Kinetics of nonequilibrium chemical reactions and separation of isotopes

N. G. Basov, É. M. Belenov, V. A. Isakov, E. P. Markin, A. N. Oraevskiĭ, V. I. Romanenko, and N. B. Ferapontov

P. N. Lebedev Physical Institute, USSR Academy of Sciences

A method is considered for the separation of isotopes in chemical reactions that take place under thermodynamically nonequilibrium conditions. Enrichment of the nitrogen oxidation products with N^{15} in a pulsed electric discharge is obtained at various temperatures of the gas mixture. Separation coefficients of ~3, 20, and 130, are attained by cooling the reactor to room temperature, to the temperature of dry ice, and to the temperature of liquid nitrogen, respectively.

PACS numbers: 82.20.M, 82.20.T

1. It is known that the difference in the reaction rate constants of isotopic molecules

$$\gamma_i = A_i \exp(-\varepsilon^*/T), \qquad (1)$$

where T is the gas temperature, is determined by the difference in the factors A_i before the exponential. Since the activation energies ε^* of the reactions of isotopic molecules are practically identical.[1] Because of the insignificant difference in the coefficients A_i, isotopic effects in chemical reactions are small and the coefficient of isotope separation in a one-step operation amounts to $\sim 10^{-2} - 10^{-1}$.[1] It turns out, however,[2,3] that in the course of a reaction under thermodynamically nonequilibrium conditions, the difference in the rate constants of the reaction for isotopic modifications of the molecules can be very substantial. Physically, the effect is connected with the fact that under such conditions, different temperatures $T^{(i)}$ correspond to the vibrational degrees of freedom of the isotopic molecules; the difference between these temperatures is the greater the lower the translational temperature of the gas.

We shall assume below that these conditions are satisfied, i.e., that a significant excess of the vibrational temperatures $T^{(i)}$ of the degrees of freedom of the gas that are active in the reaction over its translational temperature T is created in some way (for example, as a consequence of the action of resonant laser radiation on the vibrational degrees of freedom of the molecules or the excitation of vibrations of the molecules of a cooled gas in a discharge). We shall also assume—and this is natural for sufficiently high activation energies—that, as a consequence of the quasi-resonant exchange of the vibrational energies, equilibrium is established practically instantaneously (in the time scale of the chemical reaction) between the vibrational degrees of freedom of the isotopic molecules.

2. In contemporary representations,[4] the vibrational energy of the molecules plays a decisive role in chemical processes; keeping this in mind, we can generalize Eq. (1) for $T^{(i)} \gg T$ in the following way:

$$\gamma_i = A_i \exp(-\varepsilon^*/T^{(i)}). \qquad (2)$$

According to this formula, even with a small difference between $T^{(i)}$ and $T^{(j)}$ and sufficiently large activation energies ε^*, the rate constants of the reactions can differ considerably: the ratio γ_i/γ_j is now determined by the exponential factors. The temperatures $T^{(i)}$, as has already been mentioned, are not independent: the exchange of vibrational quanta between the molecules establishes a definite coupling between the $T^{(i)}$.

Thus, since the selectivity associated with pumping of a certain type of isotope is practically entirely lost because of the interaction of the vibrations of the isotopic molecules, a broadband pumping source is also suitable for stimulation of the separation reaction, exciting the entire coupled group of vibrations. As was indicated above, for example, isotopes can be separated by excitation of the molecules by electron impact.[3]

We now consider the kinetics of the processes in a gas of isotopic molecules in more detail. The establishment of equilibrium between the vibrationally excited molecules takes place through a series of stages. The first and most rapid of these is the stage of vibrational-vibrational exchange between molecules of the same isotopic composition; next is stage of cross relaxation, which establishes equilibrium between the vibrations of molecules of different types, and, finally, the vibrational-translational (V-T) exchange, leading to thermodynamic equilibrium between all the degrees of freedom of the gas. In the processes of V-T exchange and cross relaxation, energies equal respectively to the energy of the quantum and the energy difference $h(\nu^{(i)} - \nu^{(j)})$ of the vibrational quanta are transferred from the vibrational reservoir to the translational degree of freedom in a single act. As a consequence, under the conditions

$$h(\nu^{(i)} - \nu^{(j)}) \ll h\nu^{(i)}, \quad h\nu^{(i)} \gg T,$$

the time τ_{VT} of the V-T relaxation significantly exceeds the cross relaxation time: $\tau_{VT} \gg \tau_{cross}$.

