly due to the protolytic step.¹ There may, however, be a smaller effect due to physical transfer between the phase and to hydration.²

As seen from the equation

$$\alpha_0 = \alpha_{g1}[1 + (\alpha_s - 1)x_{\text{HSO}_3^-}] \quad (1)$$

(where α_{g1} and α_s relate to phase transfer and protolytic reaction, respectively) the mol fraction $\text{HSO}_3^-\text{ aq}$ should be as high as possible to obtain a high isotope fractionation factor between the gas and an aqueous solution. This can be done either by carrying out experiments in vacuum^{3,4} or by using concentrated solutions of a highly soluble hydrogen sulfite, *e.g.* NH_4HSO_3 .

In concentrated aqueous hydrogen sulfite solutions a complication may arise from the equilibrium $2\text{HSO}_3^-\text{ aq} \rightleftharpoons \text{S}_2\text{O}_5^{2-}\text{ aq}$, $K_3 = 7 \times 10^{-2}$, which must be taken into account. The following exchange reactions can be written:



with the isotope exchange coefficients α_{g1} , α_s and α_c ($\text{SO}_3^{2-}\text{ aq}$ can be neglected for solutions with $\text{pH} \leq 4.5$).

Writing the mol fractions of the species $\text{SO}_{2,\text{aq}}$, HSO_3^- and $\text{S}_2\text{O}_5^{2-}$ as $x_{\text{SO}_2,\text{aq}}$, $x_{\text{HSO}_3^-}$ and $x_{\text{S}_2\text{O}_5^{2-}}$, respectively, and defining the overall isotope enrichment factor as

$$\alpha_0 = \frac{[^{34}\text{S}/^{32}\text{S}]_{\text{aq}}}{[^{34}\text{S}/^{32}\text{S}]_{\text{g}}} \quad [4]$$

a combination of eqns. [1]–[4] gives

$$\alpha_0 = \alpha_g[x_{\text{SO}_2,\text{aq}} + \alpha_s(x_{\text{HSO}_3^-} + \alpha_c x_{\text{S}_2\text{O}_5^{2-}})] \quad [5]$$

The aim of the present work was to study the isotope fractionation factor α_0 for the sulfur isotopes ^{34}S – ^{32}S between gaseous sulfur dioxide and concentrated aqueous solutions of sulfur dioxide, especially with regard to the mol fraction $x_{\text{SO}_2,\text{aq}}$.

EXPERIMENTAL

The experiments were carried out by bubbling sulfur dioxide with a constant ^{34}S – ^{32}S isotope ratio for approximately two days through 50 ml ammonium hydrogen sulfite or perchloric acid solutions saturated with sulfur dioxide. Gradient studies established that this was sufficient to achieve isotopic equilibrium. The total sulfur concentration in the solutions was in the range ≈ 1.5 – 10 M.

The solutions contained small amounts of *N,N*-dimethyl formamide to inhibit oxidation. Gas samples were obtained from the gas phase of the equilibrated system and liquid samples by removing ~ 1 ml of the solution, acidifying with sulfuric acid and flushing out all sulfur gas formed in a vacuum system. Analysis showed that less than 0.3 % sulfur was left in solution after conversion to sulfur dioxide (presumably as SO_2,aq). Calculations based on data obtained by Rayleigh distillation^{1,2} give an error in α_0 , due to SO_2,aq loss in sample, less than 0.001.

The samples were analyzed mass-spectrometrically w.r.t. masses 64 + 65 and 66.^{1,2}

RESULTS AND DISCUSSION

The results obtained are given in Table 1 and in Fig. 1, a–c where the isotope fractionation factors α_0 at 25, 35, and 45°C are plotted *versus* the ionic fraction $(1 - x_{\text{SO}_2,\text{aq}})$.

As the ionic fraction is increased by increasing the ammonium hydrogen sulfite concentration the ratio $(\text{S}_2\text{O}_5^{2-}/\text{HSO}_3^-)$ will increase with ionic strength and a large isotope effect in the reaction $2 \text{HSO}_3^- \rightleftharpoons \text{S}_2\text{O}_5^{2-}$ should give a marked deviation from a straight line fitted to the results obtained for low ionic fractions as the $\text{S}_2\text{O}_5^{2-}$ concentration varies with the square of the hydrogen sulfite concentration. (This was not found to be the case.) However, by applying the method of least squares to the experimental data the following linear equations were obtained

$$25^\circ\text{C} \quad \alpha_0 = (1.0009 \pm 0.0004) + (0.0090 \pm 0.0006) (1 - x_{\text{SO}_2,\text{aq}})$$

$$35^\circ\text{C} \quad \alpha_0 = (1.0012 \pm 0.0002) + (0.0081 \pm 0.0005) (1 - x_{\text{SO}_2,\text{aq}})$$

$$45^\circ\text{C} \quad \alpha_0 = (1.0016 \pm 0.0003) + (0.0075 \pm 0.0005) (1 - x_{\text{SO}_2,\text{aq}})$$

