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ISOTOPE SEPARATION IN NONSTATIONARY MOLECULAR FLOW

K. D. SINEL' NIKOV, V. E. IVANOV, B. G. SAFRONOV, Iu. S. AZOVSKII, and G. G. ASEEV

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A change in the isotopic composition is observed in nonstationary molecular flow of mercury vapor. The data obtained are used to compute the time of adsorption of mercury on the surface of iron ($\tau_e^{198} = 3.4 \times 10^{-2}$ sec for $T = 290°K$) and the ratio of the adsorption times for the isotopes Hg^{198} and Hg^{204} ($\tau_e^{198}/\tau_e^{204} = 1.008$). An estimate is made of the heat of adsorption of mercury on iron (15×10^3 cal/mole).

1. A feature of stationary flow of a gas through a capillary tube is that the current is independent of the lifetime of the molecule in the adsorbed and non-adsorbed states and remains constant in time. To the contrary, as was already shown by Clausing,[1] in nonstationary flow of gas the change in the current depends substantially on the adsorption time of the molecules of the gas on the walls of the capillary tube. Gas diffusion in stationary molecular current, when $\lambda \gg r$, is accompanied by isotope separation (λ is the mean free path and r the radius of the capillary). It is interesting to determine how isotope separation changes in a nonstationary current in the presence of adsorption.

To observe the change in the isotopic composition of gas under the above conditions, it is necessary to admit gas consisting of a mixture of isotopes in one end of the capillary tube (with $\lambda \gg r$) and to measure its composition in the opposite end, from the instant that the gas appears to the instant when stationary flow is established.

Figure 1 shows the experimental setup. The working substance was mercury placed in a steel ampoule that could be cut off from the system by valve 1. Connected to the valve is iron tube 3, wound into a cylindrical coil 160 mm in diameter. The length of the tube L is 4500 mm, and its diameter $2r$ is 6 mm. The other end of the tube is connected with the ion source of the MS-2 mass spectrometer. Placed inside the coil is oven 2, with which the tube could be heated to 600°C. The temperature was monitored by thermocouple 4. The inner surface of the tube was first treated with hydrochloric and concentrated nitric acid, after which it was washed five times with distilled water at a 100°C.

The tube was trained with the MS-2 vacuum system for several days at $T \sim 450-550°C$. The qualitative composition of the separated gas was as follows: CO_2, $CO + M_2$, H_2O (no organic peaks observed). After reducing the separated gas considerably, particularly the H_2O (approximately 4 — 5 times), the training was stopped. The temperature of the tube was reduced to 20°C. The pressure in the ion source was then reduced to $1-2 \times 10^{-7}$ mm Hg, and that in the analyzer to $0.7-1.0 \times 10^{-7}$ mm Hg, remaining at this value throughout the experiment. The background value of the peak of the isotope 198 amounted to 4 — 5 divisions on the highest-sensitivity scale of the electrometer ($\sim 2 \times 10^{-15}$ amp/division). When these conditions were obtained, the valve was opened and the mercury vapor began to flow into the tube at a pressure of approximately 10^{-5} mm Hg. Within $\Delta t \sim 1$ hr, the electrometer recorded a change of approximately 10^{-15} amp in the I_{198} peak. The ion current I_{198}, which was proportional to the vapor pressure of the mercury in the ion source, was then recorded; simultaneously, the isotopic composition of the mercury was measured until stationary flow was established. The admission of mercury vapor into the tube was then stopped and the composition of the desorbed hydrogen measured. The tube was heated to accelerate the desorption.

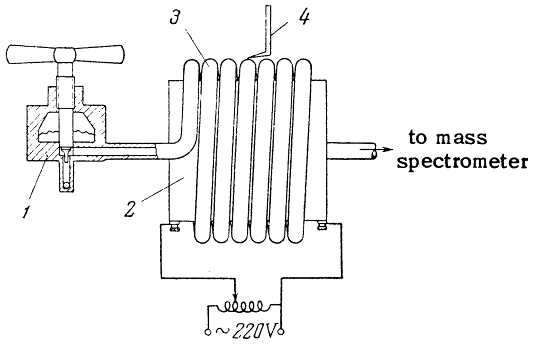

FIG. 1. Diagram of the set-up.

Measurements of the isotopic composition of the mercury were made with the single beam method relative to the extreme isotopes (198 and 204).