If the molecules take part in the reaction over the time $\tau_{cross} < t \ll \tau_{VT}$, then there exists a gap between the vibrational temperatures $T^{(i)}$ of their isotopic modifications.

3. To find the difference in the temperatures $T^{(i)}$, we first consider a model in which the vibrations of the molecules can be assumed to be harmonic. We denote by $n_v^{(i)}$ the population of the v-th vibrational level of the isotopic molecule of the ith type. Then

$$n_v^{(i)} = n_0^{(i)} \exp(-vh\nu^{(i)}/T^{(i)}), \qquad (3)$$

since the Boltzmann distribution of the molecules over the vibrational levels is established after passage of the most rapid time τ_{VV} of vibrational-vibrational exchange.

Equilibrium is also established within the time of cross relaxation between the isotopic modifications of the molecules: in particular, between the populations of the first excited levels $n_1^{(1)}$ and $n_1^{(2)}$ there should exist the relation

$$n_i^{(1)} = n_i^{(2)} \exp(-\Delta/T), \qquad (4)$$

where T is the translational temperature of the gas, $\Delta = h(\nu^{(1)} - \nu^{(2)})$ is the difference in the energies of these levels. In the derivation of (4), it has been assumed for simplicity that $n_0^{(1)} = n_0^{(2)}$; however, it is not difficult to see that this assumption has no effect on the form of the relation between $T^{(1)}$ and $T^{(2)}$ that follows from (3) and (4):

$$\nu^{(1)}/T^{(1)} - \nu^{(2)}/T^{(2)} = (\nu^{(1)} - \nu^{(2)})/T. \qquad (5)$$

Then, expressing $T^{(2)}$ in terms of $T^{(1)}$ and substituting in (2), we obtain for the ratio of the reaction rate constants

$$\frac{\gamma_1}{\gamma_2} = \exp\left[-\left(\frac{1}{T} - \frac{1}{T^{(1)}}\right) \frac{\nu^{(1)} - \nu^{(2)}}{\nu^{(1)}} \varepsilon^* \right]. \qquad (6)$$

We have neglected here the difference in the factors A_i in front of the exponential in the expression for the reaction rate constants of the isotopic molecules.

It follows from (6) that a large difference can be expected between γ_1 and γ_2 under thermodynamically nonequilibrium conditions with $T^{(1)} \gg T$. Thus, at $T = 100°K$, $\varepsilon^* = 2.5$ eV, $(\nu^{(1)} - \nu^{(2)})/\nu^{(1)} = 1/40$ (isotopes with mass number ~ 20), we get $\gamma_1/\gamma_2 = 1500$. Here the molecules that contain the heavier isotope, which has the smaller vibrational quantum energy and, consequently, the higher vibrational temperature react more rapidly.

4. We have considered above a harmonic model of the vibrational branch of the molecule. It can be shown that account of anharmonism of the vibrations has practically no effect on the expression for γ_1/γ_2. Actually, upon neglect of vibrational-translational relaxation, the distribution of the molecules over the vibrational levels is described by the Treanor distribution:[5]

$$n_v^{(i)} = n_0^{(i)} \exp[-(\sigma v + E_v^{(i)}/T)], \qquad (7)$$

where the constant σ is connected with the vibrational temperature $T_1^{(i)}$ of the first vibrational level of the molecules i in the following fashion:

$$\sigma = -(1/T - 1/T_1^{(i)}) E_1^{(i)}. \qquad (8)$$

We assume that the molecules of type i enter into the reaction beginning with the $m^{(i)}$-th vibrational level and obtain

$$\frac{\gamma_1}{\gamma_2} = \exp\left[m^{(1)} E_1^{(1)} \left(\frac{1}{T} - \frac{1}{T_1^{(1)}}\right) - m^{(2)} E_1^{(2)} \left(\frac{1}{T} - \frac{1}{T_1^{(2)}}\right) - \frac{1}{T}(E_{m^{(1)}}^{(1)} - E_{m^{(2)}}^{(2)}) \right]. \qquad (9)$$

In the derivation of (9), it was assumed that the reaction rate constant is proportional to the number of active molecules (i.e., molecules that have an energy exceeding the activation energy). The resultant expression gives practically the same result for γ_1/γ_2 as the relation (6), which was found in the harmonic approximation. We note that the use of the distribution function from Gordiets et al.[6] for calculation of γ_1/γ_2 gives results that are somewhat different (quantitatively) from (9).