The results at $x_{\text{SO}_2,\text{aq}} = 1$ and $x_{\text{SO}_2,\text{aq}} = 0$, obtained from the equations above, are given in Table 2 together with the data obtained by Rayleigh distillation.^{1,2}

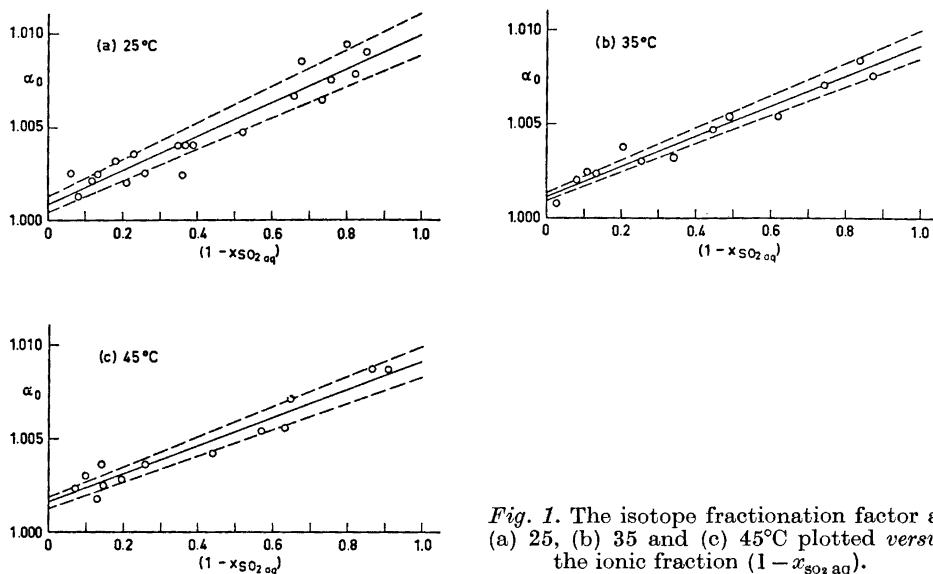


Fig. 1. The isotope fractionation factor at (a) 25, (b) 35 and (c) 45°C plotted versus the ionic fraction $(1 - x_{SO_2 aq})$.

Table 1. The exchange factor α_0 for the isotopes ^{34}S – ^{32}S between sulfur dioxide gas and aqueous solution of sulfur dioxide as a function of the ionic fraction $^a (1 - x_{SO_2 aq})$ at 25, 35, and 45°C.

Ionic fraction ($1 - x_{SO_2 aq}$)	α_0 25°	Ionic fraction ($1 - x_{SO_2 aq}$)	α_0 35°	Ionic fraction ($1 - x_{SO_2 aq}$)	α_0 45°
0.058	1.0025	0.026	1.0007	0.071	1.0023
0.081	1.0013	0.078	1.0021	0.100	1.0030
0.116	1.0021	0.106	1.0025	0.127	1.0018
0.131	1.0025	0.133	1.0024	0.143	1.0036
0.182	1.0032	0.206	1.0037	0.147	1.0025
0.209	1.0020	0.254	1.0030	0.197	1.0028
0.228	1.0035	0.342	1.0034	0.257	1.0036
0.258	1.0025	0.447	1.0047	0.442	1.0042
0.351	1.0040	0.489	1.0054	0.571	1.0054
0.357	1.0024	0.619	1.0053	0.632	1.0054
0.367	1.0040	0.744	1.0071	0.651	1.0071
0.390	1.0040	0.837	1.0084	0.867	1.0087
0.523	1.0047	0.875	1.0076	0.907	1.0087
0.661	1.0066				
0.680	1.0085				
0.758	1.0075				
0.738	1.0064				
0.801	1.0094				
0.825	1.0078				
0.854	1.0090				

^a Concentration range = 1.5–10 M.

