Sulfur Isotope Effects

I. The Isotopic Exchange Coefficient for the Sulfur Isotopes ^{34}S—^{32}S in the System $SO_{2\,g}$—$HSO_3^-{}_{aq}$ at 25, 35, and 45°C

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Measurements of the isotopic separation coefficient for the sulfur isotopes ^{34}S — ^{32}S in the system $SO_{2\,g}$ — $HSO_3^-{}_{aq}$ have been carried out at 25, 35, and 45°C by means of a method analogous to a Rayleigh distillation.

The results obtained are compared with the coefficient obtained by theoretical calculations based on statistical theory.

In 1935 Urey and Greiff[1] demonstrated by means of statistical theory that for a large number of isotopic exchange reactions the isotopic exchange coefficients or equilibrium constants differ slightly from unity and thus chemical exchange methods could be used to separate isotopes. Since then several papers have been published on the isotope effect in the system $SO_{2\,g}$ — $HSO_3^-{}_{aq}$ in which the heavy isotopes concentrate in the solution (g and aq relate to gaseous and aqueous phase, respectively).

The elementary separation factor α_t obtained ranges from 1.010 to 1.021.[2-6] (Index t chosen to mean "total".) No satisfactory explanation for the discrepancies has been given.

The aim of the present work has been to measure the elementary separation coefficient for the system $SO_{2\,g}$ — $HSO_3^-{}_{aq}$ by means of a modified Rayleigh distillation.[6]

PRINCIPLE

The isotopic separation factor between two phases, *e.g.* a gas and a solution of the gas in a liquid, might be considered as consisting of three parts: the isotope effect caused by the pure physical transfer of isotopic species between the phases, the isotope effect caused by hydration or solvation in the liquid phase, and the effects caused by further reactions in the liquid phase. It is clear that in some cases the physical transfer effect may augment the exchange factor and in others oppose it.

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Consider an aqueous solution of sulfur dioxide in which the following equilibria exist. [7-11]

$$SO_{2\,aq} \rightleftharpoons H^+_{aq} + HSO_3^-{}_{aq} \qquad\qquad K_1 = 1.72 \times 10^{-2}\ \text{M} \qquad\qquad (1)$$

$$HSO_3^-{}_{aq} \rightleftharpoons H^+_{aq} + SO_3^{2-}{}_{aq} \qquad\qquad K_2 = 6.24 \times 10^{-8}\ \text{M} \qquad\qquad (2)$$

$$2\ HSO_3^-{}_{aq} \rightleftharpoons H_2O + S_2O_5^{2-}{}_{aq} \qquad\qquad K_3 = 7 \times 10^{-2} \qquad\qquad (3)$$

The overall or effective isotope separation factor for ^{34}S and ^{32}S is defined by the equation

$$\alpha_0 = \frac{[^{34}S/^{32}S]_{aq}}{[^{34}S/^{32}S]_g} \qquad\qquad (4)$$

where $[^{34}S/^{32}S]$ is the isotopic ratio.

The overall separation factor is clearly a function of the mol fractions of $SO_{2\,aq}$, $HSO_3^-{}_{aq}$, $SO_3^{2-}{}_{aq}$, and $S_2O_5^{2-}{}_{aq}$ in the solution. However, in solution with pH < 4.5 and a total sulfur concentration < 1 M, the concentrations of $SO_3^{2-}{}_{aq}$ and $S_2O_5^{2-}{}_{aq}$ are only fractions of a per cent of the $HSO_3^-{}_{aq}$ concentration and can safely be neglected.

Thus only eqn. (1) needs to be considered.

Corresponding to phase transfer, hydration and the equilibrium (1) above, the following isotope separation coefficients are defined:

$$\alpha_{gl} = \frac{[^{34}SO_{2\,aq}/^{32}SO_{2\,aq}]}{[^{34}SO_{2\,g}/^{32}SO_{2\,g}]} \qquad\qquad (5)$$

where α_{gl} includes both phase transfer and hydration of sulfur dioxide.

$$\alpha_s = \frac{[H^{34}SO_3^-{}_{aq}/H^{32}SO_3^-{}_{aq}]}{[^{34}SO_{2\,aq}/^{32}SO_{2\,aq}]} \qquad\qquad (6)$$

(where the index s relates to solution).

