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Separation of Sulphur Isotopes by Physicochemical Methods

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Recent work on the separation of sulphur isotopes by distillation, chemical exchange, and isotope exchange methods is reviewed, and the characteristics of both laboratory and industrial apparatus for the separation of sulphur isotopes are tabulated. The direction of further developments is discussed with emphasis on a more rational organisation of the work and on the scientifically most promising approaches. 138 references.

CONTENTS

I. Introduction 213
II. Distillation 213
III. Chemical isotope exchange 215
IV. Ion exchange processes 225

Natural sulphur is a mixture of stable isotopes of mass numbers 32, 33, 34, and 36, present at relative concentrations of 95.006, 0.76, 4.22, and 0.014 at.% respectively[1]. This isotopic composition is not absolute, and depends on the source of the sulphur, suggesting fractionation of the isotopes in the course of biochemical and geochemical processes. Fluctuations in the $^{32}S/^{33}S$, $^{32}S/^{34}S$, and $^{32}S/^{36}S$ isotope ratios can be as high as 2.5%, 5%, and 10% respectively[2,3]. The sulphur of the troilite in the Canyon Diablo meteorite, with an $^{32}S/^{34}S$ ratio of 22.22, has been adopted as the international standard[4].

Sulphur isotopes are used in biology[5,6], medicine[7], geology[8-16], nuclear physics[17,18], agrochemistry[20], organic[20-23] and physical chemistry[19,20,24-26], astronomy[27,28], physiology[29], etc.

Stable sulphur isotopes (and their methods of analysis) have also been used in practice to solve problems in geological uranium prospecting[30], estimating the quality of petroleum deposits[31], monitoring the sulphur content of cast iron and steel[20], and controlling the emission of sulphur waste gases and their rate of circulation and neutralisation in the atmosphere[32]. Another important group of applications of stable sulphur isotopes includes the preparation (by nuclear processes) of new radioactive isotopes, including the very important isotopes[17,18] ^{33}P and ^{35}S. The radioactive phosphorus isotope ^{33}P, prepared by the $^{33}S(n; p)^{33}P$ reaction, has been used increasingly in medicine and biology in recent years. Another radioactive isotope of phosphorus is known (^{32}P), but it is less easy to use in biochemical, ecological, agrochemical, and medical studies because its emission energy (E_{max} = 1.71 MeV) is higher than that of ^{33}P (E_{max} = 0.25 MeV).

It is clear, from recent publications, that the use of stable sulphur isotopes is increasing not only in the traditional branches of science and technology but also in new (and unexpected) directions. This explains the decision to create reserve stocks of these isotopes in many countries.

An analysis of the literature suggests that the three most important limiting factors to the still wider exploitation of stable sulphur isotopes are:

1) the high cost of these isotopes, due to the complexity of existing methods of production;

2) the complexity and high cost of the methods of isotopic analysis;

3) the lack of cheap, simple, and effective methods of synthesising the sulphur-labelled compounds needed in science and technology.

The most serious of these problems is the first. For example, the cost of one gramme of the ^{34}S isotope with an enrichment of 40–60 at.%, prepared by electromagnetic mass separation, is 4200 roubles, and the cost of one gramme of ^{36}S with an enrichment of 1.5–2 at.% is 50000 roubles[33]. The first paper dealing specifically with the technology of the separation of sulphur isotopes was published more than 40 years ago[34], and a great deal of work, both theoretical and practical, has been devoted to the separation problem throughout this period in many countries[25,29,35,36]. The development of new methods of separation stimulated the development of new or improved methods of analysis of sulphur isotopes[16,37-39], new methods of producing pure and specially pure sulphur, and new developments in the chemistry of labelled compounds[20-23].

The fact that according to papers published between 1937 and 1980 approximately 89 sulphur isotope separation processes were investigated in 46 scientific establishments of 13 countries gives an indication of the scale of this work. These developments have created a need for a systematic analysis of the different trends in the theory and practice of sulphur isotope separation, including an assessment of the factors which determine the cost of the isotopes, aimed at identifying promising directions in the search for cheaper isotopes. This review is devoted to these problems.

II. DISTILLATION

Processes based on the distillation of hydrogen sulphide, sulphur dioxide, and sulphur trioxide have been proposed for the separation of the sulphur isotopes. The choice of these compounds was dictated not only by general considerations of ease of distillation (simple apparatus design, easy and cheap flow reversal arrangements at the ends of the cascade, absence of side-processes leading to "parasitic" take-off), but also by the wide use of these compounds in the chemical industry. The latter circumstance offers a routine basis for the production of isotopes as well as the possibility of exploiting "transit" schemes, in which an existing industrial production flow of sulphur compound is used for the extraction of the heavy sulphur isotopes. The waste flow, with a decreased content of heavy sulphur isotopes, is returned to the chemical production cycle from which it had been diverted. In this way the intrinsic cost of the product can be lowered very substantially, and the problems of environmental protection can be greatly simplified, since the waste from the isotope production process is fully utilised elsewhere. We should stress that "transit" schemes are economically attractive not only in the extraction of isotopes by distillation but in any large-scale method of isotope production[40].

The results of a study of isotope equilibria in liquid–vapour systems are summarised in Table 1. We note that the use of SO_2 or SO_3 is unattractive because the separation coefficients (α) are extremely low: these coefficients effectively determine both the capital costs and the running costs of the process [since the size of the apparatus is specified by the expression $V \propto 1/(\alpha - 1)^2$, and the energy needed for phase reversal is $E \propto 1/(\alpha - 1)$], and they also control the length of the start-up time [$\tau \propto 1/(\alpha - 1)^2$].

Table 1. Separation coefficients for liquid–vapour phase equilibrium.

T, K	α	Method	Refs.	T, K	α	Method	Refs.
	$H_2{}^{32}S$—$H_2{}^{35}S$				$^{32}SO_2$—$^{35}SO_2$		
197	1.0053±0.0017	1	[51]	238	1.0018±0.0005	1	[51]
208	1.0058±0.0020	1	[51]	250	1.0030±0.0016	1	[51]
	$H_2{}^{32}S$—$H_2{}^{34}S$				$^{32}SO_2$—$^{34}SO_2$		
197	1.0035	2	[51]	238	1.0012	2	[51]
208	1.0038	2	[51]	261	1	3*	[53]
213	1.001÷1.0008	3*	[53]	298	1.0012	4	[47]
298	1.0023	4	[47]		$^{32}SO_3$—$^{34}SO_3$		
194.4	1.0023	1	[41]				
195.5	1.0034	1	[41]	317	1.001	3**	[54]
203.6	1.0048	1	[41]				
205.6	1.0054	1	[41]				
207.5	1.0067	1	[41]				

Symbols: methods of determining α: 1) simple distillation and calculation by the Rayleigh integral equation; 2) recalculation from the experimental values of $\alpha(^{32}S/^{35}S)$ obtained by method 1; 3) from the separation (K^∞) obtained in a column of height H_K having a known number of separation steps (n); 4) calculated by the equation

$$\varepsilon=(\alpha-1)=0.2\left(\frac{\Delta V}{\Delta T d}\right)^2\cdot\left\{1-\left[0.2\left(\frac{\Delta V}{\Delta T d}\right)^2\cdot\right]^2\right\}\cdot\left(\frac{T_{cr}}{T_{nbp}}-1\right)\cdot\varepsilon_K\Delta m,$$

where $\varepsilon_K = \frac{3}{2}\cdot\frac{1}{M}$ for mono-atomic molecules and

$$\varepsilon_K=\frac{3}{2}\cdot\frac{1}{M}+\frac{\mu}{m^2};$$

for polyatomic molecules, M is the molecular weight, μ is the reduced mass, $\Delta V/\Delta T = (V_{cr} - V_l)/(T_{cr} - T_{nbp})$, V_{cr} is the critical volume, V_l is the volume of the liquid at the normal boiling point, T_{cr} is the critical temperature, T_{nbp} is the normal boiling point, d is the density of the liquid, and Δm is the difference in mass between the isotopic molecules.

*H_K = 1 m; n = 96 ($^{10}BF_3$ – $^{11}BF_3$).
**H_K = 0.74 m; K^∞ = 1.022.

However, we should also note that though the data in Table 1 on the temperature dependence of α during the distillation of H_2S suggest relatively high values of the separation coefficient they include some inconsistencies, and a critical reappraisal of these results is essential. The simple distillation method[41,50] followed by calculation of α by the Rayleigh integral equation assumes that the initial hydrogen sulphide is free from involatile impurities, and that equilibrium conditions are maintained throughout the evaporation of the liquid phase[42–46]. Neither of these assumptions is invariably obeyed[42,44]. Results obtained from the distillation of H_2S in a column with a known number of theoretical plates (n) are also not entirely reliable, because the n values (determined for the distillation of BF_3) may not be exactly applicable to the distillation of H_2S. The determination of $\alpha(^{32}S/^{34}S)$ by calculation from experimental values of $\alpha(^{32}S/^{35}S)$ is also inexact, since it assumes that the separation coefficient is proportional to the relative difference in mass of the isotopic molecules.

In spite of these shortcomings of the methods the α values for low temperatures agree tolerably well (but not those for high temperatures). For example, the parameter $\varepsilon = (\alpha - 1)$ determined[51] at 208 K differs by a factor of 1.76 from the value obtained[41] by simple distillation followed by application of the Rayleigh integral equation, whereas the values of ε obtained[47,53] at 213 and 298 K respectively are 3–7 times lower than the values expected from the temperature dependence of α given in Ref. 41. We should also stress that the experimental results[41] are inconsistent with a quantum-statistical calculation[48] based on spectroscopic data. The latter discrepancy probably arises from failure to allow, in the calculation, for the complex composition of the liquid phase [including associated groups of the $(H_2S)_n$ type[49,50]].

Table 2. Results obtained for the separation of sulphur isotopes in fractionating columns*.

