

*EFFECT OF TEMPERATURE ON THE VARIATION OF THE ISOTOPIC COMPOSITION  
OF LIQUID MERCURY IN THE ELECTRIC FIELD OF A CONSTANT CURRENT*

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Submitted to JETP editor June 16, 1959

J. Exptl. Theoret. Phys. (U.S.S.R.) **37**, 1241-1246 (November, 1959)

The temperature dependence of the change in the concentration of liquid mercury isotopes upon passage of a constant electric current through the liquid has been studied experimentally. In the stationary case the change in the concentration was found to be independent of the temperature. Some possible mechanisms of the phenomenon are discussed.

THE change in the isotopic composition of liquid metals in the passage through them of a constant electric current has recently been investigated for a whole series of metals: Hg,<sup>1-4</sup> Ga,<sup>5,6</sup> K,<sup>7</sup> In,<sup>8</sup> Li,<sup>9</sup> Cd, Zn, Sn,<sup>10</sup> and Rb.<sup>11</sup> It is characteristic of all these metals that the heavy isotopes are always concentrated at the cathode and the lighter ones at the anode; the process of the change of concentration continues until a certain stationary state is reached that determines the equilibrium between the process of enrichment and the reverse one of diffusion; the coefficient of enrichment reaches several per cent per volt.

The phenomenological theory of the process, both in the stationary and non-stationary cases, has been developed by Bresler and Pikus,<sup>12,13</sup> and also in previously published researches of the authors.<sup>3,4</sup> This theory was completely substantiated in the previous work of the authors.<sup>4</sup>

The processes described by the nonlinear differential equation:

$$\frac{d}{dx} \left[ c(1-c) \gamma \frac{\epsilon_0 E}{kT} - \frac{dc}{dx} \right] = \frac{1}{D} \frac{dc}{dt}, \quad (1)$$

where  $c$  is the concentration of one of the isotopes,  $D$  is the diffusion coefficient,  $E$  is the electric field intensity,  $T$  is the temperature,  $\epsilon_0$  is the electronic charge. Equation (1) preserves its form outside of the dependence on the assumed mechanism of separation; however, the constant  $\gamma$  entering into the equation will have a different physical meaning in each case.

Bresler and Pikus<sup>12,13</sup> assume two different mechanisms of separation. The first of these was based on the assumption that the reason for the separation was the difference in the mobilities of the heavy and light isotopes. In this case, the more mobile ions, carried along by the electric

field, congregate about the cathode. Here,  $\gamma = \Delta\mu/\mu$ , where  $\Delta\mu = \mu_1 - \mu_2$ ;  $\mu_1$  and  $\mu_2$  are the mobilities of ions of the one and the other isotope. To obtain the correct direction of the effect, it is necessary that the mobility of the ions of the heavy isotope be greater than those of the light.

The second mechanism takes into account the difference in the interaction of the electric current with ions of one or the other isotopes. If the probability of scattering of the electrons by ions of the different isotopes is characterized by the corresponding values of the electrical resistance,  $\rho_1$  and  $\rho_2$ , and the scattering by each ion takes place independently, then the isotope possessing the larger electrical resistance is carried along in greater degree by the electric current and concentrates at the anode. In this case,  $\gamma = \Delta\rho/\rho$ , where  $\Delta\rho = \rho_1 - \rho_2$ . It follows from the direction of the effect that the electrical resistance of the light isotope must be greater than that of the heavy.

A thermodynamic consideration of the phenomenon of the change of concentration of isotopes in the stationary case was given by the author<sup>3</sup> under the assumption that the separation appears as a result of the different molar volumes of the isotopes, which leads to a difference in the charges of the ions of the different isotopes per unit volume. The separation of the ions in this case takes place in a way similar to the separation of particles of different mass in the gravitational field. Here  $\gamma = \Delta V/V$ , where  $\Delta V = V_1 - V_2$ ;  $V_1$  and  $V_2$  are the molar volumes of the isotopes.

Genness<sup>14</sup> also assumes that the separation is brought about by the presence of a strong interaction of the electronic current with the ion and, applying the relations for a solid for the micro-

scopic description, he obtains the value

$$\gamma = \frac{zC}{12} \left( \frac{\Theta}{T} \right)^2 \frac{\Delta M}{M},$$

for  $\gamma$ , where  $\Theta$  is the Debye temperature,  $z$  = number of charges on a single ion,  $M$  = mass of the ion,  $\Delta M = M_1 - M_2$ ,  $C$  = coefficient of the order of unity.