If the mol fraction of $HSO_3^-{}_{aq}$ (including both isotopes ^{34}S and ^{32}S) in solution is $x_{HSO_3^-}$ the overall separation factor defined above in eqn. (4) can be written according to eqns. (4), (5), and (6)
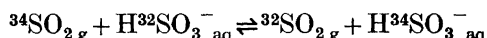
$$\alpha_0 = \alpha_{gl}\{(1 - x_{HSO_3^-}) + \alpha_s x_{HSO_3^-}\} \qquad\qquad (7)$$

or
$$\alpha_0 = \alpha_{gl}\{1 + (\alpha_s - 1)\ x_{HSO_3^-}\} \qquad\qquad (7a)$$

As seen, when the mol fraction $x_{HSO_3^-} \rightarrow 1$, i.e. $x_{SO_2\,aq} \rightarrow 0$

$$\alpha_0 \rightarrow \alpha_{gl}\ \alpha_s = \alpha_t \qquad\qquad (7b)$$

according to the hypothetical equation

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

This is the case treated in this paper. The separation factor α_t can be determined by means of a method analogous to a Rayleigh distillation.[6]

Acid is fed continuously into an aqueous solution of $HSO_3^-{}_{aq}$ and the $SO_{2\,aq}$ so formed is flushed out of the solution by a stream of inert gas which removes it from the system. If this process is carried out sufficiently slowly, isotopic equilibrium exists at all times and eqns. (5), (6), and (7b) are valid.

The natural isotopic composition of sulfur is ^{32}S: 95.0 %, ^{33}S: 0.75 %, ^{34}S: 4.2 %, and ^{36}S: 0.017 %.[20] As the concentrations of ^{33}S and ^{36}S are low they may be neglected so that a mass balance for the isotope ^{34}S gives

$$y \, \mathrm{d}S = \mathrm{d}(Sx) = x\mathrm{d}S + S\mathrm{d}x \tag{8}$$

where y is the isotope fraction ^{34}S in gas phase, x the isotope fraction ^{34}S in the solution, and S the total amount of $\mathrm{HSO_3^-}_{aq}$ in the solution.

A combination of eqns. (5), (6), and (7b) gives

$$y = \frac{x}{\alpha_t - x(\alpha_t - 1)} \tag{9}$$

Thus, combining eqns. (8) and (9) and integrating, the following equation is obtained

$$\frac{[S_1]}{[S_2]}^{\alpha_t/(\alpha_t-1)} = \frac{[x_2]}{[x_1]} \times \frac{[1-x_1]}{[1-x_2]}^{1/\alpha_t}$$

or

$$\alpha_t = \frac{\ln [S_1/S_2] + \ln [(1-x_1)/(1-x_2)]}{\ln [S_1/S_2] - \ln [x_2/x_1]} \tag{10}$$

where S_2, x_2 and S_1, x_1 are, respectively, the total amount of $\mathrm{HSO_3^-}_{aq}$ and isotopic mol fraction $\mathrm{H^{34}SO_3^-}_{aq}$ in solution before and after the distillation.

EXPERIMENTAL

The solutions were prepared by dissolving $Na_2S_2O_5$ (p.a. quality) in distilled water through which N_2 had been bubbled for more than 15 min. The total sulfur concentration C_t was determined iodometrically.[21] A small amount of N,N-dimethylformamide was added to inhibit oxidation.

Distillation. The distillation apparatus is sketched in Fig. 1. Concentrated hydrochloric acid was continuously fed into 500 ml of $\approx$ 1 M $NaHSO_3$ solution by a small pump which could be regulated to deliver from 0.03 to 30 ml h^{-1}.
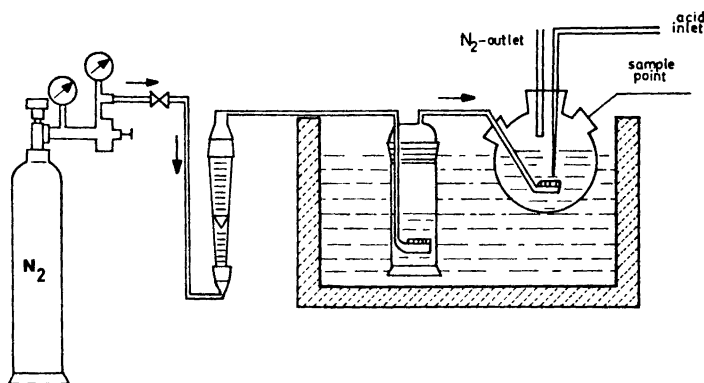

Fig. 1. Distillation apparatus.

