temperatures (20 and 400°C) were identical. The ordinate of the retarding curve I_2/I_1 obtained for $V_p = 500$ v becomes negative values starting with $V_k = 11$ v. The position of the peak of secondary electrons in the distribution curve was also obtained for $V_p = 100$ v (Fig. 3b), but the half-width of the peak of the distribution curves for $V_p = 500$ v is narrower (3 ev) than that of the curve obtained for $V_p = 100$ v (3.5 ev). The range of secondary-electron energies of the distribution curves for GeO_2, is characteristic of semiconductors.

The absence of saturation in the retarding curves in the region of positive values near zero, which leads to the appearance of electrons with "negative" energy, is explainable by tertiary electrons knocked out of the collector by the reflected primary or secondary electrons.[12]

In conclusion we regard it our agreeable duty to express thanks to V. P. Zhuze for making the germanium, and we also are thankful to B. F. Zhuravskii for his help with the measurements.

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Translated by L. B. Leder
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SOVIET PHYSICS JETP VOLUME 6(33), NUMBER 3 MARCH, 1958

CHANGE IN THE ISOTOPIC COMPOSITION OF MERCURY BY EVAPORATION

V. N. GRIGOR'EV, IA. S. KAN, N. S. RUDENKO, and B. G. SAFRONOV

Physico-Technical Institute, Academy of Sciences, Ukranian S.S.R.

Submitted to JETP editor March 13, 1957

J. Exptl. Theoret. Phys. (U.S.S.R.) **33**, 576-580 (September, 1957)

Evaporation-induced changes in the isotopic composition of mercury are investigated under various conditions. It is found that the kinetics of evaporation plays a large role at slow distillation rates. The upper limits of $\Delta p/p$ are evaluated for mercury isotopes.

INTRODUCTION

THE determination of the relative saturated vapor pressures for isotopes is important both for studying the influence of isotopic composition on the properties of matter and for isotope separation techniques. This measurement is often performed by evaporation of isotope mixtures at constant temperature. The change in the composition of a two-component mixture is then given by

$$\frac{c}{c_0} = \left(\frac{1-c_0}{1-c}\right)^{1/\alpha} \left(\frac{v_0}{v}\right)^{\frac{\alpha-1}{\alpha}}, \tag{1}$$

where c_0 and c are the concentrations of the isotope in the liquid before and after evaporation, v_0 and v are the initial and final volumes of the liquid, and α is the separation coefficient.

Under equilibrium evaporation of an ideal mixture, α is equal to the vapor pressures of the components. Such experiments may give values of v_0/v of the order of several thousands, which makes it possible to determine α to within 0.03%. An expression similar to (1) can be obtained also for many-component ideal systems.[1]

This approach was used by many authors,[2-6] but when it was possible to compare the results so obtained with direct measurements of the vapor pressure ratio, it was found that the evaporation method gives $\Delta p/p$ values that are too high. In this connection it would seem interesting to study the mechanism of isotope separation by evaporation and to clarify the possibilities of determining the vapor pressure ratio by this method. We chose mercury as the object of our studies, since it is a liquid through a wide range convenient for experiment and can be very thoroughly cleaned of impurities.

A change in the isotopic composition of mercury by evaporation has been observed by many authors,[7-9] although the investigations were performed under conditions known to be nonequilibrium no attempt was made to explain the separation mechanism.

EXPERIMENTAL PART

Evaporation with small residues was performed in the apparatus shown in Fig. 1. Between 50 and 100 cm^3 of mercury was distilled into flask A, after which the apparatus was sealed off without breaking the vacuum. The vacuum was maintained by means of a carbon trap cooled by liquid nitrogen. The evaporated mercury condensed in the tube and flowed into flask C at room temperature. To avoid possible condensation of the vapors in the upper part of A, an additional heating coil was wound at the top. Evaporation continued until between 10^{-3} and 10^{-4} of the original quantity of mercury remained, after which the remainder was analyzed in a mass spectrometer. When the experiments were performed in the temperature interval from 60 to 270°C, it was always found that the residue was enriched in the heavy isotope. The large spread in the values of α obtained, however, made it difficult to interpret the results. A decrease of the distillation rate by the introduction of a diaphragm whose diameter lay between 1 and 2 mm into A led to a decrease in the separation coefficient. Experiments in which the vapor removal rate was varied through wide limits were performed at 200°C; the removal rate was varied by altering the resistance of the tube connecting A and C (Fig. 1). When the removal rate was reduced by a factor of about 50, the separation coefficient changed from 1.0050 to 1.0008.

