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THERMODIFFUSION OF ^{32}S AND ^{34}S IN SULFUR HEXAFLUORIDE

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The article describes the experimental investigation of the separation of sulfur isotopes in a thermodiffusion column.

To obtain sulfur hexafluoride with an isotope composition different from the natural one, it becomes necessary to investigate whether thermodiffusion could be used for this purpose.

We know of only one work that presents the results concerning sulfur isotope enrichment in the gaseous phase [1]. The working medium used was sulfur dioxide. The separation efficiency was low because of the small reduced thermodiffusion constant which amounted to no more than 0.0143.

The glass column used by the authors of [1] was 3.5 m high, with 11.6-mm diameter of the working cylinder; it was heated by an electric heater of platinum wire with $d_2 = 0.4$ mm. The wire was centered by washers welded to it every 30 cm. It was heated to 100°K. The optimum pressure was 34.6 kPa at which the maximum degree of separation within 220 h was $q = 1.065$ between the isotopes ^{32}S and ^{34}S.

This result did not provide grounds for assuming that the use of sulfur hexafluoride would make it possible to attain a noticeable shift in the isotope composition. On the other hand, a calculation by the formulas of the kinetic-molecular theory on the assumption of the Lennard-Jones interaction potential being applicable to sulfur hexafluoride yielded the value $\alpha_0 = +0.254$ for $T^* = 2$ and $+0.431$ for $T^* = 3$, where the reduced temperature is $T^* = kT/\varepsilon$, and $\varepsilon/k = 200.9°K$ according to data taken from [2]. On the basis of these calculations we undertook the experimental verification of the possibility of separating the sulfur isotopes in SF_6 in a thermodiffusion column (Fig. 1).

The column consisted of two concentric cylinders, one of which was the tubular electric heater (TEH), and the second a brass tube. The working height of the column was 2.4 m, the working gap 2.25 mm; its accuracy was ensured by centering bosses of which four in each section were welded 300 mm apart to the TEH. The brass tube was cooled by circulating water. The ends of the TEH were sealed by stuffing boxes which ensured air-tight sealing in case of thermal expansion. The column was firmly mounted on a bracket, and its vertical position in two mutually perpendicular directions was checked by plumbs. The column was provided with nozzles for sampling and evacuation.

In choosing the temperature regime of column operation, we took into account the chemical properties of sulfur hexafluoride which becomes chemically active at elevated temperatures (>500°C) [3]. The experiments were therefore carried out at a temperature of the hot surface of 427°K and a mean temperature $\overline{T} = 357°K$. The temperature was measured on the basis of the change of pressure in the thermodiffusion column. If, with the heater switched off and water with $T_1 = 287°K$ circulating through the cooler, the pressure P_0 established itself, and after

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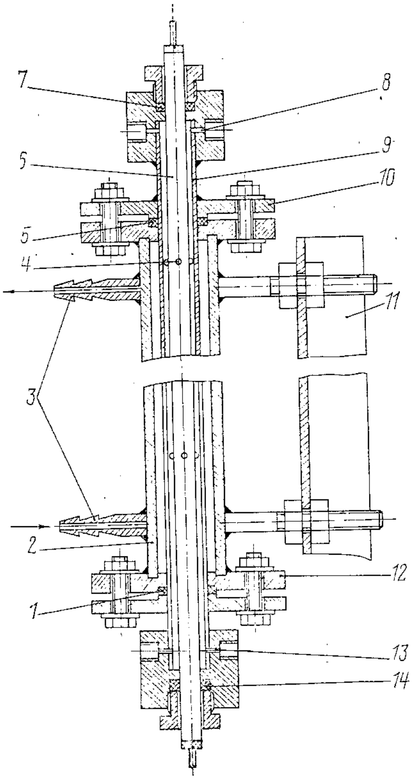

Fig. 1. Diagram of the gas thermodiffusion column: 1, 5) gaskets; 2) cooler jacket; 3) water inlet and outlet; 4) centering bosses; 6) tubular electric heater; 7, 14) stuffing boxes; 8, 13) outlet of samples for analysis; 9) brass cylinder; 10, 12) flanges; 11) bracket.

the heater was switched on the pressure became equal to P_T, then the mean temperature in the column was

$$\overline{T} = T_1 \frac{P_T}{P_0},$$

and hence

$$T_2 = 2\overline{T} - T_1; \quad \Delta T = T_2 - T_1 = 2(\overline{T} - T_1). \tag{1}$$

This method of measuring also takes into account the radiant component if sulfur hexafluoride is considered a diathermanous gas, which is perfectly admissible for the small thickness of the gaseous interlayer in the column.