A stream of nitrogen gas was fed into the solution through a fine sintered glass filter flushing out the $SO_{2\ aq}$ and thus keeping the pH ≈ 4.5. The solution and gas were thermostated to $T \pm 0.1°C$. The distillation was stopped when the hydrogen sulfite concentration in the solution was only a few per cent of the initial concentration (2 − 3 days).

The isotopic ratio $^{34}S/^{32}S$ in solution before and after distillation was determined mass-spectrometrically. Small sample volumes of the solution were taken, acidified and sulfur isolated as sulfur dioxide in a vacuum system (Fig. 2). The sulfur dioxide gas
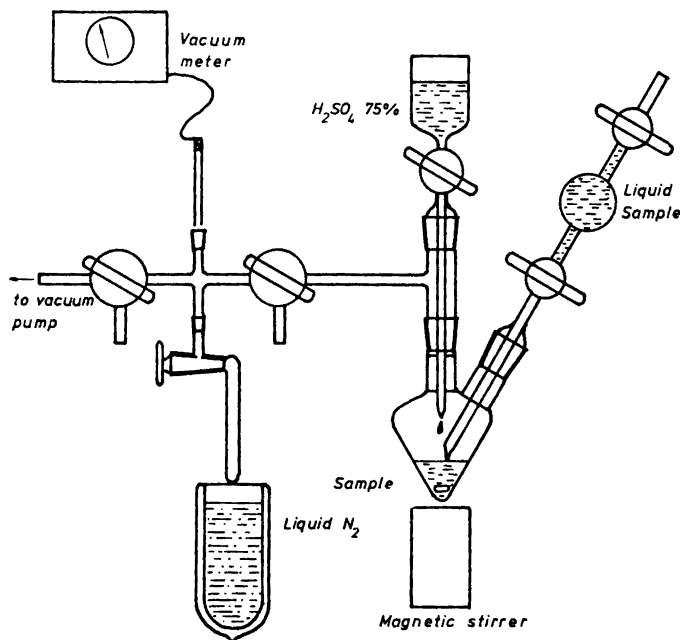

Fig. 2. Vacuum system for conversion of sulfurous species in liquid sample to sulfur dioxide.

was then transferred to gas analysis ampoules by cooling these with liquid nitrogen. A complete conversion of $HSO_3^-{}_{aq}$ to $SO_{2\ g}$ is necessary to avoid isotopic fractionation. Iodometric titrations and UV-spectrometry showed that less than 0.3 ‰ was left in the aqueous phase after conversion (presumably as $SO_{2\ aq}$).

Mass-spectrometry. As most salts and sulfur dioxide show slight differences in the $^{34}S/^{32}S$ ratio, the $Na_2S_2O_5$ used was arbitrarily taken as having the isotope ratio mentioned above and the other samples analyzed with this as standard. A slight deviation in the absolute isotopic ratio of the standard from the assumed value will have almost no effect on the calculation.

The gas samples were analyzed w.r.t. the masses (64 + 65) and 66.