Table 2. A comparison of α_0 at $x_{\text{SO}_2, \text{aq}}=0$ and $x_{\text{SO}_2, \text{aq}}=1$ from straight lines fitted to experimental data and results obtained by Rayleigh distillation.^{1,2}

$T^\circ\text{C}$	$\bar{\alpha}_0$ $x_{\text{SO}_2, \text{aq}}=1$	α_{gl}^a	$\bar{\alpha}_0$ $x_{\text{SO}_2, \text{aq}}=0$	α_{gl}^a
25	1.0009 ± 0.0004	0.9999 ± 0.0008	1.0099 ± 0.0010	1.0109 ± 0.0006
35	1.0012 ± 0.0002	1.0015 ± 0.0004	1.0093 ± 0.0007	1.0110 ± 0.0008
45	1.0016 ± 0.0003	1.0029 ± 0.0010	1.0091 ± 0.0008	1.0113 ± 0.0009

^a From Refs. 1 and 2.

As seen from Table 2 very good agreement is obtained when the ionic fraction $(1-x_{\text{SO}_2, \text{aq}})=0$, which is equal to the isotope exchange coefficient for the system $\text{SO}_{2, \text{g}}-\text{SO}_{2, \text{aq}}$. For the exchange as well as for the Rayleigh distillation experiments a slight inverted temperature effect is indicated.

At high ionic fractions (and high concentrations) the results obtained are slightly lower than the ones obtained by Rayleigh distillations,^{1,2} but the variations are within the experimental errors. The experimental data show that the combined effect of increasing ionic strength and the condensation reaction $2 \text{HSO}_3^- = \text{S}_2\text{O}_5^{2-}$ is very small.

Ultraviolet, infrared, and Raman spectral studies^{5,6} indicate that the pyrosulfite ion $\text{S}_2\text{O}_5^{2-}$ may be considered a thionite-thionate ion $\begin{bmatrix} \text{O} & \text{O} \\ \text{OS} & \text{SO} \\ & \text{O} \end{bmatrix}^{2-}$

but the partition functions for $^{34}\text{S}_2\text{O}_5^{2-}$, $^{32}\text{S}_2\text{O}_5^{2-}$, $[\text{SO}_2-\text{SO}_3]^{2-}$, $[\text{SO}_2-\text{SO}_3]^{2-}$ cannot yet be calculated because of lack of spectroscopic data.

Rutenberg and Drury⁸ have measured the isotope fractionation factor between $\text{SO}_{2, \text{g}}$ and an aqueous solution of sulfur dioxide buffered with NaH_2PO_4 . Under the given experimental conditions a large fraction of the sulfur in the liquid phase exists as $\text{SO}_{2, \text{aq}}$. The mol fraction of $\text{SO}_{2, \text{aq}}$ was estimated to be approximately 0.38. These authors obtained a fractionation

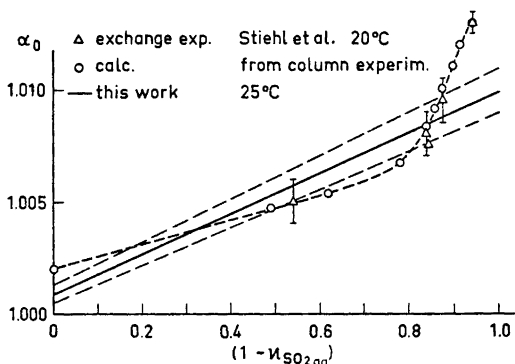


Fig. 2. The isotopic exchange coefficient.

factor at 30°C $\alpha_0 = 1.0050$ which is in good agreement with the results obtained in the present work.

Since this work was carried out two papers on the isotopic exchange system $\text{SO}_{2\text{g}} - \text{NH}_4\text{HSO}_3/\text{SO}_{2\text{aq}}$ have been published.⁹ The isotopic exchange coefficient obtained by exchange experiments at 20°C and calculated from column experiments by Stiehl *et al.* are plotted in Fig. 2 together with the straight line $\alpha_0 = (1.0009 \pm 0.0004) + (0.009 \pm 0.0006)(1 - x_{\text{SO}_{2\text{aq}}})$ computed from experimental results obtained at 25°C by the author. As seen the agreement is fairly good for ionic fractions < 0.9 , *i.e.* total sulfur concentration < 8 M whereas for higher ionic fractions the results obtained by Stiehl *et al.* are higher. The sharp increase in the exchange coefficient obtained by Stiehl *et al.* at high ionic fraction (high concentration) might indicate a greater isotope exchange coefficient for the system $\text{HSO}_3^- - \text{S}_2\text{O}_5^{2-}$ than found in this work. Stiehl *et al.* have, however, based their calculations on extrapolations without stating the uncertainty in the experimental results and a slight change in the height of a theoretical plate in the column will cause a considerable change in the exchange coefficients obtained. The exchange coefficient for the system $\text{SO}_{2\text{g}} - \text{SO}_{2\text{aq}}$ is, within the experimental error, in agreement with the results in this work.

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