Thus there are several assumptions regarding the mechanism of the change in concentration of isotopes in an electric field of a constant current. However, the experimental data currently available do not make it possible to examine critically the assumptions that have been made. For such considerations additional experimental investigations are necessary.

One of the experimental possibilities is the study of the temperature dependence of the effect. Actually, the presence of such a dependence makes it possible to consider the assumptions from the point of view of the validity of the temperature dependence of the coefficient  $\gamma$ .

Unfortunately, the information in the literature on temperature dependence<sup>6,8,10,11</sup> is quite contradictory and unreliable because of its low accuracy, inasmuch as the authors of these papers used formulas for the computation of the quantity  $\kappa = \gamma/(\Delta M/M)$  which do not take back diffusion into account. This compels them to carry out their investigations for short times of current transmission (at the beginning of the process), and consequently to use for mass spectrometric measurements slightly enriched specimens which have a strong influence on the accuracy of the measurements. An increase in the time of transmission of current increases the accuracy of the mass spectrometric measurements but lowers the accuracy of calculation of the value of  $\kappa$  because of lack of knowledge of back diffusion.

In the experiments described below, a method based on the phenomenological theory of Bresler and Pikus is employed which has already been used by the authors in reference 4.

## EXPERIMENTS

The investigation of the temperature dependence of the change of the isotopic constitution of mercury in the passage through it of a constant current was carried out in glass capillaries of internal diameter 0.4–0.5 mm and external diameter 5–6 mm (Fig. 1). The sample consisted of two sections of capillary each of length 73 mm, joined together through a reservoir. Since the concentration of isotopes in the middle of the specimen remains unchanged, the presence there of a

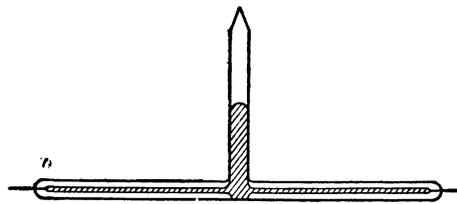


FIG. 1

mercury reservoir had no effect on the change of concentration. From the mathematical point of view, such a specimen corresponds to a homogeneous capillary of length 146 mm with closed ends at both electrodes.

The comparatively small length of the capillary was chosen for reasons of experimental convenience, because the time for establishing the stationary state in such a capillary amounted to about 20 days for the very low temperatures used in the experiments. The danger of the appearance of convection currents in the mercury for the short length of capillary was eliminated by the fact that the capillaries were horizontal at the time of the experiments (experiments carried out with capillaries in a vertical position showed that for such a length of capillary the convection currents appreciably lowered the value of the concentration change, beginning with a temperature of about 150°C).

The specimen was pumped out through the reservoir to a pressure of  $10^{-6}$  mm mercury, heated and filled with mercury by means of distillation. A constant stabilized voltage maintained with an accuracy of 2–2.5 percent was applied to molybdenum electrodes soldered to the ends of the capillary. The decrease in the voltage on the specimens at a temperature of  $-34^\circ\text{C}$  amounted to about 1 volt, for all other temperatures, about 2 volts, and was measured separately for each specimen with an accuracy no worse than 0.5 percent.

For the maximum range of temperature of liquid mercury, a succession of baths were employed in which the specimens were submerged at the following temperatures (in degrees C): acetone,  $-37 \pm 1$ , water,  $30 \pm 5$ ; lubricating oil,  $105 \pm 5$ ; and tin,  $210 \pm 5$ ,  $250 \pm 5$ ,  $300 \pm 5$ . The drop in temperature between the bath and the mercury in the capillary was determined by means of a calculation in which the coefficient of thermal conductivity of the glass used for the specimens was measured for the corresponding temperature range. For a number of specimens, the temperature of the mercury was estimated by the change in the electrical resistance. The results of the measurements coincided with the computed data.

The parts of the capillary close to the electrodes, of length about 7 mm, were cut off after the lapse of a definite time of transmission of current between the specimens, and the mercury drawn off from the cut-off capillary was analyzed by a mass spectrometer. The coefficient of separation  $P$  existing at a difference of potentials of 1 volt was computed by the formula

$$P = (\Delta a / a_0) / U,$$

where  $\Delta a = a_1 - a_2$ ;  $a_1$ ,  $a_2$ ,  $a_0$  are the ratios of the concentration of  $\text{Hg}^{198}$  to the concentration of  $\text{Hg}^{204}$  in the mercury close to the anode, close to the cathode, and in standard mercury, respectively;  $U$  = voltage on the electrodes. For each temperature, the dependence of the coefficient  $P$  on time of transmission of the current was measured, and the coefficients of separation  $P_\infty$  corresponding to the stationary state ( $t \rightarrow \infty$ ) were computed from these dependences, and also the coefficients  $\gamma = (kT/\epsilon_0) P_\infty$ .