Specific load, kg S m^{-2} s^{-1}	HETP, cm	n	T, K	K^∞	Refs.
		$H_2{}^{32}S$—$H_2{}^{34}S$			
71.5	—	—	213	1.100	[53]
81.5	—	—		1.085	[53]
117.5	—	—		1.072	[53]
163.0	—	—		1.062	[53]
		$H_2{}^{32}S$—$H_2{}^{35}S$			
0.075	2.0	51	195	1.3÷1.38	[51]
		$^{32}SO_2$—$^{34}SO_2$			
55.5÷16.5	—	96—72**	—	***	[53]
		$^{32}SO_2$—$^{35}SO_2$			
0.0015	1.0	102	248÷255	1.23	[51]

*The separation reported in Ref. 51 was in a column of height H_K = 1.02 m and diameter D_K = 12 mm, packed with Nichrome spirals (1.5 × 1.5 × 0.2 mm). The separation reported in Ref. 53 was for a column having H_K = 1.0 m and D_K = 7.6 mm and packed with Constantan rings (1.2 × 0.25 mm).
**Estimated for the distillation of BF_3 from the degree of separation of $^{10}BF_3$ and $^{11}BF_3$.
***No separation detectable within experimental error.

The characteristics of the experimental assemblies used to study the separation of sulphur isotopes by distillation are listed in Table 2: the most favourable are those for the distillation of hydrogen sulphide, offering low values of the HETP (height of the equivalent theoretical plate) as well as the possibility of achieving high specific loadings. By using the criterion W to characterise the effectiveness of unit length of the column ($W = \ln K^\infty \cdot \tau/L$, where K^∞ is the stationary separation obtained in the column, τ is the transfer of the desired isotope along the column, and L is the flow circulating in the column) Devyatykh and co-workers[51] compared the effectiveness of various sulphur isotope separation processes. The conclusion was that hydrogen sulphide is

the best working substance for the separation of sulphur isotopes by distillation ($W_{H_2S} = 1.00$, $W_{SO_2} = 0.33$†), since its molecular weight is close to the atomic weight of sulphur, and it is a naturally occurring compound as well as being in industry on a large scale (for example, in the production of heavy water by the two-temperature hydrogen sulphide method[52]). The distillation of hydrogen sulphide could be of practical interest not only as a method of separation of sulphur isotopes but also in the production of very pure sulphur and sulphides[56], the demand for which has increased sharply in recent years.

An important contributory factor to the wide use of the hydrogen sulphide distillation process for the production of heavy sulphur isotopes is the amount of information already available on this process[41,51,55]. In addition to the above data on the isotope exchange equilibrium, wide-ranging results on the hydrodynamics of the distillation of hydrogen sulphide in glass columns under vacuum can be found in the published literature. This work has established that for the column packing used in the measurements [$(2 \times 2 \times 0.3) \times 10^{-3}$ m elements made of stainless steel wire and etched with a mixture of nitric and hydrochloric acid to improve the wetting] the maximum load L^* (kg m^{-2} h^{-1}) in the temperature range 189–210.6 K is described by the equation

$$L^* = -460 + 1870(d_e\gamma_v\gamma_l)^{0.5} \quad (1)$$

where d_e is the equivalent diameter of the packing (m), and γ_v and γ_l are the density of the vapour and of the liquid respectively (kg m^{-3}).

Experimental data on the retention capacity of the packing (ΔH) under the above conditions are described by the equation

$$\Delta H = 0.11\mathrm{Re}_l^{1/3}\left(a\frac{\mu_l}{\gamma_l}\right)^{2/3} \quad (2)$$

where μ_l is the viscosity of liquid H_2S, a is the specific surface area of the packing (in the present case, 3350 $m^2 m^{-3}$), and Re_l is the Reynolds number for the liquid phase.

The measurements of the hydraulic resistance of the packing are described by the equation

$$\frac{\Delta p}{l} = \lambda\left(\frac{W_v + W_l}{2g}\right)^2 \gamma_v \frac{a}{(V_{free} - \Delta H)^3} \quad (3)$$

where W_V and W_l are the linear velocities of the flows of vapour and liquid (m s^{-1}), λ is the coefficient of friction ($\lambda = 1600/\mathrm{Re}_V$), and V_{free} is the fractional free volume.

In conclusion we note that according to the reported[41] anomalous temperature dependence of α it should be possible to carry out the distillation of hydrogen sulphide without cooling: however, in view of the doubts mentioned above, this prediction requires experimental confirmation. We should also stress that because of the high toxicity of hydrogen sulphide the cost advantage of distillation under pressure may be offset by the more stringent requirements of completely leak-free operation.

To conclude this survey of distillation processes for the separation of sulphur isotopes we should not that the technological advantages of the distillation of H_2S mentioned above may rule out the use of any other compounds, in view of the steep increase in the demand for the heavy isotope ^{34}S (now more than 10 kg per annum) in a highly enriched state (≥90%).

†At the normal boiling point of the sulphur compound.

III. CHEMICAL ISOTOPE EXCHANGE

Chemical isotope exchange processes offer values of α much greater than those found in distillation, and are widely used in the production of isotopes of the lighter elements[40,57–60]. They also play a key role in the production of the heavy sulphur isotopes[35]. A large fund of experimental information on the equilibrium and kinetics of the isotope exchange of sulphur in chemical isotope exchange processes has accumulated during the past 40 years, and furthermore the technological value of the methods has been fully characterised.

The term technological value denotes the combination of factors not directly related to the isotope exchange process in the two-phase system and yet relevant to the technology and the economics of the separation process. The latter aspects can be predominant in determining the industrial importance of a process. These factors include the availability, compatibility, toxicity, and corrosion activity of the working substances, the problems arising in organising a continuous countercurrent process, the simplicity of the phase reversal arrangements, the cost of the processes involved, the possibility of combining the isotope separation process with other industrial operations, etc.

Table 3. Data on the isotopic equilibrium of sulphur in chemical isotope exchange processes.

T, K	$10^{-5}p$, Pa	Concentration of liquid phase	$\alpha(K)$ *	Method	Refs.
		$^{34}SO_2$—$H_2{}^{32}SO_4$			
478	1	—	1.0144(1.0176)	5 (6)	[63]
573	1	—	1.0108(1.0118)	5 (6)	[63]
673	1	—	1.0088(1.0088)	5 (6)	[63]
		$^{34}SO_2$—$NaH^{32}SO_3$			
293	0.403	1.445 M $NaHSO_3$	1.0155	7*	[65]
293	0.426	1.750 M $NaHSO_3$	1.0137	7*	[65]
293	0.401	1.445 M $NaHSO_3$	1.0103	7*	[65]
293	0.975	1.503 M $NaHSO_3$	1.0150	7*	[65]
323	0.974	1.656 M $NaHSO_3$	1.0136	7*	[65]
298	1	—	1.017	5	[66]
323	1	—	1.012	5	[66]
343	1	—	1.011	5	[66]
298	1	—	1.019(1.019)	—	[64, 67]
298	0.395	$NaHSO_3$ (sat.)	1.0181	1	[68]
308	0.395	$NaHSO_3$ (sat.)	1.0170÷1.0214	1	[68]
298	0.329	—	1.010÷1.015	8	[69, 70, 71]
298	1	1 M $NaHSO_3$	1.0109	1	[72]
308	1	1 M $NaHSO_3$	1.0110	1	[72]
318	1	1 M $NaHSO_3$	1.0113	1	[72]
298	1	—	1.0110	9	[73]
308	1	—	1.0090	9	[73]
318	1	—	1.0084	9	[73]
298	1	—	1.019	5	[74]
298	1	3 M $NaHSO_3$	1.016÷1.018	5	[75]
323	1	3 M $NaHSO_3$	1.012÷1.013	5	[75]
343	1	3 M $NaHSO_3$	1.010÷1.011	5	[75]
293	1	—	1.007	—	[76]
		$^{35}SO_2$—$NaH^{32}SO_3$			
298	1	1.3 M $NaHSO_3$	1.031	10	[77]
		$^{33}SO_2$—$NaH^{32}SO_3$			
343	1	3.0 M $NaHSO_3$	1.006	3**	[75, 76]
		$^{36}SO_2$—$NaH^{32}SO_3$			
298	1	—	1.043	—	[64, 74]
343	1	3.0 M $NaHSO_3$	1.022	3**	[75, 66]
		$^{34}SO_2$—$NH_4H^{32}SO_3$			
296	1	1.5 mole SO_2 $litre^{-1}$	1.005	5	[78]
295	1	5.1 mole SO_2 $litre^{-1}$	1.0075÷1.0080	5.7	[78]
293	1	6.9 mole SO_2 $litre^{-1}$	1.0095	5	[78]
293	1	10.2 mole SO_2 $litre^{-1}$	1.0130	5	[78]
353	1	0.95 mole SO_2 $litre^{-1}$	1.0025	5	[78]
353	1	2.90 mole SO_2 $litre^{-1}$	1.0070	5	[78]
353	1	9.90 mole SO_2 $litre^{-1}$	1.0070	5	[78]
		$H_2{}^{34}S$—$NaH^{33}S$			
303	1	—	****	3***	[79]

Table 3 (contd.).

T, K	10^{-5} p, Pa	Concentration of liquid phase	$\alpha(K)$ *	Method	Refs.
		$^{34}SO_2$—$H_2{}^{32}SO_3$ *****			
303	1	—	******	3***	[79]
298	1	0.081	1.0013	1	[80]
298	1	0.116	1.0021	1	[80]
298	1	0.182	1.0032	1	[80]
298	1	2.228	1.0035	1	[80]
298	1	0.390	1.0040	1	[80]
298	1	0.523	1.0047	1	[80]
298	1	0.661	1.0066	1	[80]
298	1	0.854	1.0090	1	[80]
308	1	0.026	1.0007	1	[80]
308	1	0.078	1.0021	1	[80]
308	1	0.254	1.0030	1	[80]
		$^{34}SO_2$—$H_2{}^{32}SO_3$ *****			
308	1	0.342	1.0034	1	[80]
308	1	0.744	1.0071	1	[80]
308	1	0.837	1.0084	1	[80]
318	1	0.127	1.0018	1	[80]
318	1	0.257	1.0036	1	[80]
318	1	0.571	1.0054	1	[80]
318	1	0.907	1.0087	1	[80]
303	1	0.620	1.0050	1	[80]

Symbols: K is the equilibrium constant; methods of determining $\alpha(K)$: 5) single equilibration, 6) calculated from spectroscopic data, 7) from the kinetic curve for the accumulation of product in the column, 8) from the amount of transport in the column, 9) calculated from the experimentally determined effective separation coefficients, 10) calculated as the arithmetic mean of $\alpha(^{32}S/^{34}S)$ and $\alpha(^{32}S/^{36}S)$; other symbols as in Table 1.

