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Abstract

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ON THE POSSIBILITY OF SEPARATING NITROGEN ISOTOPES BY THE METHOD OF CHEMICAL EXCHANGE USING COMPLEX FORMATION

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By the method of chemical exchange using complex formation, first applied by us to the separation of boron isotopes ([1],[2]), the separation of isotopes of a number of light elements has by now been carried out: hydrogen ([3]), carbon ([4]), sulfur ([5]), and chlorine ([6]).

In the present communication the separation of nitrogen isotopes by this method is described.

We assumed that if a volatile nitrogen compound, in particular ammonia or nitrogen oxides, is chosen as the gas phase, and their complex compounds as the liquid phase, then fractionation of nitrogen isotopes will occur between these phases.

This assumption was tested on the example of the interaction between ammonia and its complex compound with *n*-propyl alcohol:

$$^{15}NH_3 + {}^{14}NH_3 \cdot C_3H_7OH \rightleftharpoons {}^{14}NH_3 + {}^{15}NH_3 \cdot C_3H_7OH. \qquad (1)$$

In this case, for phase reversal it is convenient to use the thermal decomposition of the complex:

$$NH_3 \cdot C_3H_7OH \rightleftharpoons NH_3 + C_3H_7OH. \qquad (2)$$

To show the practical possibility of separating nitrogen isotopes by reaction (1), a countercurrent chemical-exchange column was constructed, analogous to those that had previously been used for the separation of boron isotopes ([1],[2],[7],[8]). The schematic diagram of the apparatus is presented in Fig. 1. Solid arrows indicate the motion of the complex $NH_3 \cdot C_3H_7OH$, dashed arrows the motion of NH_3, and a wavy line the motion of *n*-propyl alcohol C_3H_7OH. During operation of the apparatus, the complex from reservoir 1 was fed at a constant rate into column 2, 140 cm long and with an internal diamet–

Table 1

Sampling duration, h	Ratio $^{14}N_2/^{14}N^{15}N$ in the sample × 10	Ratio $^{14}N_2/^{14}N^{15}N$ in the standard × 10	Separation coefficient, S
Experiment 1	**Experiment 1**	**Experiment 1**	**Experiment 1**
2.5	1.290 ± 0.004	1.336 ± 0.003	1.036
8	1.190 ± 0.004	1.336 ± 0.003	1.123
21	1.123 ± 0.004	1.336 ± 0.003	1.190
33	1.074 ± 0.004	1.338 ± 0.005	1.246
33	1.078 ± 0.003	1.338 ± 0.005	1.241
45	1.061 ± 0.005	1.345 ± 0.005	1.268
71	1.017 ± 0.002	1.283 ± 0.004	1.262
71	1.052 ± 0.002	1.345 ± 0.005	1.278
Experiment 2	**Experiment 2**	**Experiment 2**	**Experiment 2**
2	1.248 ± 0.004	1.283 ± 0.004	1.028
7.5	1.206 ± 0.005	1.283 ± 0.004	1.064
14	1.111 ± 0.006	1.336 ± 0.005	1.203
38	1.116 ± 0.007	1.336 ± 0.005	1.197

of 16 mm, filled with a packing of Levin-type stainless steel (wire diameter 0.25 mm, packing element size 2 × 2 mm). The complex leaving the column decomposed in desorber 3, heated with oil from a TC-24 thermostat to a temperature 2–3° below the boiling point of the alcohol. The ammonia evolved was sent countercurrently into column 2 and then into absorber 5, cooled with water. Here, with the aid of Patrikeev pump 4, *n*-propyl alcohol was pumped from the desorber, and in the absorber the complex $NH_3 \cdot C_3H_7OH$ was again formed, which flowed into reservoir 1. In this way, the apparatus could operate automatically for a fairly long time.

To regulate the rate at which the complex was fed into the column, we developed an electromagnetic metering device that ensured high accuracy of regulation and high reliability (the circuit of the metering device will be published later).

As the apparatus operated, samples of ammonia were taken from the lower part of the column; the ammonia was then converted into nitrogen (over copper oxide). Isotopic analysis of the nitrogen was carried out on an IM-1305 mass spectrometer using ion peaks 28 and 29 ($^{14}N_2^+$ and $^{14}N^{15}N^+$).

The results of two parallel experiments,

Fig. 1. Schematic diagram of an apparatus for isotope separation by chemical exchange

Fig. 2. Dependence of the overall nitrogen isotope separation coefficient on time

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Figure 2: Fig. 2. Dependence of the overall nitrogen isotope separation coefficient on time

carried out at a column temperature of 20° and a complex feed rate of 1.8-2.0 ml/min (desorber temperature $\sim 95°$, absorber temperature 5°), are given in Table 1.

Because of a certain scatter of the experimental data, the results obtained were processed by the method of least squares using the empirical formula (9)

$$(S-1)=\frac{(S_p-1)t}{t_{1/2}+t},$$

where S is the separation coefficient of the column corresponding to time t, S_p is the value of S at $t=\infty$, and $t_{1/2}$ is the value of t at which $(S_p-1)/2$ is reached.

It was found that $S_p \approx 1.41$, and $t_{1/2} \approx 27$. The corresponding graph is shown in Fig. 2.

Thus, analysis of the operation of the apparatus described above shows that separation of nitrogen isotopes by reaction (1) does occur; moreover, the heavy nitrogen isotope ^{15}N is concentrated in the liquid phase, i.e., in the complex $NH_3 \cdot C_3H_7OH$. All these data are preliminary. A detailed study of the process of nitrogen isotope separation is continuing.

As substances with which ammonia forms complexes, one may

also be used: other aliphatic alcohols, aromatic mono-, di-, and trihydric alcohols, aromatic and aliphatic aldehydes and ketones, hydrocarbons, cyclohexanol, ethanolamines, triethylamine, hexamethyleneimine, aniline, quinoline, cyclohexanone, carbon tetrachloride, benzene, toluene, chloroform, nitrobenzene, bromobenzene, chlorobenzene, dichloroethane, cyclohexane, benzyl chloride, ethers, carbon disulfide, organic acids, etc.

Analogous complexes may be used and found for nitrogen oxides as well.

Work in this direction is continuing.

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