The pressure was measured with a pointer-type vacuum gauge class 0.6 with a scale division of 0.005 kgf/cm^2. The temperature was kept constant by a stabilized voltage source. Samples were taken into evacuated glass ampuls, and the isotopic composition was determined on a mass spectrometer MI-1305 according to the most intensive peaks of SF_5^+ (masses 127 and 129).

The time of the transient process, during which 98% of the equilibrium value of the concentration difference between the ends of the column are attained, was calculated by the ratio

$$t_p \approx \frac{4P\delta L^2 B}{\pi^2 RT(K_c + K_d + K_p)}, \tag{2}$$

where

$$K_c = \frac{g^2 \delta^7 (\Delta T)^2 BP^4}{9! \rho D \eta^2 R^4 \overline{T}^6} \equiv K_c' P^4; \quad K_d = \rho D \delta B, \tag{3}$$

TABLE 1. Data on the Separation of $^{32}SF_6$—$^{34}SF_6$ in a Thermodiffusion Column with $\bar{T}$ = 357.3°K, ΔT = 140.6°K

No. of expt.	$P \cdot 10^{-4}$, Pa	q by (5)	$\ln q$	$(P^2/\ln q) \cdot 10^{-9}$, Pa^2	$P^4 \cdot 10^{-18}$, Pa^4	$(K_d/H'L) \times 10^{-9}$, Pa^2
38	6,080	1,158	0,1467	25,2	13,66	6,21
40	4,952	1,187	0,1714	14,3	6,01	5,95
41	3,922	1,170	0,1570	9,8	2,37	6,50
42	2,942	1,116	0,1098	7,9	0,75	6,85
44	2,452	1,093	0,0889	6,8	0,36	6,30
45	6,864	1,137	0,1284	36,7	22,20	5,84
47	1,765	1,047	0,0459	6,8	0,097	6,66
49	8,630	1,093	0,0889	83,7	55,47	6,59

and since in the thermodiffusion column that was used $d_1/d_2 = 1.27$, there is no need to take its cylindrical shape into account, and formulas (3) were taken the same as for a flat column.

In (3) we may put $\rho D \approx 1.33\ \eta$, and the value $\eta = 1.785 \cdot 10^{-5}$ Pa•sec was taken from [4]. It can be seen from (2) and (3) that t_p depends on the pressure in the column, and it assumes its maximum for

$$P^4 = \frac{K_d}{3(K_c' + K_p')}, \tag{4}$$

where $K'_p = K_p/P^4$.

On the assumption that $K'_p = 0$, calculation by (4) yielded a value of $t_p \approx 30$ h, and therefore all experiments were carried out for approximately that time, considering that the existence of parasitic convection ($K_p > 0$) led to a shorter duration of the transient process.

In the experiments we used sulfur hexafluoride with a purity of 99.4% whose mass-spectrometric analysis showed that for mass 131 we have a peak of fragments of the admixture C_5F_{10}, and the isotope ratio is $^{32}SF_6/^{34}SF_6 = 22.4$, instead of 22.5, according to the data of [5]; this divergence lies within the deviations given by the instrument, and it was reasonable to assume that on the masses 127 and 129 no fragments of any admixtures are imposed.

The results of the experiments are presented in Table 1 and graphically illustrated in Fig. 2 from which it can be seen that the maximum degree of separation

$$q = \frac{(^{34}SF_6/^{32}SF_6)\ \text{upper}}{(^{34}SF_6/^{32}SF_6)_{\text{lower}}} \tag{5}$$

is attained with $P \approx 5 \cdot 10^4$ Pa.

It can be seen from Table 1 that the degree of separation determined by (5) is in all cases larger than unity, i.e., the heavy component of ($^{34}SF_6$) is concentrated at the top of the column; this indicates that the thermodiffusion constant has a negative sign. Nevertheless, this anomalous experimental fact is not the only exception from the rule that molecules with large mass tend to the cool region and concentrate at the bottom of the column. A change of sign of the thermodiffusion constant was discovered in the mixtures: H_2—D_2 [6], $^{14}NH_3$—$^{15}NH_3$ [7], $^{13}C^{16}O_2$—$^{12}C^{16}O_2$ [8], $^{16}O_2$—$^{18}O_2$ [9], $^{13}C^{16}O$—$^{12}C^{16}O$ [10]. A feature of all the past investigations is the transition into the liquid state where the formation of dimers is possible. The above-described experiments with sulfur hexafluoride were carried out at temperatures that differed considerably from the melting point (T_{mp} = 222.2°K [3]), and therefore the hypothesis of the formation of dimers in this case seems improbable.