*H_K = 19.2 m; D_K = 50.8 mm.
**H_K = 1.0 m; D_K = 20 mm; n = 34.
***H_K = 1.8 m.
****Separation observed, but α not measured.
*****For this system the total concentration of sulphur in solution is given (calculated as SO_2).
******No separation.

The ratios of partition functions (β-factors) have been calculated[61,62,85] by inserting spectroscopic data into a model for many isotopically substituted sulphur-containing molecules and ions, and the equilibrium constants of the isotope exchange reactions of inorganic sulphur compounds have been obtained. By combining these results with experimental studies of sulphur isotope exchange equilibria (see Tables 3 and 4) and with phase equilibrium data we can identify and characterise a number of special features of the parameter α. The recognition of correlations in isotope effects in different systems can be useful not only in a rational search for the most effective working substances but also in optimising existing separation processes. However, we should note that many of the working systems listed in Refs.61 and 85 and in Tables 3 and 4 cannot be used in controlled sulphur isotope separation processes for a number of reasons (low rate of isotope exchange (see Table 5), low single-pass isotope effect, or difficulty in arranging the phase reversal at the ends of the separation cascade).

1. Hydrogen Sulphite Process

The hydrogen sulphite process, which relies on isotope exchange between gaseous SO_2 and the hydrogen sulphite ion HSO_3^-, satisfies most of the above requirements[35,60,75,78]. The slight discrepancies in the experimental values of α (Table 3) may be due to inadequacies in the methods employed or, in some cases, to failure to allow for the presence of other ions (e.g. SO_3^{2-} and $S_2O_5^{2-}$) in an aqueous solution of hydrogen sulphites containing dissolved SO_2.[72,73,80] The relative contribution of these spurious reactions to the overall separation effect is determined by the factors which influence the equilibrium between the various ions in the liquid phase: temperature, pressure, concentration of hydrogen sulphite, and pH.

Table 4. Data on the isotopic equilibrium of sulphur in chemical isotope exchange processes between SO_2 and its complexes (p = 0.1 MPa).

Workings system	T, K	r	α	Method	Refs.	Notes
$^{33}SO_2$— xylidene ·$^{32}SO_2$*	293	1.2	1.008	11**	[81,82]	—
$^{34}SO_2$— xylidene ·$^{32}SO_2$*	293	—	1.008	11**	[81,82]	—
$^{33}SO_2$— dimethylaniline · ·$^{32}SO_2$	293	—	1.009	11***	[81,82]	—
$^{34}SO_2$— dimethylaniline · $^{32}SO_2$	293	—	1.013	11***	[81,82]	—
»	297	1.55	1.001	3	[54]	H_K=0.84 m; K^∞=1.013
$^{34}SO_2$— triethylaniline · ·$^{32}SO_2$	303	1.82	1.002	3	[54]	H_K=0.84 m; K^∞=1.022
$^{34}SO_2$— aniline ·$^{32}SO_2$	303	1.47	1.002	3	[54]	H_K=0.84 m; K^∞=1.028
$^{34}SO_2$— nitrobenzene · $^{32}SO_2$	303	—	****	3	79]	H_K=1.8 m
$^{34}SO_2$— methanol·$^{32}SO_2$	273	—	****	3	[79]	H_K=1.8 m
$^{34}SO_2$— $(CH_3CO)_2O$·$^{32}SO_2$	273	—	1.0005	—	[83]	—
$^{34}SO_2$—$B(OCH_3)_3$·$^{32}SO_2$	—	—	*****	—	[83]	—
$^{34}SO_2$—CH_3CN·$^{32}SO_2$	—	—	*****	—	[83]	—
$^{34}SO_2$— complex $^{32}SO_2$******	298	—	1.0022	—	[83]	—
$^{34}SO_2$— $H^{32}SO_3^-$	298	—	1.014	12	[47]	—
$^{36}SO_2$— $H^{32}SO_3^-$	298	—	1.028	12	[47]	—
$^{34}SO_2$—$(CH_3)_2O$·$^{32}SO_2$	273	58% SO_2 42% $(CH_3)_2O$	1.0005	3	[84]	n=15; K^∞=1.008
$^{34}SO_2$— pyridine ·$^{32}SO_2$	303	1.24	1.002	3	[54]	H_K=0.84 m; K^∞=1.027
$^{34}SO_2$— ethylene oxide · ·$^{32}SO_2$	288	0.6	1.000	3	[54]	H_K=0.84 m; K^∞=1.008
$^{34}SO_2$— thiophen $^{32}SO_2$	303	—	****	3	[54]	H_K=0.84 m;
$^{34}SO_2$— tetrahydrofuran ·$^{32}SO_2$	303	—	****	3	[54]	H_K=0.84 m;
$^{34}SO_2$— phenol·$^{32}SO_2$	303	—	****	3	[54]	H_K=0.84 m;
$H_2{}^{32}S$ — $H^{34}S^-$	298	—	1.003	12	[47]	—
$^{34}SO_2$—water·$^{32}SO_2$	298	—	****	3	[79]	H_K=1.8 m

Symbols: r is the composition of the complex (mole SO_2 $mole^{-1}$ complex former). Methods of determining α: 11) repeated equilibration; 12) calculated by the equation

$$\varepsilon=(\alpha-1)\simeq 0.7\,\varepsilon_\lambda \Delta m,$$

where

$$\varepsilon_\lambda=\left[\left(\frac{3}{2}\frac{1}{M_{AC}}+\frac{\mu_{AC}}{m^2}\right)-\left(\frac{3}{2}\frac{1}{M_{AB}}+\frac{\mu_{AB}}{m^2}\right)\right];$$

other symbols as in Tables 1 and 3.

*Xylidene diluted with water (1:2 ratio).
**Five-fold equilibration.
***Three-fold equilibration.
****No separation.
*****Separation observed, but α not measured.
******Complex of $^{32}SO_2$ with an azeotropic mixture of pyridine (43%) and water.

Many workers have studied the influence of these factors on the separation process (see Table 6): in most cases the measurements were made with aqueous solutions of sodium

or ammonium hydrogen sulphite[65,66,71,75,76,78,83,88,89]. The optimum conditions for the separation of the sulphur isotopes were found to be: temperature 343 K, concentration of hydrogen sulphite in solution 3–4 mole litre^{-1}, pressure ~0.03 MPa, and preferably using a solution of ammonium hydrogen sulphite.

Table 5. Studies of the rate of isotope exchange.

T, K	Experimental data		τ, s	References
	$10^{-3}t$, s	a, %		
	$^{32}SO_2$—$H^{35}SO_4^-$			
298	173	0	—	[86]
298	75.6	0	$>85\cdot10^7$	[86]
298	4920	$<0.4\pm0.1$	—	[86]
373	173	5	—	[86]
374	1200	1.6 ± 0.2	$\sim50.4\cdot10^6$	[86]
410	554	19 ± 0.3	$177.5\cdot10^4$	[86]
408	905	30.6 ± 0.4	—	[86]
433	25.2	3.8 ± 0.2	$53.6\cdot10^4$	[86]
433	188.5	18.8 ± 0.3	—	[86]
484	5.4	14.2 ± 0.2	$27\cdot10^3$	[86]
484	10.8	22.5 ± 0.3	—	[86]
553	<18	100	—	[86]
	$H^{35}S$—$^{32}S^{32}SO_3^{2-}$			
373	3.6	*	—	[87]
373	86.4	100	—	[87]
	$(HS^{33}S)=(H^{35}SS)^-$			
363÷373	3.6	100	—	[87]
	$^{35}SO_3^{2-}$—$^{32}S_2O_3^{2-}$			
293	72	0	—	[87]
330	3.6	*	—	[87]
330	75.6	100	—	[87]
373	3.6	100	—	[87]
	$^{32}S^-$—$^{35}SO_4^{2-}$			
373	129.6	**	—	[87]
	$^{32}SO_3^{2-}$—$^{35}SO_4^{2-}$			
373	129.6	**	—	[87]
373	126	**	—	[87]
	$^{32}SO_2$—$^{35}SO_3$			
553	61.2	**	—	[87]
608	86.4	*	—	[87, 86]
	$^{32}SO_2$—($^{35}SO_3+H_2O$)			
323	10.8	**	—	[87, 86]
	$^{32}SO_2$—($^{35}SO_3+{}^1/_3H_2O$)			
553	54.0	*	—	[87, 86]
	$^{32}SO_2$—($^{35}SO_3$+Pt on asbestos)			
553	14.4	*	—	[87, 86]
	$C^{32}S_2$—$H_2{}^{35}S$—N_2			
673	10.8	5÷6	—	[22]
	$C^{32}S_2$—[$Fe^{35}S$]***—N_2****			
473	—	1	—	[22]
573	—	11÷13	—	[22]
773	—	26	—	[22]
673	$10\cdot10^{-3}$	100	—	[22]
	$H_2{}^{32}S$—[$Fe^{35}S$]***—N_2****			
473	—	2.2	—	[22]
573	—	26.0	—	[22]
673	—	73.0	—	[22]
673	*****	100.0	—	[22]
	$CO^{32}S$—[$Fe^{35}S$]—N_2******			
473	—	13	—	[22]

Table 5 (contd.)

T, K	Experimental data		τ, s	References
	$10^{-3}t$, s	a, %		
	$C_4H_4{}^{32}S$—[$Fe^{35}S$]—N_2******			
473	—	0	—	[22]
573	—	1	—	[22]
673	—	15	—	[22]
723	—	27	—	[22]

Symbols: t is the duration of the experiment, a is the fractional amount of exchange, τ is time of half-exchange.

*Partial exchange.
**No exchange.
***[$Fe^{35}S$] is a sulphidised nickel–chromium catalyst of composition 87.95% Fe_2O_3, 7.9% CO_3^{2-}, 3.66% SO_4^{2-}, 0.31% CaO, 0.18% MgO.
****Experiments under dynamic conditions, with a volume feed rate of the gas mixture of 1200 h^{-1}.
*****Several seconds.
******Experiments under static conditions.

