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NOTE

Theoretical Calculation of the Sulfur Isotope Separation Factor in the Distillation of Hydrogen Sulfide

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Natural sulfur comprises four stable isotopes ^{32}S, ^{33}S, ^{34}S, and ^{36}S with relative abundances of 95.02, 0.75, 4.21, and 0.02%, respectively (*1*). Sulfur isotopes can effectively be separated by the sulfur dioxide–bisulfite exchange process and by liquid-phase thermal diffusion (*2*, *3*).

Distillation of sulfur-containing compounds, such as H_2S, represents a possible alternative to the above processes (*3*, *4*). This is based on the difference in the volatilities of $H_2{}^{32}S$ and $H_2{}^{34}S$, and this difference can be characterized by the isotope separation factor (α) for the equilibrium between a liquid phase and its saturated vapor:

$$\alpha = (X'/X)_{\mathrm{vap}}/(X'/X)_{\mathrm{liq}} \tag{1}$$

where X' and X are the mole fractions of $H_2{}^{32}S$ and $H_2{}^{34}S$, respectively, in the vapor and liquid phases.

Since the separation factor is not much different from unity, determination of reliable values of α requires multiplication of the elementary separation process. One such multiplying method is that of Rayleigh distillation; in this case a mixture of two components, with known quantity and isotope concentration, is evaporated under equilibrium conditions until just enough residue for isotope analysis remains (*5*). This technique was used by Devyatykh et al. (*6*) who obtained values of 1.0053 and 1.0058 for the $^{32}S/^{34}S$ separation factor at −76 and −65°C, respectively. These values were obtained from data on the $^{32}S/^{35}S$ isotope effect by correcting for the mass difference between $H_2{}^{34}S$ and $H_2{}^{35}S$. The Rayleigh distillation technique was used by Postnikov et al. (*7*) to determine the temperature

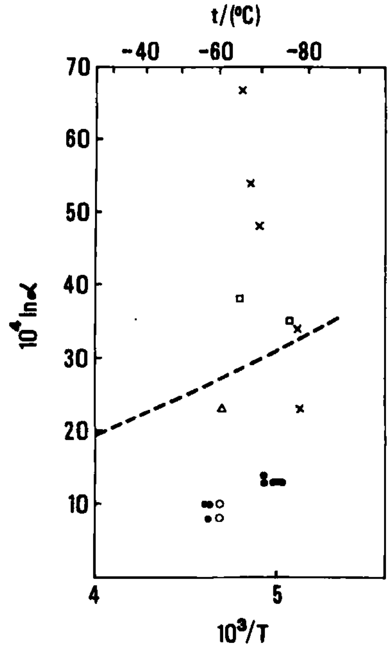

FIG. 1. The $^{32}S/^{34}S$ separation factor (α) in the distillation of H_2S: (□) (*6*); (×) (*7*); (○) (*8*); (●) (*4*); (△) (*9*); (- - -) our calculated line.

dependence of the separation factor, and they found that the magnitude of α increased with increasing temperature (Fig. 1).

A large multiplication of the elementary separation can be achieved with distillation columns. Gverdtsiteli et al. (*8*) determined values of 1.001–1.0008 for α at −60°C by fractionation experiments on natural hydrogen sulfide in a packed column. The number of theoretical plates was obtained by measuring ^{10}B enrichment during the rectification of BF_3 in the same column. From distillation experiments carried out at column pressures from 45 to 125 kPa, Mills (*4*) found a variation of separation factors between 1.0008 and 1.0014. In this case, NO, with a well-known isotope separation factor, was used to determine the number of theoretical plates in the column.

The only available estimation on the $^{32}S/^{34}S$ separation factor in the distillation of H_2S is that of Kuznetsova et al. (*9*) who obtained a value of 1.0023 for α at the boiling point by using a calculation of a very approximate nature.

As can be seen in Fig. 1, the isotope separation factors obtained by different methods show a large scatter, and the increase of α with rising temperature (*7*) can hardly be rationalized by theoretical considerations. Therefore, we decided to calculate the $^{32}S/^{34}S$ separation factor by using the theory of condensed-phase isotope effects (*10*, *11*).

In the harmonic oscillator approximation using a simplified cell model for the liquid phase, the separation factor can be calculated from the internal and external vibrational frequencies of the isotopic molecules by the equation (*11*, *12*)

$$\alpha = \prod_{\text{int.freq.}}^{3N-6} \frac{(u_i/u_i')_c}{(u_i/u_i')_g} \times \frac{\exp((u_i' - u_i)_c/2)(1 - \exp(-u_i')_c)/(1 - \exp(-u_i)_c)}{\exp((u_i' - u_i)_g/2)(1 - \exp(-u_i')_g)/(1 - \exp(-u_i)_g)} \times \prod_{\text{ext.freq.}}^{6} \frac{u_i}{u_i'}\left\{\exp\left(\frac{u_i' - u_i}{2}\right)\right\}\left\{\frac{1 - \exp(-u_i')}{1 - \exp(-u_i)}\right\} \tag{2}$$

where $u_i = hc\nu_i/kT$; c and g refer to the condensed and gas phase; N is the number of atoms in the molecule; ν_i is the ith normal mode frequency in cm^{-1}; and the prime refers to the lighter isotopic species (H_2S). In the case of hydrogen sulfide there are three internal vibrational frequencies (ν_1: symmetrical S—H stretch; ν_2: H—S—H bend; ν_3: antisymmetrical S—H stretch) as well as three hindered translational (ν_{trans}) and three hindered rotational (ν_{rot}) frequencies. The vibrational frequencies can be computed by using the Wilson FG matrix method (*13*) with an isotope independent force constant matrix (F). The isotope dependence of the normal mode frequencies arises through the isotope dependence of the G matrix which can be calculated from the geometry of the molecule and the atomic masses.