From the equations describing the process, it is simple to obtain

$$P_\infty = \gamma \frac{\epsilon_0}{kT} = P \left[ 1 - \sum_{n=0}^{\infty} \frac{8}{\pi^2 (2n+1)^2} \times \exp\left[-\frac{\pi^2 D (2n+1)^2 t}{4l^2}\right] \right]^{-1}, \quad (2)$$

for  $\gamma \ll 1$  and  $\Delta a/a_0 \ll 1$ , where  $\epsilon_0$  = electronic charge,  $l$  = length of the capillary (73 mm). Under such conditions, Eq. (2) is valid not only for a two component mixture, but also for any pairs of isotopes of a mixture consisting of many components.

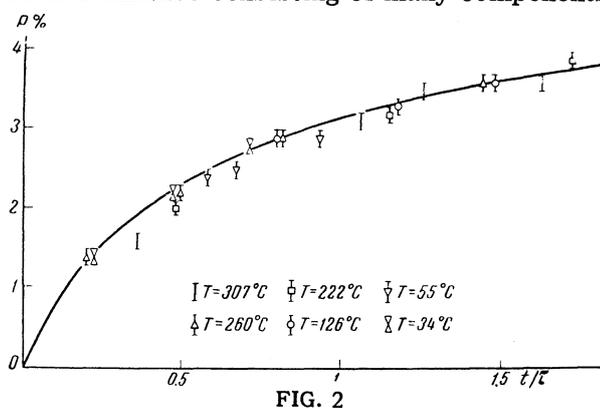


FIG. 2

The dependence of the change of concentration of  $\text{Hg}^{198}$  and  $\text{Hg}^{204}$  on the time of transmission of the current is plotted in Fig. 2 for different temperatures. The reduced time  $t/\tau$  is plotted along the abscissa, where  $\tau = 4l^2/\pi^2 D$  is the time required to establish the steady state. Here, the coefficient of self-diffusion  $D$  was computed according to the empirical formula<sup>15</sup>

$$D = 1.260 \cdot 10^{-4} \exp[-1160/RT].$$

It is seen from the graph that for equal times the coefficient  $P$  does not depend on the temperature. It also follows from the graph that the maximum change in the concentration (for large time of transmission of current)  $P_\infty$  remains constant for the whole temperature range of liquid mercury.

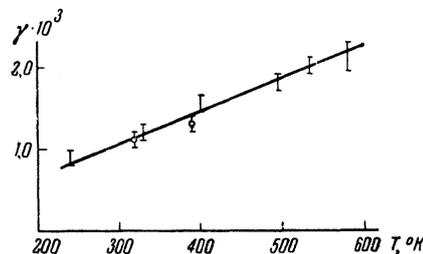


FIG. 3

The dependence of the coefficient  $\gamma$  on temperature is shown in Fig. 3. Points corresponding to temperatures 318°K and 388°K were obtained from the results of the previous work of the authors.<sup>4\*</sup> As is seen from the graph the coefficient  $\gamma$  in which we are interested increases in proportion to the increase in temperature.

## DISCUSSION OF RESULTS

The observed linear growth of  $\gamma$  with increase in temperature permits us to evaluate the assumptions of the nature of the process.

The temperature dependence that is obtained contradicts the assumption of Gennes inasmuch as it is necessary to assume that the product  $zC$  increases proportionally to  $T^3$  in order that the condition  $\gamma \sim T$  be satisfied. The density of charges per ion can increase with temperature; however, one does not have to rely on its rapid increase. The change of the coefficient  $C$  with temperature depends on the difference in activation energy of diffusion and viscosity and it is uncertain that it can depend so strongly on the temperature.

The assumption that the determining role in the process of concentration change is played by the difference in the molar volumes of the isotopes  $\Delta V/V$  is also not capable of explaining the dependence  $\gamma \sim T$ . Although the molar volumes

\*A mistake was made by the authors in reference 4. In Eq. (12) the quantity  $L/2$  should appear for  $L/4$  in front of the brackets. For this reason, the quantity  $\kappa$  computed for mercury from the results of the research and given in the Table is twice too large, and one must regard the values of  $L$  and  $\Delta\mu/\mu$  as referring to the mercury isotopes  $\text{Hg}^{198}$  and  $\text{Hg}^{204}$ .

for metallic isotopes were not studied experimentally, experiments with isotopes of hydrogen and helium show a decrease, and not an increase, in the relative difference of molar volumes, with increase in temperature. Some further support can be found from the fact that the theoretical estimates of  $\Delta V/V$  carried out with reference to the solid state also show a decrease in this quantity with increase in temperature.