Solutions of sodium or ammonium hydrogen sulphite were found to be prone to "ageing" effects[65,71,75] associated with oxidation by dissolved atmospheric oxygen in the presence of ultraviolet light. It was noted[89] that the "ageing" of hydrogen sulphites takes place in two steps: in the first, sulphate, thiosulphate, and polythionates are formed, and in the second the thiosulphate and polythionates are converted into sulphate and free sulphur (generating small quantities of sulphate). The solution develops a colour, due to colloidal sulphur. The formation of colloidal sulphur takes place mainly by the reaction

$$S_2O_3^{2-} + 2H^+ \rightleftarrows H_2S_2O_3 \rightleftarrows H_2O + SO_2 + S$$

in the reactor of the lower flow reversal unit, in parallel with the decomposition of the hydrogen sulphite by sulphuric acid at $T \cong 373$ K. All these side-reactions in the solution of hydrogen sulphite should, in principle, disturb the technological regime and cause a loss of enriched product, since the exchange between HSO_3^-, SO_3^{2-}, and SO_4^{2-} ions is negligible both in acid and in alkaline solutions (as is also the exchange between thiosulphates, polythionates, and colloidal sulphur).

Many attempts to "moderate" the ageing of hydrogen sulphite solutions by various means have been reported, including additions of oxidation inhibitors, degassing of the solutions, improved designs of the lower flow reversal unit, and a search for an oxidation-resistant source of hydrogen sulphite ions. It was found that small amounts of hydroquinone[68] or *N*,*N*-dimethylformamide[80] can be used as oxidation inhibitors in solutions of ammonium hydrogen sulphite. Auto-oxidation was also shown to be avoidable[65] by degassing the initial solutions and by displacing the air in the column with an inert gas.

Many workers have found that the oxidation of hydrogen sulphite depends on the method of preparation of the solutions[75] and on their purity[71]. Thus the formation of colloidal sulphur can be largely suppressed by using freshly prepared solutions of sodium hydrogen sulphite[75]. A comparative study of different sources of hydrogen sulphite ions ($NaHSO_3$, $KHSO_3$, NH_4HSO_3, $Na_2S_2O_5$) showed that industrially the best results are obtained with sodium pyrosulphite[90] supplied in a crystalline form, which allows solutions of $Na_2S_2O_5$ to be

Table 6. Separation of sulphur isotopes in chemical isotope exchange processes.

n_{st}	N *	Shape, material, and size of packing	H_K, m	D_K, mm	c	10^4 G, $m^3\ m^{-2}\ s^{-1}$	HETP, cm	T, K	$-p$, MPa	K^{∞} (Y^{∞})	w, kg $^{34}S\ s^{-1}$	Refs.
					$^{32}SO_2$—$NaH^{34}SO_3$							
1	5×4.5	ceramic saddles, 6 mm	24	70	3.2 M	1.13	—	298	0.0329	(8% ^{34}S)	$3.70\cdot10^{-8}$	[67], [71]
2	3×4	glass Fenske helices, 6 mm	12	22	3.2 M	4.38	—	298	—	(15% ^{34}S)		
3	1×4.5; 1×3.0	glass Fenske helices, 6 mm	7.5	10	3.2 M	5.51	—	298	—	(27% ^{34}S) **		
1	1	spirals of Kh18N10T stainless steel wire, 1.8 × 1.6 × 0.2 mm	1.0	20	3.0 M	1.665	9.6	298	0.1	1.19	—	[75]
					3.0 M	1.665	3.6	333	0.1	1.36		
					3.0 M	1.665	2.9	343	0.1	1.45		
					3.0 M	1.665	3.3	353	0.1	1.40		
					4.0 M	1.665	4.4	333	0.1	1.31		
					4.0 M	1.665	2.9	343	0.1	1.45		
					4.0 M	1.665	3.4	353	0.1	1.38		
1	1	ceramic Raschig rings, 6.3 mm	19.2	50.8	1.445 M	6.46	3.13	293	0.0487	1.32	—	[65]
					1.445 M	3.25	2.35	293	0.0401	1.35		
					1.503 M	4.91	3.68	293	0.0975	1.36		
					1.750 M	4.33	2.67	293	0.0426	1.321		
					1.635 M	4.96	2.21	323	0.0975	1.485		
1	1	circular spirals, 1.6 × 1.6 × 0.2 mm	0.5	20	1.0 M	1.85	—	293	0.1	1.098	—	[76]
					2.1 M	1.82	—	293	0.1	1.165		
					3.0 M	1.765	—	292.5	0.1	1.212		
					4.1 M	1.765	—	293	0.1	1.192		
					5.0 M	1.735	—	293	0.1	1.193		
					3.0 M	1.765	—	313.5	0.1	1.287		
					3.0 M	1.765	—	333	0.1	1.327		
					3.0 M	1.765	1.82	292.5	0.1	1.212		
					3.0 M	4.6	3.13	292.5	0.1	1.118		
					3.0 M	6.72	5.47	292.5	0.1	1.066		
1	1	—	20	12	—	—	—	—	—	***		[69]
					$^{32}SO_2$—$NaH^{35}SO_3$							
1	1	carbon, AG grade	3.0	13	0.558 N	—	—	298	0.1	1.089	$2.68\cdot10^{-7}$ ($K=1.203$)	[77]
					1.020 N	—	—	298	0.1	1.160		
					1.300 N	0.338	—	298	0.1	1.115		
					1.300 N	0.752	—	298	0.1	1.202		
					1.300 N	0.880	—	298	0.1	1.168		
					1.300 N	1.005	—	298	0.1	1.118		
					1.300 N	1.257	—	298	0.1	1.060		
					1.300 N	—	50	298	0.1	1.203		
					1.580 N	—	—	298	0.1	1.157		
					2.040 N	—	—	298	0.1	1.142		
					2.51 N	—	—	298	0.1	1.105		
					$^{32}SO_2$—$NH_4{}^{34}SO_3$							
1	1	circular spirals of stainless steel, 1.6 × 1.6 × 0.2 mm	0.5	20	1.3 M	1.85	—	292.5	0.1	1.21	—	[78]
					1.9 M	1.85	—	293	0.1	1.20		
					3.4 M	1.765	—	293	0.1	1.26		
					5.1 M	1.680	—	293	0.1	1.24		
					6.0 M	1.765	—	292.5	0.1	1.22		
					6.9 M	1.765	—	293.5	0.1	1.20		
					10.2 M	1.765	—	295	0.1	1.12		
					2.9 M	1.765	—	353	0.1	1.463		
					6.6 M	1.765	—	353	0.1	1.32		
					7.3 M	1.765	—	353	0.1	1.32		
					9.9 M	1.765	—	353	0.1	1.182		
					3.0 M	1.765	0.93	353	0.1	1.46		
					4.0 M	1.765	1.00	353	0.1	1.42		
					5.0 M	1.765	1.09	353	0.1	1.38		
					6.0 M	1.765	1.20	353	0.1	1.34		
					7.0 M	1.765	1.34	353	0.1	1.30		
					8.0 M	1.765	1.52	353	0.1	1.26		
					9.0 M	1.765	1.76	353	0.1	1.22		
					10.0 M	1.765	2.12	353	0.1	1.18		
					1.3 M	1.765	1.23	293	0.1	1.21		
					1.9 M	1.765	1.27	293	0.1	1.232		
					3.4 M	1.765	1.45	293	0.1	1.26		
					$^{32}SO_2$—$NH_4H^{34}SO_3$							
1	1	circular spirals of stainless steel, 1.6 × 1.6 × 0.2 mm	0.5	20	5.1 M	1.765	1.93	293	0.1	1.24	—	
					6.0 M	1.765	2.29	293	0.1	1.22		
					6.9 M	1.765	2.74	293	0.1	1.20		
					8.0 M	1.765	3.50	293	0.1	1.17		
					9.0 M	1.765	4.30	293	0.1	1.15		
					10.2 M	1.765	5.50	293	0.1	1.12		
1	1	circular spirals of wire, 1.6 × 1.6 × 0.2 mm	0.5	20	5.0 M	1.915	3.85	293	0.1	1.11	—	[88]
1	1	extended circular spirals of wire, 1.6 × 1.6 × 0.2 mm	—	20	5.0 M	1.93	1.72	293	0.1	1.275	—	[88]

Table 6 (contd.).

n_{st}	N*	Shape, material, and size of packing	H_K, m	D_K, mm	c	10^4 G, $m^3\ m^{-2}\ s^{-1}$	HETP, cm	T, K	p, MPa	K^{∞} (Y^{∞})	w, kg $^{34}S\ s^{-1}$	Refs.
1	1	triangular spirals of wire, 1.6 × 1.6 × 0.2	0.5	20	5.0 M	1.85	1.79	293	0.1	1.25	—	[88]
1	1	extended triangular spirals of wire, 1.6 × 1.6 × 0.2 mm	0.5	20	5.2 M	1.80	1.30	293	0.1	1.36	—	[88]
1	1	extended square spirals of wire, 1.6 × 1.6 × 0.2 mm	0.5	20	5.0 M	1.93	2.87	293	0.1	1.15	—	[88]
1	1	acid-resistant spirals No.316	3.0	40	3.0 M 3.0 M 3.0 M 3.0 M 3.0 M 3.0 M	0.833 1.665 2.500 1.665 0.833 1.665	5.50 10.00 13.00 5.10 1.44 3.30	298 298 298 322 343 343	0.1 0.1 0.1 0.1 0.1 0.1	a column 5.5 m high gave 100 litre of SO_2 containing 50 at.% ^{34}S		[29]
					$H_2{}^{32}S$—$NaH^{34}S$							
1	1	glass spirals	8.0	10	sat.soln.	—	—	298	0.1	1.063 (^{34}S becomes concentrated in the gas)		[79]
					$^{32}SO_2$—$Na_2{}^{34}S_2O_5$							
1	1	triangular spirals of stainless steel wire, 2.2 × 2.2 × 0.2 mm	8.0	27	3.0 *M*	3.50	6.4	343	0.1	—	—	[90]
2	1	triangular spirals of stainless steel wire, 1.8 × 1.6 × 0.2 mm	12.0	21	3.0 *M*	2.42	5.0	343	0.1	****	—	[90]

Symbols: N is the number of columns in the cascade step, n_{st} is the number of steps in the cascade, c is the concentration of hydrogen sulphite, G is the specific load, Y^{∞} is the stationary concentration, w is the output rate.