5. In the present study, the isotopes ^{14}N and ^{15}N were separated in the oxidation reaction of nitrogen in a pulsed electric discharge. The mechanism of this reaction, according to Zel'dovich and Raizer,[4] is

$$O + N_2 = NO + N - 75.5 \text{ kcal/mole}$$
$$N + O_2 = NO + O + 32.5 \text{ kcal/mole}$$
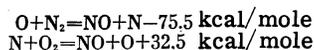
The rate of the entire reaction is determined principally by the first, endothermic reaction, which requires an activation energy $\epsilon^* \approx 3.3$ eV. The second reaction takes place practically without activation (so that the reaction $N_2 + O_2 = 2NO$ cannot be used for separation of the oxygen isotopes). Vibrations of the nitrogen molecules are effectively excited by electron impact; therefore, in accordance with the theory developed above, nitrogen molecules containing the heavy isotope should take part in the reaction preferentially in an electric discharge with the cooling of the gas mixture.

Thus, the products of the reaction (NO molecules) should be enriched in the isotope ^{15}N. The condition $\tau_{cross} < t \ll \tau_{VT}$ should obviously be satisfied here, where t is the time of participation of the excited molecules in the reaction. The condition $\tau_{cross} < t$ is satisfied practically always because of the smallness of the isotopic frequency shift in nitrogen ($\Delta\nu/\nu \sim 1/60$). The condition $t \ll \tau_{VT}$ should be satisfied for $\tau_p \ll \tau_{VT}$, where τ_p is the duration of the discharge pulse. Actually, in view of the large activation energy, the reaction rate of oxidation of the nitrogen should decrease rapidly with decreasing energy of the reacting molecules, or, in this specific case, with decreasing vibrational temperature of the nitrogen molecules. Thus, the V-T reaction not only lowers the separation coefficient of the isotopes as a result of the increase in the translational temperature of the gas, but also quenches the reaction itself noticeably. The relatively high yield of reaction products in our experiments ($\sim 10^{-3} - 10^{-4}$ for a single discharge pulse) indicates that a significant fraction of the nitrogen molecules entered into the reaction before there was appreciable vibrational deexcitation.

The experiment was carried out on the apparatus diagrammed in Fig. 1. We used air as the initial reagent (the natural ratio of nitrogen isotopes is ^{14}N/^{15}N ~ 250). Air enters the nitrogen trap 1 through a flow regulator which allows regulation of the pressure in the reaction chamber. The low-boiling components of the gas (water, CO_2 and so on) are frozen out in the trap. Then the air passes to the reaction chamber 2. The reactor was immersed in coolant. The experiments were performed at the temperatures of liquid nitrogen and dry ice and room temperature.

The reactor consisted of a U-shaped quartz tube of diameter 20 mm and length 600 mm with tungsten electrodes immersed in a dewar filled with the coolant. A high voltage was applied to the electrodes from a power supply in pulsed operation. For the supply pulses, we used the discharge of a 0.04 μF capacitor across a pulse transformer with a 60 V output. The discharge energy amounted to 4 J. The pulse duration reached several microseconds; the repetition rate was 0.5–0.3 Hz. The gas pressure in the discharge tube was maintained at ~ 5 Torr. The trap 3 was placed at the output of the reactor and the reaction products were frozen there.
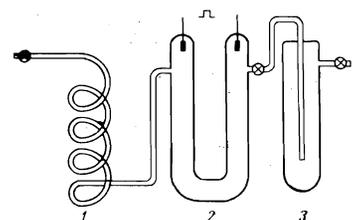

FIG. 1. Diagram of experimental setup: 1, 3—nitrogen traps, 2—reactor.

N. G. Basov et al.

Analysis of the composition of the mixture after the reaction was carried out in an SN-8 mass spectrometer.

A number of processes going on in the discharge increase the translational temperature T of the gas. The single process opposing the increase in T is heat conduction. Therefore, with the aim of stabilization of the translational gas temperature, pumping was provided; it guaranteed a change in the gas mixture located in the reactor within the time between discharge pulses. This allowed us to assign the gas the temperature of the walls of the reactor before the beginning of the pulse.