In order to evaluate the vapor pressure ratio at low temperatures, one may make use of evaporation by molecular distillation, for which the mean free path λ of a vapor molecule is much greater than the distance d to the condenser. In this case $\alpha = (p_1/p_2)\sqrt{M_2/M_1}$, where p_1 and p_2 are the vapor pressures of the isotopes, and M_1 and M_2 are their atomic weights. Due to the very low evaporation rate, the Rayleigh distillation method cannot be used, and therefore the apparatus shown in Fig. 2 was used to remove a small quantity of the vapor.* The low-temperature kerosene bath A was cooled by means of heat conductor B immersed in liquid nitrogen. The vapor condensed on the inner wall of a Dewar flask cooled by liquid nitrogen. The amount of condensed vapor was no greater than 10^{-4} of the original mercury, so that the composition of the liquid could be assumed constant. Under such conditions the ratio of the concentrations in the distillate and residue gives the separation coefficient. Experiments were performed at temperatures of −20, −30, and −38°C. In all cases the separation coefficient was found to be equal to the square root of the isotope mass ratio within the experimental limits, regardless whether the mercury was stirred or not.

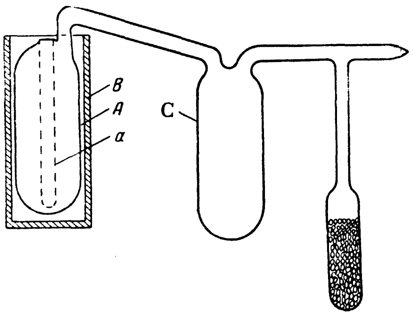

FIG. 1. Distillation apparatus. B — electric mercury heater; a — thermometer tube.

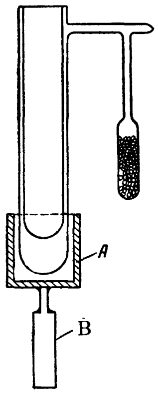

FIG. 2. Apparatus for removing the vapor at low temperatures.

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*L. S. Kan took part in developing this method.

Distillations with small residues were performed at temperatures from 10 to 90°C under conditions close to molecular distillation. The separation coefficient decreased as the tmperature increased and as the distance to the condenser increased. Experiments on fractional distillation were performed under similar conditions in the apparatus shown in Fig. 3. Mercury on the outside wall 1 of the Dewar flask was heated by water vapor and condensed on the inner wall 2 which was cooled by liquid nitrogen. The evaporation continued until half the original mercury remained in the apparatus. The remainder (the so-called "heavy" fraction) was removed from the apparatus through the narrow rubber tube 3. After the nitrogen evaporated, the "light" fraction was removed. The "light" and "heavy" fractions thus obtained were subjected to further distillation. In this way we obtained fourteen fractions of "light" and twelve fractions of "heavy" mercury.

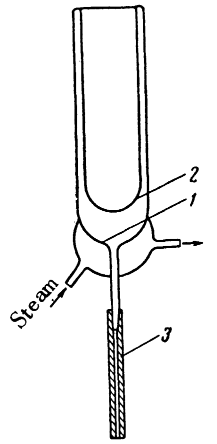

FIG. 3 Apparatus for fractional distillation.

MASS-SPECTROMETRIC ANALYSIS

A preliminary measurement established the fact that the change in the concentration of a given isotope in a sample is related linearly to the difference between the atomic weight of this isotope and the mean atomic weight of the mixture. We therefore performed an analysis to measure the change in the concentration ratio $a = c^{198}/c^{204}$ for the isotopes Hg^{198} and Hg^{204}. The measurements were performed on MS-2 and MS-4 mass spectrometers according to the following scheme: ordinary mercury — sample investigated — ordinary mercury. The background before the measurements on the sample of ordinary mercury was no greater than 3% of the operating intensity. No "memory" effect, (i.e., influence of the absorbed vapors on later measurements) was observed.

DISCUSSION OF RESULTS

The results of the experiments are shown in the tables and in Fig. 4. The tables give the temperatures at which the experiments were performed, the ratio v_0/v of the initial and final volumes, the ratio of the mean evaporation rate calculated by Langmuir's formula (G_{calc}) to the mean distillation rate as found from the time of evaporation (G_{exp}), the change of the concentration ratio of Hg^{198} and Hg^{204} of the residue as compared with ordinary mercury, and the calculated separation coefficient.

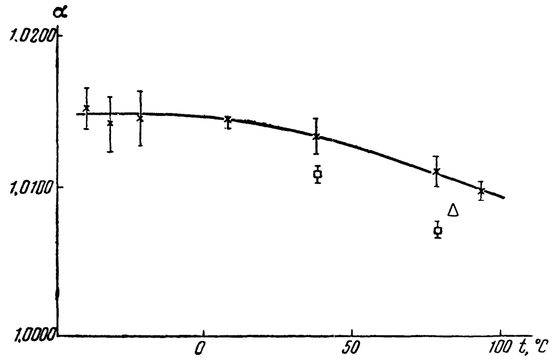

FIG. 4. The separation coefficient as a function of temperature for molecular distillation × — distillation in an apparatus with d = 2 cm, □ — d = 10 cm, Δ — mean value of α for fractional distillation.