*The first figure is the number of columns, the second is the height of the columns in metres.
**Non-stationary concentration reached in ~18 × 10^5 s.
***Concentrations of 10.2% ^{34}S and 1.5% ^{33}S reached; non-stationary, though reached without take-off.
****Concentrations of 45% ^{34}S, 2.7% ^{33}S, and 0.9% ^{36}S reached.

prepared immediately before the separation process. Furthermore, by using a reactor incorporating three separately heated sections[75] and carrying out the lower phase reversal operation at successively higher temperatures (50, 75, 95, and 100–105 °C) the precipitation of colloidal sulphur was suppressed to a large extent and quantitative evolution of the SO_2 was obtained though its concentration in the effluent solution was very low (5 × 10^{-3} kg m^{-3}). Small amounts of colloidal sulphur were precipitated after lengthy boiling of the solutions, but they were easily entrained by the liquid and did not interfere with the separation.

An isotopic analysis of the colloidal sulphur precipitated during the separation was carried out[75] in order to determine whether the precipitation causes a loss of enriched product. Though the laboratory apparatus produced a concentration of ^{34}S of 6.2% at the lower end of the column in a stationary regime, the isotopic composition of the sulphur was identical to that of the initial solution, showing that the precipitation of colloidal sulphur had not caused a loss of enriched product. This conclusion is of the utmost importance in determining the possibility of obtaining sulphur isotopes at high concentrations by the hydrogen sulphite process, and it requires experimental confirmation by the same method but at higher levels of enrichment of ^{34}S in the column.

Another important series of studies on the hydrogen sulphite process was aimed at developing improved apparatus designs and lowering the unit cost of the process. Perhaps the most significant of these were the search for a more effective type of column packing[66,71,88] and the work on minimising the cost of flow reversal. The need for these improvements was dictated by the very high values of the HETP (from 0.25 to 1.1 m) reported in the early publications[65, 71,77] (see Table 6) and by the excessive consumption of relatively expensive high-purity reagents in the flow reversal process.

One of the earliest attempts[71] to increase the efficiency of the packing (by improving its wetting by the working solution) relied on the addition of small amounts of technical octanol, but the performance of the packing (glass saddles or Fenske helices) was not measurably improved. Nevertheless the use of additives to improve the wetting of the packing and to increase the rate of diffusion processes in the liquid phase should not be dismissed, especially if the additives also act as oxidation inhibitors for the hydrogen sulphite ions, if they assist the flow reversal or protect the apparatus from corrosion, or if they favour the mutual solubility of the phases participating in the separation. An alternative method of increasing the effectiveness of the

packing relies on etching the surface with acid solutions (in the case of stainless steel packings). This method is interesting, and its effectiveness has been noted in a number of studies of different isotopic mixtures using different packings[54,91,93].

The most systematic investigation of possible ways of improving the effectiveness of column packings for the hydrogen sulphite process was reported by Stiehl and coworkers[88]. By studying five types of stainless steel packing of different geometrical form they showed that the best packing consists of extended triangular spirals, which offer a large free volume and a low retention for aqueous solutions of hydrogen sulphites. These workers calculated that by using this type of packing for the separation of sulphur isotopes in the NH_4HSO_3–SO_2 system an apparatus not exceeding 35.4 m in height can give a fractional take-off of 90%-enriched ^{34}S equal to 0.2677×10^{-3} of the flow (L) circulating in the column. The calculations apply to an aqueous solution of NH_4HSO_3 with a total concentration of SO_2 of 9 mole litre^{-1}, assuming a working temperature of 353 K and a specific loading (with liquid) of 1.765×10^{-4} m^3 m^{-2} s^{-1}.

At the current level of production of sulphur isotopes (up to 2 kg of 50–90% ^{34}S per annum[90]) the most important item in the overall cost of manufacture is that of the flow reversal arrangements (in addition to the labour costs)[35].

One of the most promising methods of minimising this cost in the hydrogen sulphite process is to combine this separation with the separation of nitrogen isotopes in the NO–HNO_3 chemical exchange system[76] (see Fig.1)#, which can itself easily be combined with the low-temperature distillation of NO to yield oxygen isotopes[96]. A combination of these processes by the scheme shown in Fig.1 minimises the flow reversal costs of both the hydrogen sulphite and the HNO_3–NO process as well as solving the problem of by-product utilisation. Any practical embodiment of this scheme should include provisions for removing dissolved SO_2 from the sulphuric acid emerging from the lower flow reversal unit of the "nitric acid" assembly: otherwise, the acid will cause a serious dilution of the enriched sulphur isotopes when admitted to the lower flow reversal unit of the "hydrogen sulphite" assembly.

The problem of removing dissolved SO_2 from the sulphuric acid is made much simpler by organising the flow reversal in the NO–HNO_3 process as shown in Fig.2. This allows the concentration of the H_2SO_4 issuing from the flow reversal unit to reach 70–75% [100] (since the solubility of SO_2 in H_2SO_4 goes through a minimum as the concentration increases to 80% [99]). The concentration of SO_2 in the sulphuric acid is lowered also by heating the acid, since the solubility varies inversely with temperature. For example, according to standard Tables[98] the solubility of SO_2 in 95% H_2SO_4, which is 25 m^3 SO_2 m^{-3} H_2SO_4 at 298 K, falls to 4 m^3 SO_2 m^{-3} H_2SO_4 at 363 K. This suggests that failure to control the SO_2 content of the sulphuric acid used for flow reversal in "hydrogen sulphite" plants may be responsible for the reported[76,83] discrepancies in the HETP obtained for isotope exchange between the hydrogen sulphite ion and SO_2 in counter-current packed columns and in ion exchangers[17,101] (see also Tables 6 and 9). In the latter case the motion of the Spedding zone was achieved by using hydrochloric rather than sulphuric acid (thus avoiding the presence of dissolved SO_2). We also note from the results in Table 6 that substantially different values of the HETP were obtained by different workers using H_2SO_4 for flow reversal in counter-current columns under similar conditions (identical temperature, pressure, concentration of hydrogen sulphite ion, load (and shape and size) of the packing, and similar column diameters).

#The production of a kg of ^{15}N by the NO–HNO_3 process requires a supply of more than 50000 kg of sulphur dioxide for flow reversal[97]. This gas is a waste product in the hydrogen sulphite process, and at the same time the waste product of the NO–HNO_3 process (sulphuric acid) can be utilised (after suitable treatment) to induce flow reversal in the hydrogen sulphite process.

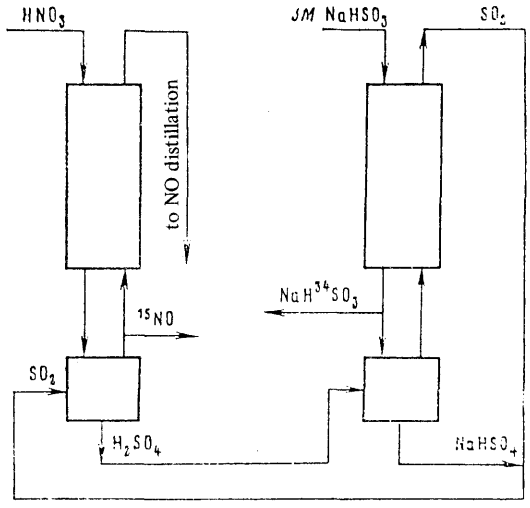


Figure 1. Combination of the hydrogen sulphite sulphur isotope separation and the NO–HNO_3 nitrogen isotope separation process.

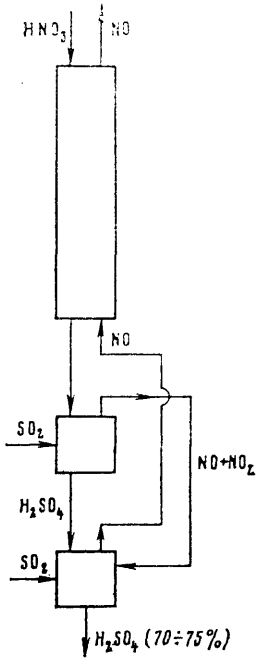


Figure 2. Flow reversal scheme suggested[100] for the lower unit in the nitrogen isotope separation process.

Knowing the maximum solubility of SO_2 in sulphuric acid[98] we can calculate the possible isotopic dilution of the product caused by the SO_2 of natural isotopic composition contained in the sulphuric acid added to the flow reversal unit. For a concentration of ^{34}S of 4.2 at.%, and a separation coefficient of the ^{32}S and ^{34}S of $\alpha = 1.008$ (at 20 °C), the production of 1 kg of ^{34}S in an apparatus without take-off requires the treatment of a flow of raw materials containing $L = p/x_0\Gamma \cong$ 3000 kg of sulphur, as well as an input of 9000 kg of H_2SO_4 for flow reversal. At 293 K the solubility of SO_2 is 0.0365 kg SO_2 kg^{-1} H_2SO_4, and as a result of isotopic dilution the ^{34}S content of the product may fall from $x_K = 100\%$ to $x_K = 4.79\%$. At higher temperatures the solubility of SO_2 decreases, but not to a negligibly low value. For example, at 90 °C the solubility is 0.00475 kg SO_2 kg^{-1} H_2SO_4, which can also lead to marked isotopic dilution ($x_K = 8.5\%$). Evidently, failure to allow for these effects may have been responsible for serious errors in the determination of the HETP from experimental values of the degree of separation obtained, and hence it may explain the large discrepancies between HETP values reported from different laboratories.

