

Isotope separation in chemical reactions occurring under thermodynamic nonequilibrium conditions

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An isotope separation method is proposed, based on the difference between the rates of chemical reactions of the isotopes under thermodynamic nonequilibrium conditions. A 20-fold enrichment with N^{15} was obtained in the products of nitrogen oxidation in an electric discharge.

1. It is known^[1] that, with the exception of the case of the hydrogen isotopes, the isotope separation coefficient

$$\beta = r'/r - 1, \quad (1)$$

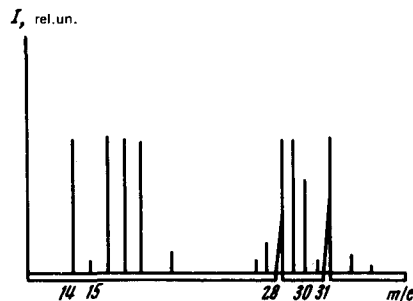
where r' and r are the isotopic ratios before and after separation, amounts to $\sim 10^{-2} - 10^{-3}$ in the case of a one-step operation. We propose here an isotope separation method that permits an appreciable increase of β , and report the first experiments on the separation of nitrogen isotopes by this method.

The idea of the proposed method is to use chemical reactions that occur under thermodynamic nonequilibrium conditions, with a large difference between the vibrational and translational temperatures. Owing to the peculiarities of the vibrational exchange mechanism, equilibrium between the isotopic modifications of the molecules sets in at different vibrational temperatures. This difference is larger the lower the translational temperature T of the gas.^[2] Physically this effect is due to the fact that the ratio of the probability of transferring a vibrational quantum to the heavier molecule to that of the inverse process increases with decreasing temperature. The difference between the vibrational

temperatures brings about in turn a difference between the reaction rates of the isotopic modifications of the molecules. It can be shown that the rate constants γ_i of the reactions are connected by the relation

$$\frac{\gamma_1}{\gamma_2} = \exp \left[h\nu_1 m_1 \left(\frac{1}{T} - \frac{1}{T_1} \right) - h\nu_2 m_2 \left(\frac{1}{T} - \frac{1}{T_2} \right) - \frac{E_{m_1}^{(1)} - E_{m_2}^{(2)}}{T} \right], \quad (2)$$

where $h\nu_1$ and $h\nu_2$ are the energies of the first vibrational levels of the molecules, T_1 and T_2 are their temperatures, m_1 and m_2 are the level numbers starting



Mass spectrum of the mixture following the reaction.

with which the molecules can enter in the reaction, and $E_{m1}^{(1)}$ and $E_{m2}^{(2)}$ are the energies of these levels.

Expression (2), which was obtained for the Morse oscillator model, coincides in fact with the analogous result of the harmonic model of the molecule^[3]

$$\frac{\gamma_1}{\gamma_2} = \exp\left(\frac{\mathcal{E}}{T} \frac{\nu_2 - \nu_1}{\nu_1}\right), \quad (3)$$

where \mathcal{E} is the reaction activation energy.

Putting $T \approx 300^\circ\text{K}$, $(\nu_2 - \nu_1)/\nu_1 \sim 1/40$ (isotopes with mass number ~ 20), and $\mathcal{E} \approx 2$ eV, we obtain $\gamma_1/\gamma_2 \sim 10$, with the heavier molecules reacting more speedily.

2. The indicated method was used to separate the nitrogen isotopes in the reaction $\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$ occurring in an electric discharge. The reaction requires an appreciable activation energy (not less than $\mathcal{E} \approx 3.3$ eV^[4]), and at a low translational gas temperature the reaction products should become considerably richer in the isotope N^{15} . The experiment was performed in accordance with the following scheme: Air at a pressure ~ 20 Torr was contained in a discharge tube cooled with liquid nitrogen. The nitrogen oxidation reaction was

stimulated by a pulsed electric discharge with pulse duration 5×10^{-6} sec and an off-duty cycle ~ 15 sec. The gas was analyzed with an SN-8 mass spectrometer.

The figure shows the mass spectrum of the mixture after the reaction. The concentrations of the N^{14}O and N^{15}O molecules are proportional to the intensities of the mass-spectrum lines I_{30} and I_{31} , respectively. The intensity ratio obtained after subtracting the background, $I_{31}/I_{30} \approx 1/12$, is much larger than the isotopic ratio $[\text{N}^{15}]/[\text{N}^{14}] \approx 1/250$ in air, thus indicating an appreciable enrichment ($\beta \approx 20$) of the reaction products with the isotope N^{15} .

¹S. F. Peterson and R. G. Wymer, *Chemistry in Nuclear Technology*, Addison-Wesley, 1963.

²C. E. Treanor, I. W. Rich, R. C. Rehm, *J. Chem. Phys.* **48**, 1798 (1963).

³E. M. Belenov, E. P. Markin, A. N. Oraevskii, and V. I. Romanenko, *ZhETF Pis. Red.* **18**, 196 (1973) [*JETP Lett.* **18**, 116 (1973)].

⁴Ya. B. Zel'dovich and Yu. P. Raizer, *Fizika udarnykh voln i vysokotemperaturnykh gidrodinamicheskikh yavlenii* (Physics of Shock Waves and High-Temperature Hydrodynamic Phenomena), Nauka, 1966 (Academic, 1966).