Isotope separation in a supersonic stream

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Nitrogen isotopes were separated by ultrasonic expansion of a hot mixture of the reagents through a nozzle. The results uncover a possibility of separating the isotopes of reagents with high freezing temperature.

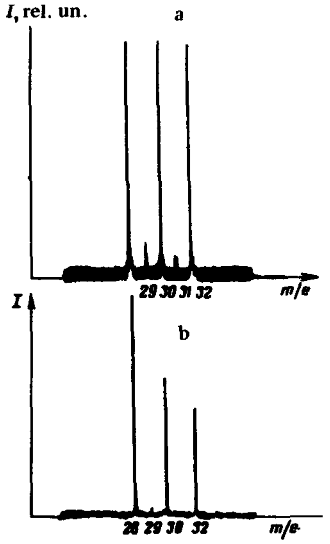
In chemical reactions that occur under thermodynamic disequilibrium conditions, isotope separation becomes possible. From the results obtained in [1,2] it follows that the separation efficiency increase rapidly with decreasing translational temperature of the gas. This may impose a significant limitation on the separation of the isotopes of many reagents with a high freezing temperature. This difficulty can be circumvented by rapid cooling of the gas, say in a supersonic stream. It is known that a gas escaping through a nozzle can be cooled to temperatures much below its freezing point. The deviation of the vibrational temperature of isotopic molecules from the translational temperature of the gas can be realized either by subsequently exciting, in one manner or another, the vibrational degrees of freedom of the molecules, or by using the difference between the velocities of the vibrational and translational relaxations of the molecules. In the latter case, two isotopic-separation schemes are realized.

1. *Lowering of the translational temperature of isotopic molecules.* A gas heated to a high temperature and consisting of isotopic molecules is passed through a nozzle. Its translational temperature is then greatly decreased, whereas the vibrational temperature changes insignificantly. If a cold binding agent is now added to the gas, then a chemical reaction will take place, in which the molecules containing the heavier isotope enter at a higher rate.[1,2]

2. *Lowering of the translational temperature in a reagent mixture under thermodynamic equilibrium.* The separation of the isotopes of element A occurs in a reaction of the type

$$A_i C + BD \rightleftarrows A_i B + CD \qquad (i = 1,2). \tag{1}$$

The equilibrium concentrations of the reagent molecules and of the reaction products are determined from the relation



Mass spectrum of the reaction products: the scale of spectrogram b is one-tenth the scale of spectrogram a. The mass peaks 28, 30, and 23 of spectrogram a are shown under conditions when the apparatur is saturated.

$$k_{1i}[A_iC][BD] = k_{2i}[A_iB][CD], \tag{2}$$

where k_{1i} and k_{2i} are the rate constants of the direct and inverse reactions.

We shall assume that the vibrational temperature of the reagent molecules varies slowly enough with time. In this case, a quasistationary equilibrium state can be reached when the quantities that enter in (2) depend only on the translational and vibrational temperatures at the given instant of time.

We assume futher that the direct reaction is due to the vibrational temperature of the molecules AC. If the activation energy ϵ_2^* of the inverse reaction is much lower than the activation energy ϵ_1^* of the direct reaction, or if the rate of the $V-T$ relaxation for the molecules AB and CD is much larger than for the molecules AC, then when the vibrational temperature of the molecules AC deviates from the translational temperature of the gas, the constants k_{1i} and k_{2i} satisfy the relations[1]

$$k_{11}/k_{12} = \exp\left(\frac{\Delta\nu}{\nu}\ \frac{\epsilon_1^*}{T}\right), \quad k_{21} \approx k_{22}, \tag{3}$$

where $\Delta\nu/\nu$ is the relative shift of the vibrational frequency of the molecules A_i, C, and T is the translational temperature of the gas in energy units (with the constant k_{1i} larger for the molecules A_iC containing the heavier isotope).

Let the mixture of molecules AC and BD be heated to a high temperature T_0, and let the reaction (1) take place. The concentration of the reaction products is determined by relation (2), where the reaction rate constants k_{1i} and k_{2i} are calculated at the temperature T_0. If we now cool the mixture as it escapes from the nozzle to a temperature $T \ll T_0$ then, owing to the large difference between the rates of the vibrational and translational relaxation in the system there can be established a quasistationary state, in which a deviation of the vibrational temperature of the molecules AC from the translational temperature is realized. It follows from (2) and (3) that under these conditions the reaction products (the molecules AB) will be enriched with the heavy isotope of element A.

For an experimental verification of the possibility of separating the isotopes by cooling the gas of reagents in a supersonic stream, we used the nitrogen-oxidation reaction. In an explosion chamber, where the mixture $H_2:O_2:N_2$ (N_2O) (0.1: 0.15: 0.4 atm) was exploded, the molecules O_2 and N_2 entered in the reaction $N_2 + O_2 = 2NO$ at a temperature 2500–3000 °K. This gas mixture was then expanded through a nozzle in a low-pressure chamber, and its translational temperature was then lowered to 300–350 °K. The reaction products (the NO molecules) were frozen out in a nitrogen trap. The NO was analyzed with an SN-8 mass spectrometer using a chromatograph. The obtained mass spectrum is shown in the figure. The concentration of the ^{14}NO and ^{15}NO molecules corresponds to the peaks I_{30} and I_{31}, respectively. The ratio of these peaks, $I_{31}/I_{30} \sim 1/100$, indicates that the NO molecules have become enriched with ^{15}N by more than a factor of two compared with its natural content ($\sim 1/250$).

[1] É. M. Belenov, E. P. Markin, A. N. Oraevskiĭ, and V. I. Romanenko, ZhETF Pis. Red. 18, 196 (1973) [JETP Lett. 18, 116 (1973)].

[2] N. G. Basov, É. M. Belenov, L. K. Gavrilina, V. A. Isakov, E. P. Markin, A. N. Oraevskiĭ, V. L. Romanenko, and N. B. Ferapontov, ZhETF Pis. Red. 19, 336 (1974) [JETP Lett. 19, 190 (1974)].