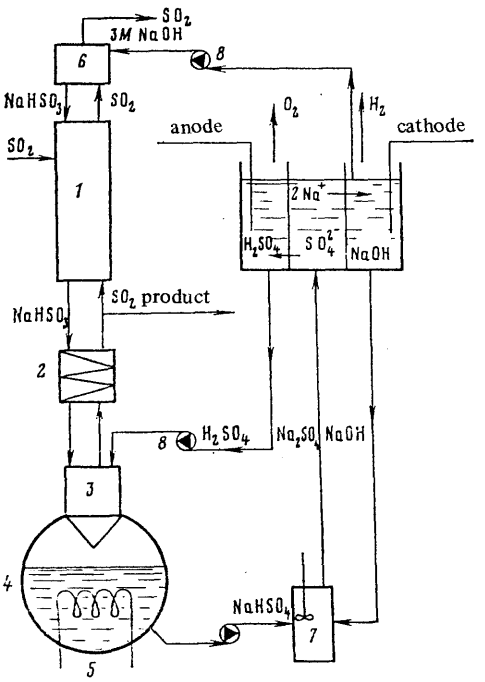


Figure 3. Flow reversal using an electro-dialysis system in the hydrogen sulphite process: *1*) exchange column, *2*) condenser, *3*) hydrogen sulphite decomposition column, *4*) boiler, *5*) heater, *6*) reactor of upper flow reversal unit, *7*) hydrogen sulphite converter, *8*) pump.

In order to reduce the cost of the reagents used for flow reversal (sulphuric acid in the lower unit and sodium hydroxide in the upper unit for flow reversal in a "hydrogen sulphite" apparatus with take-off) an electro-dialysis system has been used[19,25,35,36] to regenerate NaOH and H_2SO_4 from the $NaHSO_4$ formed in the lower flow reversal unit (Fig.3). The additional consumption of electrical energy in this case is 3500 kJ per mole of $NaHSO_4$.[35]

The advantages of the electro-dialysis scheme include inducing flow reversal by using electrical energy, and the possibility of using a gas as feed-stock (thus allowing the process to be combined with the "nitric acid" process, or, using the "transit" scheme, with the sulphuric acid process based on SO_2). Furthermore this scheme avoids the difficulties arising from the need to use freshly prepared solutions of hydrogen sulphite, and minimises "ageing" effects.

The problem of using HETP data obtained for small-diameter columns in the design of large industrial isotope separation plant is still unsolved. However, for the hydrogen sulphite process this problem is easily solved by using the abundant experimental information on HETP values available for columns of widely different diameter (up to 0.07 m [71]) and using packing of different shape and size (see Table 6).

We shall conclude this discussion of the hydrogen sulphite process with a brief review of the characteristics of industrial assemblies and of the results of experiments in large laboratory apparatus and in pilot plant. The first separation of sulphur isotopes by the hydrogen sulphite process was achieved in a fairly large laboratory cascade assembly[67,70,71] whose main parameters are listed in Table 6. Because of the low flow rate of gaseous SO_2 the pressure drop in the columns was also low, and therefore the cascade could be operated without intermediate gas compressors. A stationary distibution of ^{34}S concentration was reached after 21 days' operation of the cascade. It was found that 3.0×10^{-5} m^3 of enriched $NaHSO_3$ solution (3.2×10^{-3} kg of sulphur) could be taken daily from the last column of the cascade with a concentration of ^{34}S not less than 25%. Having determined experimentally the hold-up of ^{34}S in the column, Thode and co-workers[70] calculated the average rate of transfer (1.272×10^{-8} kg ^{34}S s^{-1}).

It was subsequently found[69] that the heavy sulphur isotopes could be concentrated to the level of 10 at.% ^{34}S and 1.5 at.% ^{33}S in the $NaHSO_3$–SO_2 system by using an apparatus with columns 20 m high. In the early 1970's a cascade consisting of two columns 8 and 12 m high was built in the Soviet Union, and this gave an enrichment of 45 at.% for ^{34}S, 2.7 at.% for ^{33}S, and 0.9 at.% for ^{36}S in 20 days. From these results a design was produced for a three-column cascade apparatus capable of producing 0.5 kg $year^{-1}$ of sulphur containing 90 at.% of ^{34}S or 0.1 kg $year^{-1}$ of sulphur containing 3 at.% of ^{36}S. The estimated cost[90] was 117000 roubles per kilogramme of ^{34}S and 580000 roubles per kilogramme of ^{36}S.

A group of French workers[29] described a series of tests on a large-scale apparatus consisting of a column 5.5 m long and 0.04 m in diameter filled with Helipak 316 packing. By using the NH_4HSO_3–SO_2 system these workers studied the effect of load and temperature on the HETP at atmospheric pressure and 3 M concentration of the aqueous hydrogen sulphite solution. Their results are given in Table 6. A comparison of these results with those obtained[75] under otherwise similar conditions for the $NaHSO_3$–SO_2 system in a column 0.02 m in diameter confirms the report[76,102] that the HETP for the NH_4HSO_3–SO_2 system is lower than the corresponding value for the $NaHSO_3$–SO_2 system. These pilot experiments established that the apparatus can produce 0.1 m^3 day^{-1} of SO_2 containing 50% of ^{34}S.

The development of a large-scale apparatus for separating sulphur isotopes at the Mound laboratory (USA) has recently been described[25,35,36]. It is based on the laboratory's five-step cascade process for the production of carbon-13 by the amine–carbamate method[36,103]. The consumption of reagents for flow reversal is minimised by adopting an electro-dialysis system in conjunction with the $NaHSO_3$–SO_2 working system.

The separation is carried out at 343 K with a 3 M concentration of sodium hydrogen sulphite in water. For a feed rate of $(1.157–3.48) \times 10^{-5}$ kg SO_2 per day this plant is expected to produce 5×10^{-8} kg of ^{34}S with a concentration of 90 at.% per day at a cost between 100000 and 200000 dollars per kilogramme. It is also proposed[36] to use some of the product in the Mound laboratory's thermo-diffusion apparatus[25,36] to produce ^{33}S at high concentration.

In addition to the hydrogen sulphite process, the exchange of isotopes between potassium xanthate $S{=}C(OR)(SK)$ and carbon disulphide CS_2 has also been studied as a means of separating sulphur and carbon isotopes simultaneously[104,105]. The lower flow reversal in this process uses the reaction

$$RO{-}C(SK){=}S + HCl \rightarrow ROH + KCl + CS_2$$

and the upper flow reversal uses the reaction

$$CS_2 + KOH + ROH \rightarrow RO{-}C(SK){=}S + H_2O\ .$$

This process is not very attractive for the separation of sulphur isotopes, because sulphur isotope exchange is very slow in the C–S and O–S bonds[20]. Furthermore, the practical value of the method is very doubtful in view of its reliance on expensive chemical flow reversal arrangements.

Table 7. Separation of sulphur isotopes in chemical isotope exchange processes between SO_2 and its thermally unstable complexes (p = 0.1 MPa).

Working system	ϵ	10^4G, $m^3\ m^{-2}\ s^{-1}$	T, K	K^∞ (Y^∞)	Refs.
$^{32}SO_2$–[pyridine/H_2O] × $^{34}SO_2$* (43% pyridine)	5.5 M	4.72	357	(4.55% ^{34}S)	[94]
ditto	4.5 M	4.72	323	(1.15% ^{34}S; 1.075% ^{33}S)	[94]
$^{32}SO_2$–[pyridine/H_2O].$^{34}SO_2$ (4.7 mole C_5H_5N litre^{-1})	4.5 M	4.72	323	1.15	[95]
$^{32}SO_2$–[pyridine/H_2O/H_3PO_4] × $^{34}SO_2$ (3.15 mole H_3PO_4 litre^{-1}, 2.86 mole C_5H_5N litre^{-1})	1.95 M	1.88÷2.2	295	1.13	[95]
$^{32}SO_2$–[pyridine/H_2O/H_3PO_4] × $^{34}SO_2$ (3.33 mole H_3PO_4 litre^{-1}, 2.77 mole C_5H_5N litre^{-1})	1.5 M	2.05	294	1.135	[95]
$^{32}SO_2$–[pyridine/H_2O/H_3PO_4] × $^{34}SO_2$ (4.39 mole H_3PO_4 litre^{-1}, 2.89 mole C_5H_5N litre^{-1})	1.56 M	1.732	293	1.08	[95]
$^{32}SO_2$–H_2O.$^{34}SO_2$	0.9 M	2.83÷3.46	293	1.075	[95]

*H_K = 1.85 m, D_K = 25 mm, triangular spirals of V2A steel wire, 1.6 × 1.6 × 0.2 mm.
**H_K = 2.0 m, D_K = 25 mm.

Symbols: as in Table 6.

2. Systems Using Thermal Flow Reversal

The possibility of using complexes of SO_2 with various organic compounds has been studied in several laboratories (see Tables 4 and 7). The systems examined include xylidene and dimethylaniline[55,81,82,87], pyridine[55] and its mixtures with water and phosphoric acid[94,95], and also diethyl and dimethyl ether, anisole, and phenetole[75,84,106], trimethoxyborane and acetonitrile[83], and aniline, triethylaniline, ethylene oxide, phenol, and tetrahydropyran[55]. Other sulphur-containing complexes have also been studied, including those formed by the reaction of H_2S, $(CH_3)_2S$, CS_2, COS, $SOCl_2$, SCl_2, and S_2Cl_2 with complexing agents such as diborane, boran trifluoride, boron triaryls and trialkyls, and also aluminium trialkyls (in particular, $(CH_3)_3Al$ and $(C_2H_5)_3Al$).[107] The largest isotope effect was obtained for a mixture of SO_2 and the complex of SO_2 with the pyridine–water azeotropic mixture: on a column 1.85 m long this gave a separation of the ^{32}S and ^{34}S isotopes of $K^\infty = 1.15$.[95]

Though these systems offer the great advantage of thermal flow reversal, they are not serious competitors of the hydrogen sulphite system for the separation of sulphur isotopes. In most cases their α values are extremely low (see Table 4), and the low stability of the complexing agent towards atmospheric oxygen and water vapour can create serious practical problems. As a result, the separation has to be carried out in an inert atmosphere, and provisions for continuous (or periodic) drying have to be made, together with provisions for removing the decomposition products of the complexing agent. We should also note that the complexing agents and the sulphur-containing compounds listed above are, in most cases, highly toxic and corrosive.

However, these difficulties should not be used as an argument to stop the research in these areas, because analogous systems have long been used with success in industrial plant for the separation of boron isotopes[108].