It is known that isotope separation by evaporation can be due to two mechanisms: an equilibrium mechanism related to the difference in the vapor pressures, and a nonequilibrium mechanism which depends on the difference of the evaporation rates. As mentioned above, in the second case $\alpha = (p_1/p_2)\sqrt{M_2/M_1}$. From experiments performed with molecular distillation conditions, it follows that $\alpha \approx \sqrt{M_2/M_1}$, so that the difference in the vapor pressures does not exceed the error of these experiments. It is seen from Fig. 4 that the separation coefficient begins to decrease already at $\lambda \sim d$, which is an indication of the effect of molecular collisions in the vapor.

In the first experiments on evaporation with a small residue, the calculated evaporation rate exceeded the rate of vapor removal by a factor of several times ten. This would seem to assure conditions sufficiently close to equilibrium. The poor reproducibility of the results alone, however, makes it reasonable to suppose that the dependence of α on the distillation conditions is related to differences in the contributions from nonequilibrium processes. This point of view is supported by the experimental increase of the separation coefficient when the removal rate is changed, that is on approaching equilibrium. It is seen from Table III that the vapor removal rate is a very important parameter in the process of isotope separation by evaporation. In experiments performed at very low distillation rates, G_{calc}/G_{exp} was of the order of several thousands, yet in these cases one cannot assert that the separation is due only to the difference in the

TABLE I

t °C	$\frac{v_0}{v}$	$\frac{G_{calc}}{G_{exp}}$	$\frac{\Delta a}{a}$, %	α	$\Delta\alpha\cdot 10^4$	Remarks
70	2040		2.4	1.0031	6	
80	19000	40	2.6	1.0031	5	
100	5560	30	2.9	1.0036	5	
100	524		1.7	1.0030	4	Distillation with water vapor;
110	5880		2.2	1.0028	3	
120	2710	70	2.8	1.0036	3	
120	9000	100	1.6	1.0020	4	
140	2000		1.2	1.0017	5	
160	9700	150	2.9	1.0037	7	
160	183	170	1.7	1.0023	4	Distillation with a constant mercury surface
200	7750	200	1.8	1.0022	5	
250	532	3200	0.3	1.0004	2	

TABLE II

t °C	$\frac{v_0}{v}$	$\frac{G_{calc}}{G_{exp.}}$	$\frac{\Delta a}{a}$, %	α	$\Delta\alpha\cdot 10^4$
100	2700	90	2.6	1.0033	4
160	8950	600	0.8	1.0007	2
200	15200	1000	1.9	1.0022	3
270	1960	3100	1.2	1.0013	3
270	10300	5000	0.5	1.0004	2

TABLE III

$t = 200°$ C

$\frac{G_{calc}}{G_{exp}}$	$\frac{v_0}{v}$	α	$\Delta\alpha\cdot 10^4$
100	5780	1.0051	4
800	2260	1.0019	4
1200	5380	1.0022	3
3000	209	1.0010	3
5000	256	1.0008	3

vapor pressures.

The influence of the evaporation kinetics is particularly important in the evaporation of small drops, which leads to anomalously large separation coefficients at v_0/v of the order of several times ten thousand and to a decrease of α for evaporation from a constant surface. It would seem that the evaporation kinetics plays an important role in distillation in the presence of an inert gas, since when the distillation is performed in the presence of water vapor the separation coefficient obtained is about the same as for ordinary distillation.

The literature cited in the introduction, unfortunately, does not contain data which can be used to evaluate the state of equilibrium of the evaporation. One can only suggest that the large values of the $C^{12}H_4$ and $C^{13}H_4$ vapor pressures obtained by several authors[5,6] may be explained in this way.

The experiments performed can be used to evaluate the upper limits of the relative vapor pressure difference of Hg^{198} and Hg^{204}. These are $\Delta p/p \leq 2 \times 10^{-3}$ at $t = -20°C$, and $\Delta p/p \leq 8 \times 10^{-4}$ at $t = 200°C$. These results do not contradict the $\Delta p/p$ value as calculated on the basis of the work of I. Lifshitz and Stepanova,[10] namely $\Delta p/p = 3 \times 10^{-4}$ at $t = 20°C$ and $\Delta p/p = 4 \times 10^{-5}$ at $t = 200°C$ for mercury vapor.

In conclusion we take this opportunity to thank B. G. Lazarev for discussions.

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Translated by E. J. Saletan
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