The temperature dependence of the relative difference in mobilities  $\Delta\mu/\mu$  is still not clearly established; however, there is an experimental fact which does not support the use of the assumption of  $\Delta\mu/\mu$  as the reason for the effect. Lazarus and Okkerse<sup>16</sup> measured the coefficients of diffusion for two isotopes of iron Fe<sup>55</sup> and Fe<sup>59</sup> in silver and found that the light isotope of iron Fe<sup>55</sup> possessed the greater mobility. At the same time, as was pointed out above, for a correct explanation of the direction of the change of concentration in the electric field of a constant current by such a mechanism, it is necessary that the lighter isotope possess a smaller mobility than the heavier. The fact that in one case we are talking about self diffusion in a liquid metal, and in the other about diffusion in a solid material is evidently not decisive for the sign of the difference of mobility of the isotopes.

An excellent opportunity of testing the assumptions connected with the difference in the electrical resistance of the isotopes is provided by a comparison of the value of  $\Delta\rho/\rho$  and its dependence on temperature, obtained from experiments on the concentration change in the electric field of a current, with the value and temperature dependence of  $\Delta\rho/\rho$  determined directly for the same isotopes. Such investigations, which also possess an interest in their own right, were carried out by the authors for the isotopes of mercury. The results of preliminary experiments do not eliminate the possibility of the explanation of the effect of the change of concentration in the electric field of a current by the presence of a difference in the electrical resistances of the isotopes.

In the present work we have not considered the mechanism proposed by Klemm,<sup>17</sup> inasmuch as the large number of parameters coming into consideration do not permit us to confirm this mechanism by an experimental test.

We can thus make the following comments regarding the assumptions discussed here. The assumption connected with the difference in the mo-

bilities of the isotopes, the assumption on the difference in the molar volumes, and the consideration of Gennes, contradict the measured temperature dependence. The assumption connected with the difference in the specific electrical resistances of the isotopes represents the most probable of the mechanisms discussed; however, it requires further verification.

<sup>1</sup>E. Haeffner, *Nature* **172**, 775 (1953).

<sup>2</sup>Haeffner, Sjoborg, and Lindhe, *Z. Naturforsch.* **11a**, 71 (1956).

<sup>3</sup>Rudenko, Grigor'ev, Dolgoplov, and Bogoyavlenskii, Works (Trudy) of the Session of the Academy of Sciences, Ukr. S.S.R. on the Peaceful Utilization of Atomic Energy, 1956. Acad. Sci. Press, 1958.

<sup>4</sup>Bogoyavlenskii, Grigor'ev, Rudenko, and Dolgoplov, *JETP* **33**, 581 (1957); *Soviet Phys. JETP* **6**, 450 (1958).

<sup>5</sup>G. Nief and E. Roth, *Compt. rend.* **239**, 162 (1954).

<sup>6</sup>Goldman, Nief, and Roth, *Compt. rend.* **243**, 1414 (1956).

<sup>7</sup>Lunden, Reuterswård, and Lodding, *Z. Naturforsch.* **10a**, 924 (1955).

<sup>8</sup>Lodding, Lunden, and Ubisch, *Z. Naturforsch.* **11a**, 139 (1956).

<sup>9</sup>Lunden, Lodding, and Fischer, *Z. Naturforsch.* **12a**, 268 (1957).

<sup>10</sup>A. Lodding, *Z. Naturforsch.* **12a**, 569 (1957).

<sup>11</sup>A. Lodding, *Z. Naturforsch.* **14a**, 7 (1959).

<sup>12</sup>S. E. Bresler and G. E. Pikus, *J. Tech. Phys. (U.S.S.R.)* **26**, 109 (1956); *Soviet Phys.-Tech. Phys.* **1**, 102 (1956).

<sup>13</sup>S. E. Bresler and G. E. Pikus, *J. Tech. Phys. (U.S.S.R.)* **28**, 2282 (1958), *Soviet Phys.-Tech. Phys.* **2**, 2094 (1958).

<sup>14</sup>P. G. Gennes, *J. phys. Rad.* **17**, 343 (1956).

<sup>15</sup>R. E. Hoffman, *J. Chem. Phys.* **20**, 1567 (1952).

<sup>16</sup>D. Lazarus and B. Okkerse, *Phys. Rev.* **105**, 1677 (1957).

<sup>17</sup>A. Klemm, *Z. Naturforsch.* **9a**, 1031 (1954).