Mass spectra of the mixture after the reaction are shown in Fig. 2. The peaks I_{28}, I_{29}, I_{30}, I_{31} and I_{32} pertain to the molecules $^{14}N^{14}N$, $^{14}N^{15}N$, $^{14}N^{16}O$, $^{15}N^{16}O$ and $^{16}O^{16}O$, respectively. We obtained the following values of the separation coefficient β of the nitrogen isotopes from the ratio of the peaks I_{31} and I_{30} (after subtraction of the background): 130 in the case of cooling of the reactor to liquid nitrogen temperatures, 20 at the temperature of dry ice, and 3 at room temperature.

We note that the identification of the peak I_{31} is not generally unique. Not only may $^{15}NO^+$ ions be responsible for its appearance, but also $H^{14}NO^+$ ions formed as a result of ion-molecular reactions during the mass-spectrometric measurements. In our case, such reactions could be

$$OH^+ + NO = HNO^+ + O, \quad 2NO + O_2 = 2NO_2,$$
$$OH^+ + NO_2 = HNO^+ + O_2$$
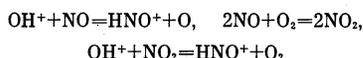
(the OH^+ ions are formed from molecules of water present both in the gaseous mixture and in the background of the mass spectrometer). However, if we assume that the intensity of the peak I_{31} is determined by the HNO^+ ions, the ratio I_{31}/I_{30} will depend significantly on the measurement conditions, but not on the conditions of the course of the chemical reaction in the reactor, or, in particular, on the temperature of the walls. The conditions of the measurements did not vary. On the other hand, if the intensity of the peak I_{31} is determined by the $^{15}NO^+$ ions, then this ratio should depend strongly on the temperature of the gas mixture (see (6)), as it clearly did in the results obtained.

Quantitative comparison of the experimental results with the estimates obtained from Eq. (6) gives values for the activation energy ϵ^* of the reaction $N_2 + O_2 \rightarrow 2NO$ that lie in the range from 2 to 3 eV. This scatter of the values can evidently be connected with the fact that, by virtue of the exponential dependence of β on T, comparatively small changes in T appear to be significant in the degree of separation of the isotopes. Thus, since the temperature T changes during the course of the reaction (the change in the temperature is produced by the processes of vibrational-translational relaxation, the thermal effect of the reaction itself, partial heating of the gas mixture in the discharge), the reaction will be characterized by some average separation coefficient $\bar{\beta}$, which can differ appreciably from the value of β at the beginning of the reaction.
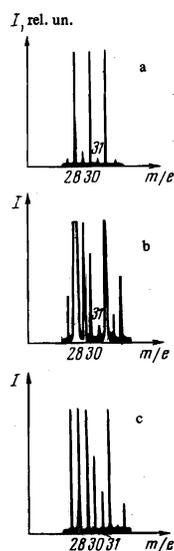
FIG. 2. Mass spectra of mixture after the reaction with cooling of the reactor to the temperature of: a) the room, b) dry ice, c) liquid nitrogen. The intensities of the peaks for m/e = 30 and m/e = 31 are proportional to the concentrations of ^{14}NO and ^{15}NO, respectively.

[1] L. Melander, Isotope Effects on Reaction Rates, Ronald, 1960.
[2] E. M. Belenov, E. P. Markin, A. N. Oraevskiĭ, and V. I. Romanenko, ZhETF Pis. Red. 18, 196 (1973) [JETP Lett. 18, 116 (1973)].
[3] N. G. Basov, E. M. Belenov, L. K. Gavrilina, V. A. Isakov, E. P. Markin, A. N. Oraevskiĭ, V. I. Romanenko, and N. B. Ferapontov, ZhETF Pis. Red. 19, 336 (1974) [JETP Lett. 19, 190 (1974)].
[4] Ya. B. Zel'dovich and Yu. P. Raĭzer, Fizika udarnykh voln i vysokotemperaturnykh gidrodinamicheskikh yavleniĭ (The Physics of Shock Waves and High Temperature Hydrodynamic Phenomena), Nauka, 1966.
[5] C. E. Treanor, I. W. Rich, and R. C. Rehm, J. Chem. Phys. 48, 1798 (1968).
[6] B. F. Gordiets, Sh. F. Mamedov, and L. A. Shelepin, Zh. Eksp. Teor. Fiz. 67, 1287 (1974) Sov. Phys.-JETP 40.