The most important outcome of these investigations is the establishment of clear correlations between the parameter α and the physicochemical of structural properties of the complexes. However, before examining these correlations we should briefly consider the reliability of the α values listed in Table 4 for the SO_2 complexes. These values were obtained either by repeated equilibration or by separating a mixture of isotopes on a column. The weakness of the latter method has already been stressed in this review. The main weakness of the repeated equilibration method is its reliance on a strict preservation of the material balance[109–112], which cannot always be ensured owing to mechanical losses or to the volatility of the gaseous sulphur compounds. The results may be distorted also by kinetic isotope effects in the evolution of the gaseous sulphur compound from the complex former (or its absorption). Furthermore, errors in the determination of α may arise from fluctuations (from step to step) in the amount of flow contraction assumed for the calculation[109,110,117].

These factors may be responsible for the large discrepancies in the α value for the SO_2–SO_2·dimethylaniline system (see Table 4) and for the good agreement of the α values in the SO_2–SO_2·xylidene system for the ^{34}S–^{32}S and ^{33}S–^{32}S isotope mixtures. Another possible reason for the poor reproducibility of experimental data is the dependence of the separation coefficient α on the composition of the complex (or, more exactly, on the parameter r, which is the ratio of the number of moles of the sulphur-containing compound in the complex, D, to the number of moles of complexing agent, R). This dependence is due to the presence in the liquid phase of free molecules of the sulphur-containing compound, leading to inter-phase isotope exchange (in addition to ordinary isotope exchange) between the sulphur compound in the gas phase and in the liquid complex former respectively. Therefore the observed effective separation coefficient α depends on the fractional amount m of free sulphur compound in the liquid phase according to the equation

$$\alpha = mK_{ph} + (1-m)K$$

where K is the equilibrium constant of the isotope exchange reaction between the sulphur compound in the gas phase and its complex in the liquid phase, and K_{ph} is the separation

coefficient for the inter-phase isotope exchange between the free sulphur compound in the gas phase and in the liquid phase respectively.

A rational search for efficient working systems by quantum-statistical calculations can be based on the ratio of the partition functions (β-factors) of the isotopic forms of the sulphur compounds[61,113]. In addition to an estimate of the equilibrium constants for different sulphur compounds this calculation gives an indication of the trends in the dependence of the β-factor on various characteristics of the compounds, as in the earlier work on boron compounds[113–116]. However, the calculation assumes that the vibration frequencies and the anharmonicity factors for both the normal and the isotopic molecules are experimentally known, and in the case of the more complex molecules these measurements are extremely difficult[115]. Reported calculations[61,85] suggest that the SO_3 and SO_2 molecules should have the highest β-factor of all gaseous sulphur compounds. At the same time these calculations point to the advantages of using a thermally unstable complex (e.g. a complex of H_2S) for the separation of sulphur isotopes.

A relationship has been reported[118,119] between the parameter α for sulphur isotopes and the ionisation potential J of the complexing agent. These calculations were based on the wave function

$$\varphi_N = a\varphi_0(\mathrm{RD}) + b\varphi_1(\mathrm{R}^+ + \mathrm{D}^-)$$

which describes the ground state of the complex molecules ($R + D \rightleftharpoons RD \rightleftharpoons R^+ + D^+$), and assumed a linear dependence of the separation coefficient α on the ionisation potential J of the donor: $\alpha = m - nJ$, where m and n are constant coefficients, equal to 1.0109 and 9.8×10^{-4} respectively for the separation of the sulphur isotopes ^{32}S and ^{34}S in SO_2–SO_2(complex) systems at 293 K.

The above equation is not acceptably consistent with experiment[118], and it assumes that the isotope effect is negligible for $J = 11.1$ eV. Since the potential J usually decreases as the size of the molecule increases, we can expect[118] α to increase with the molecular weight of the donor. As Table 4 shows, this expectation is not borne out in general: for different homologous series the parameter α tends to increase with the molecular weight of the complexing agent, but within any one homologous series no such tendency is observed.

It has also been pointed out[118] that the choice of a linear correlation between α and J is purely empirical, and there may be exceptions arising from steric hindrance to the formation of additive compounds, from orientation effects, or from the screening effect of free electrons. Furthermore, the assumed correlation between the ionisation potential and the properties of the resulting donor–acceptor complex has been shown[120] to be valid only if the complex forming power and the ionisation potential are referred to the same system of electrons in the donor molecule. In aliphatic or in saturated cyclic ethers, sulphides, or amines both these quantities refer to the properties of the unshared pair of electrons on the hetero-atom, but in aromatic or unsaturated compounds containing a hetero-atom the ionisation potential may relate to the excitation of a π-electron whereas the formation of the complex takes place through an n-electron of the hetero-atom. Furthermore, the use of the ionisation potential of the donor molecule to characterise the donor–acceptor interaction fails to take account of the overlap of the orbitals involved in the formation of the intermolecular bond and of "spatial" factors.

It has therefore been suggested[120] that the donor–acceptor interaction (and therefore also the parameter α) could be more accurately characterised by using the overlap integrals of the atomic orbitals of the donor and the acceptor. The possibility was demonstrated[120] for the complexes of BF_3 with a class of amines, ethers, and thio-ethers in which α varies in the order $\alpha_S > \alpha_O > \alpha_N$ whereas the overlap integrals calculated by using the Slater functions for the B–O, B–N, and B–S bonds vary in the opposite order (B–S < B–O < B–N). It is interesting to note that in these classes of compounds the ionisation potential decreases in the sequence $J_O > J_S > J_N$.[121] This tends to support the correlation proposed in Ref.118.

A dependence of α (or of the equilibrium constant K of the isotope exchange reaction) for a series of compounds of a given type has been noted[108] as a function of the nature of the electron-donor atom in the complex former R, of the nature and position of the complex former in the homologous series, of the presence of polar or easily polarisable groups in the molecule, and of the structure of R. The effects were ascribed to the factors listed above and their influence on the stability of the complexes, and in particular to the heat of formation of the complex ΔH_{form}. The relationship between α and the heat of formation of the complex was specially stressed[108]. In the case of boron complexes of a single type the parameter α was found to increase as the stability of the complex decreases, i.e. as ΔH_{form} decreases. In such a series of complexes the stability decreases as the atomic number of the donor atom increases, due not only to the larger size of the atom but also to the screening of the inner electrons from the electrons in the outer sphere of the donor atom. These considerations led to the suggestion[107] that the α values for a series of sulphur complexes of a given type including B, Al, Ga, In, or Tl as the electron-donor atom should decrease in the sequence Tl > In > Ga > Al > B. At the same time, the data on the boron complexes indicate that in the case of sulphur complexes the α values should decrease in the sequence Se > S > O > N.

Clearly, in the sulphur complexes (as in the BF_3 complexes) the maximum value of α is found in the second member of the homologous series of complex formers. This was confirmed experimentally[55,75] in a study of the separation of sulphur isotopes by using the complexes of SO_2 with phenol[55] and with anisole and phenetole[75]. Whereas by using phenol no separation was obtained in a column 0.84 m long, by using anisole in a column 1 m long with a packing of particle size ($1.6 \times 2.0 \times 0.2$) $\times 10^{-3}$ m a stationary distribution of ^{32}S and ^{32}S corresponding to a separation of $K^{\infty} = 1.06$ was obtained, and this was greater than the separation obtained in the same column by using phenetole. The maximum in the α values for the second member of the homologous series of complex formers has been ascribed[108], in the case of the separation of boron isotopes, to the influence of the geometry of the R molecule on the energy of the bond between the donor atom and the boron atom, and hence on the parameter α. This explanation can be extended to the complexes formed by sulphur-containing compounds, since the influence of the structure of the complex former on α is unmistakable in the results (Table 4) for the complexes of SO_2 with aniline ($\alpha = 1.002$)[55] and with dimethylaniline ($\alpha = 1.013$)[81]. The presence of two methyl groups on the donor (nitrogen) atom of dimethylaniline causes steric hindrance to the formation of a donor–acceptor bond between the sulphur and the nitrogen atom, thus lowering the stability of the complex and as a result raising α.

In the case of the BF_3 complexes the introduction of polar or easily polarisable groups into the complex-forming molecule lowers the stability of the complex: conversely, the stability is increased by the introduction of electron-donor substituents[108]. Thus the parameter α can be varied by inserting appropriate groups into the complex-forming molecule. However, we should not that the tendency of α to

increase in response to a decrease in the stability of the complex (by the introduction of polar or easily polarisable groups) also leads to a decrease in r. We also note that because of the scarcity and unreliability of the published data on the heat of formation of the complexes of sulphur-containing compounds it may be necessary to use the composition r (at saturation) as a measure of the stability of these complexes.

Table 8. Vapour pressure of the complex (p) against composition (258 K, SO_2 partial pressure 0.1 MPa).[106]

SO_2:$(C_2H_5)_2O$ *	p, MPa	SO_2:$(C_2H_5)_2O$ *	p, MPa
1.000	0.01167	0.334	0.0526
0.845	0.01395	0.227	0.0625
0.570	0.0295	0.111	0.0721
0.510	0.0334	0.000	0.0796

*Molar ratio.

Some data on the phase equilibria in systems including sulphur complexes are given in Table 4. The properties of complexes of the $(CH_3)_2O\cdot SO_2$ and $(C_2H_5)_2O\cdot SO_2$ type have also been studied[84,106]: for $(C_2H_5)_2O\cdot SO_2$ the dependence of the vapour pressure p on the composition r was determined for 258 K and a partial pressure of SO_2 of 0.1 MPa (see Table 8), whereas for $(CH_3)_2O\cdot SO_2$ an azeotrope containing 58% SO_2 and 42% $(CH_3)_2O$ was observed at 273 K. The degree of dissociation of the latter complex in the vapour phase at 273 K was found to be 0.93. The melting point and boiling point of the $(CH_3)_2O\cdot SO_2$ complex are given[84] as 177.5 and 263 K respectively, and its heat of formation as ~15.5 kJ mole^{-1} (the composition of the saturated complex r = 1 mole SO_2 mole^{-1} $(CH_3)_2O$ is reached at 263 K and 0.1 MPa). The boiling point of $(C_2H_5)_2O\cdot SO_2$ is given[106] as 258 K, and its heat of formation as ~29.4 kJ mole^{-1}.