The measured currents were used to calculate $\beta = I_{198}/I_{204}$, each value of which was obtained by averaging ten measurements. The time requiring for each series was approximately two minutes. It was shown by means of special measurements that after approximately two days, the standard ratio β_0 remained unchanged. The standard isotopic composition was taken to be the composition of the stationary stream of mercury through the tube. The standard was measured before and after the experiment, and the tube was heated to approximately 300°C to accelerate the establishment of the stationary flow.

Analogous measurements were made with glass and copper tubes. In all cases, the diffusion resistances of the tube were the same.

2. The results obtained with iron and glass tubes are shown in Fig. 2. Curve 1 of the upper graph represents the change in the flow of mercury through an iron tube at $T = 20°C$, while Curve 2 is for $T = 290°C$. Curve 3 corresponds to a change in the flow through a glass tube. The lower graph shows the corresponding curves for the variation of the isotopic composition $\Delta = (\beta - \beta_0)/\beta_0$, where $\beta = f(t)$ (a common time axis is used).

It is seen from Curve 1 (lower plot) of Fig. 2 that the initial mercury stream contains an excess of the lighter isotope and approximately eight hours are required to make the composition standard. Section AB of the curve corresponds to the desorption of mercury at $T = 20°C$, while section BC corresponds to desorption at 300°C. It is seen from the lower plot that the desorbed mercury is enriched with the heavier isotope.

In the case of a glass tube (see Fig. 2), the time to establish the flow and the composition is one tenth that required for an iron tube at $T = 20°C$. The appearance time was approximately 10 sec in this case. The mercury adsorption on the glass was vanishingly small.

Figure 3 shows the results of the measurements of the flow and of the isotopic composition with a copper tube at $T = 20°C$. (Curves 1). The curves for copper and for iron are qualitatively the same. Section AB of Curves 1 corresponds to desorption at $T = 20°C$, while section BC corresponds to desorption at $T \sim 150°C$, while CD is for $T \sim 230°C$. The composition of the desorbed mercury in section AB of Fig. 3 can be attributed to the uneven evaporation and to the difference in the isotopic composition of the adsorbed mercury along the length of the tube. Curves 2 of Fig. 3 show the same relations for a copper tube with a diffusion resistance that is one third as large as for the case of Curves 1.

3. P. Clausing[1] solved the diffusion problem for a nonstationary molecular flow, with allowance for the adsorption time. His solution is independent of the degree of jacketing, is subject to the initial and boundary conditions of the present work, and fits very well the experimental Curve 1 (dotted curve of Fig. 2) for a certain value of the parameter α. This indicates that it is proper to employ these calculations for the flow of mercury vapors through an iron tube.

Combining the flow equation[1] for the isotope 198 with the flow equation for the isotope 204, we obtain

$$\Delta = \frac{\beta - \beta_0}{\beta_0}$$

$$= \frac{1 - 2\,[\exp(-t/\alpha_1) - \exp(-4t/\alpha_1) + \exp(-9t/\alpha_1)]}{1 - 2\,[\exp(-t/\alpha_2) - \exp(-4t/\alpha_2) - \exp(-9t/\alpha_2)]} - 1, \tag{1}$$

where the indices 1 and 2 refer to the lighter and heavier isotopes, with

$$\alpha = \frac{L^2}{\pi^2 D} = \frac{3}{\pi^2}\left(\frac{L}{2r}\right)^2\left(\frac{2r}{u} + \tau_e\right), \tag{2}$$

where τ_e is the average adsorption time, u the average thermal velocity, and L and r the length and radius of the tube. The value of α_2 is deter-