Although the object of the present investigation was not to explain the possible causes of the mentioned anomaly in the behavior of sulfur hexafluoride, we nevertheless add some considerations concerning this question.

It is known that in the steady state [11]

$$\frac{P^2}{\ln q} = \frac{K_c' + K_p'}{H'L} P^4 + \frac{K_d}{H'L}, \tag{6}$$

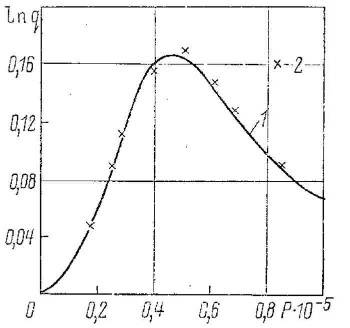

Fig. 2

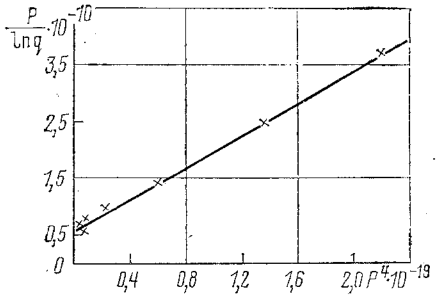

Fig. 3

Fig. 2. Dependence of the logarithm of the degree of separation by (5) on the pressure: 1) theory taking into account parasitic convection and the value of α in accordance with (11); 2) experiment. $P \cdot 10^{-5}$ Pa.

Fig. 3. Graphic illustration of the dependence (6). $P/\ln q \cdot 10^{-19}$ Pa^2; $P^4 \cdot 10^{-19}$ Pa^4.

where

$$H = \frac{\alpha g \delta^3 (\Delta T)^2 B P^2}{6! \eta R^2 \bar{T}^4} \equiv H' P^2. \tag{7}$$

It can be seen from (6) that between $P^2/\ln q$ and P^4 there must be a linear correlation; this is confirmed by Fig. 3. The slope of the straight line is

$$\frac{K_c' + K_p'}{H'L} = 1.39 \cdot 10^{-9}\ \mathrm{Pa}^{-2}. \tag{8}$$

By using the data of Table 1, we can find from formula (6) that

$$\frac{K_d}{H'L} = \frac{P^2}{\ln q} - 1.39 \cdot 10^{-9} P^4. \tag{9}$$

The values thus obtained are contained in the last column, and they yield

$$\frac{K_d}{H'L} = (6.362 \pm 0.445) \cdot 10^9\ \mathrm{Pa}^2. \tag{10}$$

If we determine by the second equation of (3) $K_d = 3.114 \cdot 10^{-9}$ kg·m/sec and calculate from (7) the value $H' = 1.938 \cdot 10^{-16}\ \alpha$ kg/Pa^2·sec, we find from (10) that

$$\alpha = -(1.058 \pm 0.07) \cdot 10^{-3}; \quad \alpha_0 = \alpha \frac{148 + 146}{148 - 146} = -(0.156 \pm 0.011), \tag{11}$$

where the minus sign in front of the brackets shows that the heavy component is concentrated in the upper part of the column.

The obtained results enable us to determine the effect of parasitic convection on the separation process, i.e., the magnitude of the ratio K'_p/K'_c which, according to (8), is determined by the expression

$$\frac{K_p'}{K_c'} = 1.39 \cdot 10^{-9} \frac{H'L}{K_c'} - 1. \tag{12}$$

If we calculate by the first ratio of (3) the value $K'_c = 5.397 \cdot 10^{-28}$ kgm/Pa^4·sec and take into account the values of H', α, and L presented above, we find that $K'_p/K'_c = 0.27 \pm 0.08$, i.e., the effect of parasitic convection was within acceptable limits.

Returning now to the question of the negative value of the reduced thermodiffusion constant, we have to point out that the kinetic-molecular theory admits the existence of points of inversion for α_0 for a certain kind of interaction potentials. This applies to the Lennard-Jones potential for reduced temperature $T^* = 0.4$ and $T^* = 0.95$. However, the calculated

TABLE 2. Values of the Collision Integrals with Potential (13) (m = 9, γ = 0), Reduced Second Virial Coefficients B*, and Thermodiffusion Constants α_0, and Also Data on the Parameters ε/k and σ