Attempts to relate the separation coefficient to the polarisability and dipole moment of the complex former have been described[122,124]. The more readily polarisable the complex former, and the larger the dipole moment of the complex, the weaker is the bond formed in the complex. Therefore we can expect α to increase with the dipole moment of the complex. This expectation has been confirmed experimentally for the complexes of BF_3 with the lower olefins, and is probably equally valid for the complexes of sulphur-containing systems. The dipole moments of some selenium, sulphur, and phosphorus compounds and their complexes are listed in Ref.125.

The importance of establishing the correlation between α and the parameters which describe the electronic and structural properties of the donor molecules and their substituents has been stressed[126,127]. By classifying the effect of substituents on the properties of the donor molecule as inductive, steric, mesomeric, etc. we can write the following expression for α in terms of the Hammett–Taft equation

$$\lg \alpha/\alpha_0 = \rho\Sigma\sigma + \Delta n\cdot h + \delta E_S + \psi$$

where α_0 and α are the separation coefficients of the sulphur isotopes for the initial and the substituted compound respectively, σ is the inductive constant (a measure of the effective electronegativity of the substituents), E_S is the steric constant of the substituent, Δn is the difference in the numbers of hydrogen atoms involved in hyperconjugation in the initial and the substituted compound, ρ, δ, and h are the parameters of the reaction series (a measure of the sensitivity of the reaction to the inductive, steric, and hyperconjugation effects respectively), and ψ is the coefficient which reflects the contribution from the conjugation of any π system to the reaction centre. Values of σ, E_S, and Δn are available for almost any substituent[128]. Often some of the effects can be ignored, and the equation becomes simpler.

In conclusion we note that all the complexes of SO_2 and of other sulphur compounds can be arbitrarily divided into two large groups. The first group includes complexes whose vapour pressure is lower than that of the complex former (for example, $(CH_3)_2O\cdot SO_2$ and $(C_2H_5)_2O\cdot SO_2$). These are only partially dissociated in the vapour phase, and as a result the gaseous sulphur compound included in the complex cannot be separated from the complex former. This group of compounds can be used in the separation of sulphur isotopes by chemical isotope exchange combined with distillation, involving isotope exchange between the liquid and the partially dissociated vapour of the complex. The lower flow reversal is achieved by evaporation of the liquid complex.

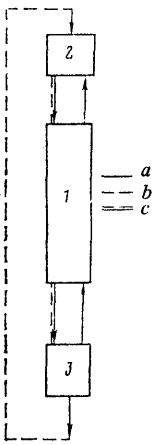


Figure 4. Process for the separation of sulphur isotopes by chemical isotope exchange with thermal phase reversal: *1*) exchange column, *2*) adsorber, *3*) desorber; *a*) gas flow, *b*) flow of complex former, *c*) flow of complex.

The second group of complexes includes those whose vapour pressure is greater than that of the complex former (for example, $C_6H_5OCH_3\cdot SO_2$, $C_6H_5OC_2H_5\cdot SO_2$). These complexes are almost fully dissociated in the vapour phase. By heating them to the boiling point of the complex former it is possible to strip the sulphur-containing gas almost quantitatively from the complex, since the vapour pressure of the complex former is relatively low. This makes possible the separation of sulphur isotopes by counter-current exchange between a gaseous sulphur-containing compound and its liquid complex, i.e. by "clean" chemical isotope exchange (Fig.4). Flow reversal at the ends of the separation cascade is achieved by thermally dissociating the complex in the desorber to the sulphur-containing gas and the complex former. The complex former is cooled and re-used to absorb the gas emerging from the separating column in the upper flow reversal unit, which is also an apparatus of the column type[108].

We should stress that the possibility of exploiting this group of compounds for separating sulphur isotopes was first demonstrated by Soviet workers[81]. Evidently, solid complexes of sulphur-containing gases could also be used, as in the gas–solid hypersorption processes proposed for the separation of hydrogen, nitrogen, and oxygen isotopes[129–131]. High values of r and α can be expected with these complexes. Furthermore, solid complexes of gaseous sulphur compounds can be used in separation processes as liquid solutions in solvents inert towards both the compounds and their complexes. However, the use of a solvent may have an unfavourable effect on the economics of the process because of the energy cost of heating, cooling, and transporting the solvent, and also because of the decreased throughput of the column. Nevertheless the use of a solvent could improve the rate of isotope exchange in the columns.

Table 9. Sulphur isotopic equilibrium data for ion exchange systems at 298 K.

R	α	Method	References
	$H_2{}^{34}SO_3$–$RH^{32}SO_3$		
Wofatit L	1.0064	3,13	[101]
SBW	1.0064	3	[101]
SBR	1.0064	3	[101]
	$^{34}SO_2$–$RH^{32}SO_3$		
Wofatit L	1.010	13	[101]
SBW	1.010	13	[101]
SBR	1.010	13	[101]
	$NH_4H^{34}SO_3$–$RH^{32}SO_3$		
Dowex 2-x 8.5-100 mesh	1.010	13	[17]

Symbols: methods of determining α: *13*) chromatographic; other symbols as in Table 1.

Table 10. Separation of sulphur isotopes by ion exchange* (T = 293 K, P = 0.1 MPa).[101]

c, mol litre^{-1}	v, m s^{-1}	HETP, cm	K_τ
0.5	15.5	6.0	1.13
1.0	15.5	10.0	1.10
1.0	15.5	7.0	1.15
0.4	1.332	1.3	1.42
0.4	4.0	2.1	1.36
0.4	8.5	4.5	1.21
0.4	14.33	4.6	1.20
1.0	0.833	1.1	1.59
1.0	8.5	1.9	1.44
0.125	8.33	5.3	1.19
0.6	4.17	2.6	1.11
0.4	4.0	2.8	1.35
0.4	4.34	3.8	1.38
0.4	4.17	5.6	1.24
0.4	4.17	11.7	1.32
1.0	5.0	2.8	1.38
0.4	4.17	4.6	1.64
—	—	0.2	23% ^{34}S **

Symbols: c is the concentration of the solution, v is the velocity of the liquid phase, K_τ is the degree of separation achieved.

*Separation carried out in the $RH^{32}SO_3$–$NH_4H^{34}SO_3$ system, where R is Dowex 2-X (8.5)-100 mesh, H_K = 12 m, D_K = 25 mm.

**Data from Ref.117; the maximum concentration of ^{34}S reached is stated. The same system was used, with H_K = 0.85 m and D_K = 47 mm.

IV. ION EXCHANGE PROCESSES

Extensive work carried out during the 1960's in Sweden[17], East Germany[83,101,132,133], and France[60] demonstrated the possibility in principle of using ion exchange processes in the separation of sulphur isotopes (see Tables 9 and 10), and resulted in the production of gramme quantities of the isotopes[17]. Separation in columns was achieved by using Spedding's method[134] of organising a counter-current process on ion exchangers without motion of the solid phase. However, the low HETP values thus obtained are insufficient compensation for the disadvantages of ion-exchange separation, including the high consumption of reagents for flow reversal and regeneration of the resin (thus, the production of 1 mole of ^{33}S in the NH_4HSO_3–Dowex resin system requires[17] the expenditure of 4×10^4 mole of HCl and $\sim 5 \times 10^4$ mole of NH_4HSO_4), and also the complexity of the apparatus, due to the difficulty of arranging a continuous counter-current process in this type of system[135–137]. Similar problems are encountered in processes using liquid anion exchangers. Isotopic mixtures of ^{32}S and ^{34}S have been separated in an experimental column at 298 K by using the following working systems: CCl_4/tri-n-octylamine $H \cdot HSO_3/H_2SO_3$, C_6H_6/tri-n-octylamine $H \cdot HSO_3/H_2SO_3$, n-octanol/tri-n-octylamine $H \cdot HSO_3/H_2SO_3$, toluene/tri-n-octylamine $H \cdot HSO_3/H_2SO_3$, cyclohexane/tri-n-octylamine $H \cdot HSO_3/H_2SO_3$, tetralin/tri-n-octylamine $H \cdot HSO_3/H_2SO_3$, nitrobenzene/tri-n-octylamine $H \cdot HSO_3/H_2SO_3$, pentane/tri-n-octylamine $H \cdot HSO_3/H_2SO_3$, and hexane/tri-n-octylamine $H \cdot HSO_3/H_2SO_3$. Separation was observed in every case, but the α and HETP values were not determined[83]. In spite of the almost two-fold saving in materials achieved by combining the ion-exchange separation of sulphur isotopes with the separation of carbon isotopes[83, 132,133], the disadvantages of the method still make it unacceptable in practice. A possible combined scheme, relying on the use of acids of different strength for the separation, is shown in Fig.5.

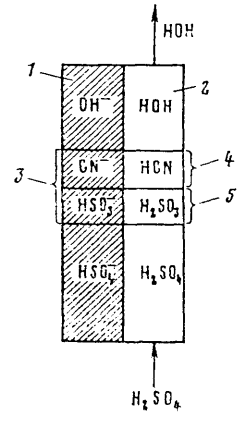


Figure 5. Combined ion-exchange separation process for sulphur and carbon isotopes: *1*) solid phase, *2*) liquid phase, *3*) separation part of the column, *4*) carbon isotope separation zone, *5*) sulphur isotope separation zone.

A far more promising method is based on continuous counter-current adsorption processes, analogous to those previously used to separate nitrogen or oxygen isotopes[130,138],

since these offer α values usually much greater than those obtained in ion exchange or in distillation as well as the possibility of thermal flow reversal.

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Thus we may conclude that studies of equilibrium two-phase counter-current processes for the separation of sulphur isotopes have not yet led to the development of a really efficient process, combining low cost with other desirable attributes, in spite of the pressing need for such a process in both scientific and industrial practice. The most promising directions for future development work include: a search for new and more effective working systems, optimisation of the technological parameters of the separation processes, the development of rational technological schemes for combining the separation of sulphur isotopes with other chemical or isotopic production processes, and a search for means of using cheaper energy sources for phase reversal, and for means of utilising the waste products.

The main aim of the work should be to establish relationships between the physicochemical properties of the working systems and their separation coefficients, rate of isotope exchange, and other characteristics of the separation process.

From the industrial point of view it would be desirable to investigate new systems compatible with thermal flow reversal. The most promising of these are the various adsorption processes, and also the chemical isotope exchange between SO_2 and its thermally unstable complexes in the solid form, or dissolved in an inert solvent.

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