The natural isotopic compositions of sulfur and oxygen are [25]

^{32}S	95.018 %		^{16}O	99.759 %
^{33}S	0.75 %		^{17}O	0.037 %
^{34}S	4.215 %		^{18}O	0.204 %
^{36}S	0.017 %			

Assuming the isotopic abundance of ^{16}O, ^{17}O, and ^{18}O to be as tabulated above a mass balance gives

mass 64: $^{32}S^{16}O_2$

mass 65: $^{33}S^{16}O_2 + {}^{32}S^{16}O^{17}O$

mass 66: $^{34}S^{16}O_2 + {}^{32}S^{17}O_2 + {}^{33}S^{16}O^{17}O + {}^{32}S^{16}O^{18}O$

$$\left[\frac{64+65}{66}\right] = R = \frac{{}^{32}S^{16}O_2 + {}^{33}S^{16}O_2 + {}^{32}S^{16}O^{17}O}{{}^{34}S^{16}O_2 + {}^{32}S^{17}O_2 + {}^{33}S^{16}O^{17}O + {}^{32}S^{16}O^{18}O}$$

$$\frac{1 + [{}^{33}S/{}^{32}S] + 2[{}^{17}O/{}^{16}O]}{[{}^{34}S/{}^{32}S] + [{}^{17}O/{}^{16}O] + 2[{}^{33}S/{}^{32}S] \times [{}^{17}O/{}^{16}O] + 2[{}^{18}O/{}^{16}O]}$$

Since the isotopic fractions $[{}^{33}S/{}^{32}S]$ and $[{}^{17}O/{}^{16}O]$ are very small, the product terms are neglected and the isotope fraction $[{}^{34}S/{}^{32}S]$ calculated from the equation

$$[{}^{34}S/{}^{32}S] = \left[\frac{66}{64+65}\right] - 2[{}^{18}O/{}^{16}O] - [{}^{17}O/{}^{16}O]$$

or

$$[{}^{34}S/{}^{32}S] = \left[\frac{66}{64+65}\right] - 0.00446$$

RESULTS

The results obtained are tabulated in Table 1.

Table 1. The separation coefficient α_t for the sulfur isotopes $^{34}S - {}^{32}S$ in the system $SO_{2\ g} - HSO_3^-{}_{aq}$ at 25, 35, and 45°C.

α_t 25°C	α_t 35°C	α_t 45°C
1.0115	1.0118	1.0117
1.0081	1.0070	1.0121
1.0109	1.0131	1.0131
1.0088	1.0115	1.0098
1.0112	1.0126	1.0098
1.0117	1.0102	
1.0111		
1.0118		
1.0130		
1.0110		
$\bar{\alpha}_t$ 1.0109 ± 0.0006	1.0110 ± 0.0008	1.0113 ± 0.0009

DISCUSSION

The equilibrium constant for an isotope exchange reaction can be calculated by means of statistical theory according to a formula derived by Biegeleisen and Mayer [12]

$$K = \frac{s/s' \, f(H^{34}SO_3^-/H^{32}SO_3^-)}{s/s' \, f(^{34}SO_{2 \, g}/^{32}SO_{2 \, g})} \tag{11}$$

where s/s' f, the ratio of the partition functions of two isotopic molecules, can be written

$$s'/s \, f = \prod_i^{3n-6} \frac{u_i}{u_i'} \times \frac{e^{-u_i/2}}{e^{-u_i'/2}} \times \frac{1 - e^{-u_i'}}{1 - e^{-u_i}} \tag{12}$$

$$s'/s \, f = 1 + \sum_i^{3n-6} G(u_i) \, \Delta u_i \tag{13}$$

where
$$G(u_i) = \frac{1}{2} - \frac{1}{u_i} + \frac{1}{e^{u_i} - 1} \tag{14}$$

u_i refers to the light isotopic molecule, u_i' refers to the heavy isotopic molecule and $u_i = hc\omega_i/kT$ where ω_i is the i'th fundamental molecular vibration frequency.

The so-called reduced partition functions of $H^{34}SO_3^-$ and $H^{32}SO_3^-$ cannot yet be calculated because of lack of spectroscopic data. The reduced partition function ratios, based on vibrational data, have, however, been calculated for the system $SO_{2 \, g} - SO_3^{2-}{}_{aq}$ by Vojta and Koch. [15,16]
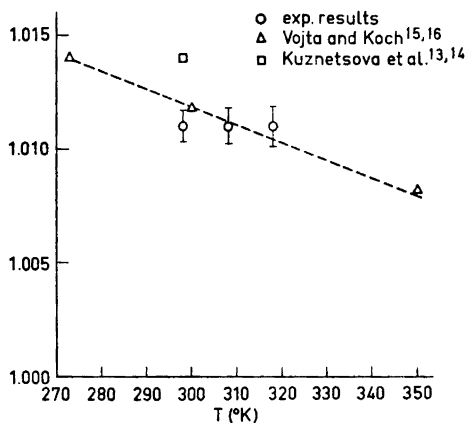

Fig. 3. Plot of experimentally found exchange coefficients and coefficients calculated by Vojta and Koch,[15,16] and Kuznetsova [13,14] vs. temperature.