T^*	$\Omega_{(1,1)^*}$	$\Omega_{(1,2)^*}$	$\Omega_{(1,3)^*}$	$\Omega_{(2,2)^*}$	α_0 by (14)	B^*	ε/k, °K		$\sigma \cdot 10^{10}$ m		
							expt.	by (16)	by second virial coeff.	by (16)	by (1 6
0,7500	1,75663	1,40569	1,20950	1,96465	—0,167	—5,59066	472	426	3,03	4,16	4,9
0,8263	1,65897	1,33444	1,15658	1,85480	—0,145	—4,71146	429	426	3,21	4,29	4,9

values of α_0 for sulfur hexafluoride in this interval of values of T* are in absolute magnitude considerably smaller than those obtained in the experiment, and e.g., for T* = 0.65 α_0 = −0.124, yet ε/k = 549, which does not agree with any literature data whatsoever, and the value of σ does not describe the experimental data on viscosity. Great possibilities of explaining these results are provided by the potential

$$\varphi = \varepsilon\left\{\frac{1}{m-6}(6+2\gamma)\left(\frac{\sigma}{r}\right)^m \frac{1}{m-6}[m-\gamma(m-8)]\left(\frac{\sigma}{r}\right)^6 - \gamma\left(\frac{\sigma}{r}\right)^8\right\}, \tag{13}$$

suggested in [12], where ε is the depth of the potential well; σ is the collision diameter; m, γ are parameters. Klein et al. [12] present comprehensive tables of values of the second virial coefficient and of collision integrals for different T*, and with their use and by the Chapman–Cowling formula

$$\alpha_0 = \frac{15(6C^*-5)(2A^*+5)}{2A^*(16A^*-12B^*+55)}, \tag{14}$$

where

$$A^* = \frac{\Omega^{(2,2)^*}}{\Omega^{(1,1)^*}}; \quad B^* = \frac{5\Omega^{(1,2)^*}-4\Omega^{(1,3)^*}}{\Omega^{(1,1)^*}}; \quad C^* = \frac{\Omega^{(1,2)^*}}{\Omega^{(1,1)^*}},$$

the values of α_0 were calculated with different T* for m = 9 and γ = 0. According to (11), the experimental values of α_0 lie within the interval −0.145 to −0.167, and consequently we obtain by interpolation that T* = 0.8263-0.75, and hence, taking into account the mean experimental temperature $\overline{T}$ = 354.3°K, we find the value ε/k (Table 2). From the mentioned temperatures and by the tables of [12] the values of the reduced virial coefficients and the parameter σ were found; the latter can be calculated according to the data on viscosity:

$$\sigma = \left(\frac{2.6693 \cdot 10^{-26}\sqrt{M\overline{T}}}{\Omega^{(2,2)^*}\eta}\right)^{1/2}. \tag{15}$$

The parameters ε/k and σ are correlated with such characteristics of the substances as V_{cr} and T_{mp} by the empirical relationships [13]:

$$\frac{\varepsilon}{k} \approx 1.92T_{mp} \qquad \sigma \approx 8.392 \cdot 10^{-10}V_{cr}^{1/3}, \tag{16}$$

where V_{cr} = 0.1961 m³/kmole is the critical volume, and T_{mp} = 222.2°K is the melting point [14].

An examination of Table 2 permits the conclusion that the parameter ε/k considerably exceeds the one calculated according to the second virial coefficient for the Lennard-Jones model [2], but it is fairly close to the value ε/k = 414 obtained in [15] for the potential

$$\varphi = \frac{\varepsilon}{3}\left[\left(\frac{\sigma}{r}\right)^{28} - 4\left(\frac{\sigma}{r}\right)^7\right]. \tag{17}$$

As regards the parameter σ, its values determined according to the second virial coefficient and viscosity differ from each other by 33%, and from the data of [13] by 17%.

Thus, potential (13) yields satisfactory agreement with experiments in the part pertinent to the transport properties of sulfur hexafluoride, but it does not satisfy its equilibrium properties. Unfortunately, for the potential (17) the collision integrals have not been calculated, and it is therefore not possible to evaluate its applicability for describing the process of thermodiffusion. However, it can be seen from the above-explained that the anomalous behavior of sulfur hexafluoride isotopes in the thermodiffusion column may be explained on the basis of the choice of a certain potential model.

NOTATION

$T^* = kT/\varepsilon$, reduced temperature; $\overline{T} = (T_2 + T_1)/2$; T_2, T_1, temperatures of the hot and cold surfaces, respectively; $\Delta T = T_2 - T_1$; K_c, K_d, H, coefficients of the transport equation, see (3), (7); δ, size of the gap; P, pressure; L, height of the column; B, perimeter of the gap; R, gas constant; D, η, diffusion coefficient and coefficient of dynamic viscosity, respectively; ρ, density; q, degree of separation, see (5); α, thermodiffusion constant; $\alpha_0 = \alpha(M_1 + M_2)/(M_1 - M_2)$; M_1, M_2, masses of the isotopic molecules; K_p, parameter taking parasitic convection into account; φ, potential function.

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