We used the values of gas- and liquid-phase force constants obtained in a model calculation performed for the interpretation of the difference between the vapor pressures of H_2S and D_2S (*14*). The reliability of these force constants is warranted by the good agreement between the calculated values and the H_2S/D_2S experimental data (*15*, *16*). Thus, for example, the calculations predicted that the vapor pressure of H_2S becomes smaller than that of D_2S above 225 K, and this was corroborated by a recent experimental investigation (*17*). The calculated vibrational frequencies obtained by using the force constants given in Ref. *14* are listed in Table 1. The calculated $^{32}S/^{34}S$ distillation separation factors, obtained by substituting the vibrational frequencies in Eq. (2), are shown as a function of temperature in Fig. 1.

TABLE 1
Vibrational Frequencies of $H_2{}^{32}S$ and $H_2{}^{34}S$ in Gas and Liquid Phases in cm^{-1}

	$H_2{}^{32}S$		$H_2{}^{34}S$	
	Gas	Liquid	Gas	Liquid
ν_1	2722.4	2681.3	2720.2	2679.1
ν_2	1214.4	1203.0	1213.3	1201.9
ν_3	2733.8	2692.6	2731.2	2690.1
$\nu_{trx} = \nu_{try} = \nu_{trz}{}^a$		93.0		90.4
ν_{rotx}		176.0		175.7
ν_{roty}		178.9		178.8
ν_{rotz}		181.4		181.4

[a] x, y, and z denote the three inertial axes of the molecule.

It can be seen that α decreases with increasing temperature; therefore, the temperature dependence observed by Rayleigh distillation (*7*) is of the wrong sign. We have also determined that the Rayleigh distillation method gave false temperature dependences for the $^{10}B/^{11}B$ separation factors in BF_3 and BCl_3 distillations too (*18*, *19*). This may be due to the difficulty in maintaining equilibrium conditions of the evaporation during Rayleigh distillation.

Although the temperature dependence of α obtained by distillation (*4*) is consistent with calculation, the magnitudes of the separation factor (*4*, *8*) are much smaller than the calculated values. This discrepancy can possibly be ascribed to the assumption that the number of theoretical plates in the column is equal to that obtained in the rectification of NO (or BF_3). Accurate determination of the number of plates would be possible by measuring the separation of hydrogen and deuterium during distillation, since the separation factor is well known in this case and it can reasonably be assumed that in a given distillation the number of effective theoretical plates is the same for all isotopic species.

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REFERENCES

1. J. MacNamara and H. G. Thode, *Phys. Rev.*, *78*, 307 (1950).
2. W. M. Rutherford and W. J. Roos, in *Proceedings, Isotope Ratios as Pollutant Source and Behaviour Indicators*, IAEA, Vienna, 1975, p. 295.
3. B. M. Andreev and A. S. Polevoi, *Usp. Khim.*, *52*, 373 (1983).

4. T. R. Mills, in *Proceedings, Synthesis and Applications of Isotopically Labeled Compounds* (W. P. Duncan and A. B. Susan, eds.), Elsevier, Amsterdam, 1983, p. 409.
5. P. Baertschi and M. Thürkauf, *Helv. Chim. Acta, 43,* 80 (1960).
6. G. G. Devyatykh, Yu.N. Suloev, and A. D. Zorin, *Tr. Khim. Khim. Tekhnol., 1*(2), 24 (1958).
7. A. A. Postnikov, Ya.D. Zel'venskii, and A. E. Kovalenko, *Tr. MKhTI im. D. I. Mendeleeva, 73,* 179 (1973).
8. I. G. Gverdtsiteli, T. A. Gagua, and Yu. V. Nikolaev, *At. Energy, 4,* 294 (1958).
9. E. M. Kuznetsova, Z. V. Gryaznova, and G. M. Panchenkov, in *Abh. Dtsch. Akad. Wiss. Berl., Kl. Chem., Geol., Biol.,* p. 51 (1965).
10. J. Bigeleisen, *J. Chem. Phys., 34,* 1485 (1961).
11. G. Jancsó and W. A. Van Hook, *Chem. Rev., 74,* 689 (1974).
12. M. J. Stern, W. A. Van Hook, and M. Wolfsberg, *J. Chem. Phys., 39,* 3179 (1963).
13. E. B. Wilson Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations,* McGraw-Hill, New York, 1955.
14. B. Gellai and G. Jancsó, *Ber. Bunsenges. Phys. Chem., 75,* 156 (1971).
15. I. Kiss, L. Matus, and I. Opauszky, *Kernenergie, 5,* 329 (1962).
16. E. C. W. Clarke and D. N. Glew, *Can. J. Chem., 48,* 764 (1970).
17. A. G. Cubitt, C. Henderson, L. A. K. Staveley, I. M. A. Fonseca, A. G. M. Ferreira, and L. Q. Lobo, *J. Chem. Thermodyn., 19,* 703 (1987).
18. G. Jancsó, *Isotopenpraxis, 13,* 118 (1977).
19. G. Jancsó, *Ber. Bunsenges. Phys. Chem., 78,* 648 (1974).

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