The following values are given

T K	s/s' $f(^{34}SO_2/^{32}SO_2)$	s/s' $f(^{34}SO_3^{2-}/^{32}SO_3^{2-})$
273.15	1.04568	1.0604
300	1.03967	1.0520

Thus according to eqn. (11)

$$\alpha = \begin{matrix} 1.01410 \\ 1.01186 \end{matrix} \qquad \begin{matrix} 273.15 \text{ K} \\ 300 \text{ K} \end{matrix}$$

Approximate calculations of the isotopic exchange coefficient for the system $HSO_3^-{}_{aq} - SO_3^{2-}{}_{aq}$ might, however, be carried out if the following assumptions are made.

The species HSO_3^- and SO_3^{2-} are regarded as derived from the sulphate ion, i.e. the sulfur is surrounded by a total of four bonds or lone electron pairs. Thus SO_3^{2-} has three $S-O$ bonds and one lone pair while HSO_3^- has three $S-O$ bonds and one σ-bond to H. The effect of replacing a lone pair on sulfur by a bond to H should be a slight strengthening of the $S-O$ bonds. The fundamental vibration frequencies for SO_3^{2-} and the $(^{34}S/^{32}S)$ isotopic shifts given by Vojta and Koch [15] and the corresponding vibration frequencies for HSO_3^- given by Simon and Waldmann [9] are tabulated below.

SO_3^{2-}	ω (cm^{-1})	968	932 (2)	618	465 (2)
	$\Delta\omega$	-6.3	-12.3	-6.9	-1.3
HSO_3^-	ω	1089	1019 (2)	586	457 (2)

Neglecting the isotope effects in the $H-S$ vibrations as the change in the reduced masses are small and assuming the isotopic effects in corresponding vibration frequencies of HSO_3^- and SO_3^{2-} to be the same, the reduced partition functions and the equilibrium constant are calculated to be

$$s/s'\ f(^{34}SO_3^{2-}/^{32}SO_3^{2-})\ = 1.0527$$
$$s/s'\ f(H^{34}SO_3^-/H^{32}SO_3^-) = 1.05893$$
$$\alpha = 1.0059$$

Thus the equilibrium constant α_t for the isotope exchange system $SO_{2\ aq} - HSO_3^-{}_{aq}$ is calculated to be $\alpha_t \simeq 1.018$.

Another approach to the theoretical treatment has been given by Kuznetsova et al.[13,14]

An approximate equation based on a rigid rotator, harmonic oscillator molecular model [1,17] has been derived.

By disregarding geometrical differences in the isotopic molecules taking only zero point vibrational energies into consideration and assuming $\alpha = 1$ at 800 K (an examination of experimental data shows that the temperature T_0 where $(\varepsilon = (\alpha - 1) = 0$ is in the range $600 - 1000$ K for the majority of isotopic exchange reactions (8)) the exchange coefficient is given by the equation

$$\alpha - 1 = \varepsilon = 0.7 \left[\left(\frac{3}{2} \times \frac{1}{M_1} + \frac{\mu_1}{m^2} \right) - \left(\frac{3}{2} \times \frac{1}{M_2} + \frac{\mu_2}{m^2} \right) \right] \Delta m \qquad (12)$$

where M_1 and M_2 are the molecular weights of the isotopic molecules, μ_1 and μ_2 are the reduced masses, m is the mass of the isotopic atom in M_1, and Δm the mass difference of the isotopic atoms.