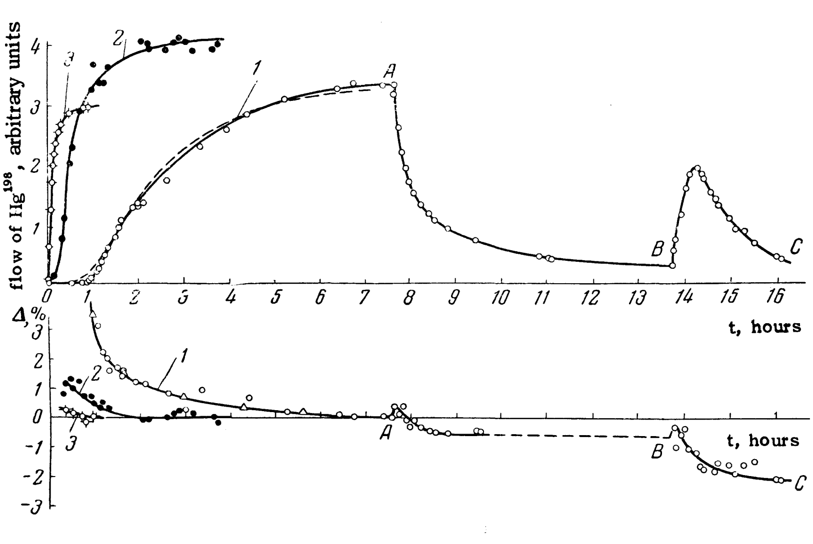

FIG. 2. Variation of stream and of isotopic composition of mercury vapors passing through iron and glass tubes.

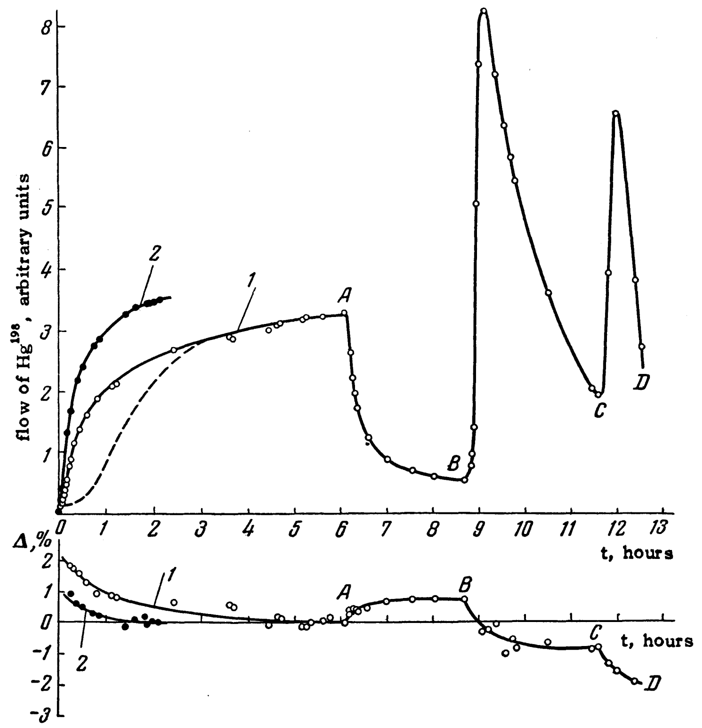

FIG. 3. Variation of flow and isotopic composition of mercury vapors passing through copper tubes.

mined by means of formula (1) from the known values of Δ and α_1, obtained from Curve 1 of Fig. 2. As a check, using the computed values of α_1 and α_2, formula (1) was used to compute points (triangles on Fig. 2), which fit well on the experimental curve.

Analogous calculations for the copper tube have shown that it is possible to describe the variation of the flow and the isotopic composition in terms of the Clausing equations, this being a consequence (see Fig. 3) of the discrepancy between the experimental curve 1 and the calculated one (dotted one). The difference between the curves for the flows through iron and copper tubes can be explained by the presence of dissolution and diffusion of mercury in the wall of the copper tube.

The following values of τ_e were computed from the experimental results with the iron tube:

for $T = 293°\text{K}$ $\tau_e^1 = 3.4\cdot 10^{-2}$ sec, and $\tau_e^2/\tau_e^1 = 1.008$;
for $T = 563°\text{K}$ $\tau_e^1 = 1.0\cdot 10^{-2}$ sec.

Using the values of τ_e^1 for two temperatures, it is possible, after Frenkel',[2] to estimate the heat of adsorption on mercury on iron. It turns to be approximately 15×10^3 cal/mole.

It is thus shown that the different adsorption times of the isotopes, for a nonstationary molecular flow, lead to a separation of the isotopes. The phenomenon described must be taken into account in exact mass-spectrometric measurements, for it is one of the sources of the non-systematic errors.

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[1] P. Clausing, Ann. Physik 7, 489 (1930).
[2] Ia. Frenkel', Z. Physik 26, 117 (1924).

Translated by J. G. Adashko
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