For the system $SO_{2\ g} - HSO_3^-{}_{aq}$ Kuznetsova et al.[13] give the separation coefficient $\alpha = 1.014$ at 298 K. It should, however, be emphasized that the T_0 concept is very approximate, and for reactions in which T_0 is very different from 800 K the calculated coefficients may be considerably in error. In addition, the statistical formulas given above are based on an ideal gas model with no molecular interaction. The coefficients should therefore be multiplied by a coefficient taking account of the interionic and intermolecular forces. This

has as yet only been done for simple molecules.[23] (As the hydrogen sulphite ions are gradually replaced by chloride ions during experiments, the ionic strength is kept constant, but the intermolecular and interionic forces will, of course, vary.)

Although Rayleigh distillation has been shown to give values slightly too low,[19] probably due to the vapour pressure of the solvent and some entrainment of liquid by the gas stream, the separation coefficient obtained in this work is somewhat lower than expected from the theoretically calculated coefficients given above. The temperature effect is not significant compared with the experimental error.

REFERENCES

1. Urey, H. C. and Greiff, L. *J. Am. Chem. Soc.* **57** (1935) 321.
2. Stewart, W. and Cohen, K. *J. Chem. Phys.* **8** (1940) 904.
3. Thode, H. G., Graham, R. L. and Ziegler, J. A. *Can. J. Res.* **B 23** (1945) 40.
4. Clusius, V. K. and Heimerl, H. *Z. Naturforsch.* **3a**, No. 11 (1948) 611.
5. North, E. D. and White, R. R. *Ind. Eng. Chem.* **43** (1951) 2390.
6. Agaljtsov, A. M. and Zelvenskij, J. D. *Zh. Fiz. Khim.* **29** (1955) 2244.
7. Ley, H. and König, E. *Z. phys. Chem.* **B 41** (1938) 365.
8. Falk, M. and Giguère, P. A. *Can. J. Chem.* **35** (1957) 1195; **36** (1958) 1121.
9. Simon, A. and Waldmann, K. *Z. anorg. allgem. Chem.* **281** (1955) 113, 135; **284** (1956) 63; Simon, A., Waldmann, K. and Steger, E. *Ibid.* **288** (1956) 131.
10. Golding, R. M. *J. Chem. Soc.* **1960** 3711.
11. Schaeffer, K., Niggermann, H. and Köhler, W. *Z. Elektrochem.* **21** (1915) 181; Schaeffer, K. and Köhler, W. *Z. anorg. allgem. Chem.* **104** (1918) 212.
12. Biegeleisen, J. and Mayer, M. G. *J. Chem. Phys.* **15** (1947) 261.
13. Kuznetsova, E. M., Gryaznova, Z. V. and Panchenkov, G. M. Dritte Arbeitstagung über Stabile Isotope, Leipzig 1963, *Abhandlungen der Deutschen Akademie der Wissenschaften zu Berlin*, Akademie-Verlag, Berlin 1965, p. 51.
14. Panchenkov, G. M. *J. Chim. Phys.* **60** (1963) 107.
15. Vojta, G. and Koch, D. *Z. phys. Chem. (Leipzig)* **225** (1964) 295.
16. Vojta, G. *Z. phys. Chem. (Leipzig)* **217** (1961) 337.
17. Urey, H. C. *J. Chem. Soc.* **1947** 562.
18. Vojta, G. In Hertz, G. *Lehrbuch der Kernphysik*, B. G. Teubner Verlagsgesellschaft, Stuttgart 1962, p. 100.
19. Holmberg, K. E. *Acta Chem. Scand.* **13** (1959) 717; **14** (1960) 1660; **16** (1962) 2117.
20. Strominger, D., Hollander, J. M. and Seaborg, G. T. *Rev. Mod. Phys.* **30** (1958) 614.
21. Eriksen, T. E. *Chem. Eng. Sci.* **22** (1967) 729.
22. Pratt, H. C. R. *Countercurrent Separation Processes*, Elsevier, Amsterdam — London — New York 1967, p. 300.
23. Rabinovich, I. B. *Russ. Chem. Rev.* **31** (1962) 51.
24. Prigogine, I. *The Molecular Theory of Solutions*, North-Holland, Amsterdam 1957, Ch. 18 — 20.
25. Haïssinsky, M. *Nuclear Chemistry and Its Applications*, Addison-Wesley, Reading 1964, p. 56.