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VARIATIONS IN THE ISOTOPIC COMPOSITION OF MERCURY IN A DC ELECTRIC FIELD

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Direct current was passed through liquid mercury and the time variation of the isotopic composition of the mercury was studied. The experiments were carried out at two temperatures. We investigated the variation of isotope concentration along the electric field, and the relation between the isotopic composition at the cathode and the applied voltage. The experimental data are compared with some phenomenological calculations and possible causes for the effect are discussed.

THERE are many papers[1] devoted to the effect that direct current has on the constitution of binary metallic solutions. None of the theories which have been proposed to explain the effect has given satisfactory agreement with experiment, and the underlying mechanism remains obscure. The question is most conveniently considered if we take a mixture of metal isotopes as the object to be investigated.

It has recently been observed that changes in isotopic constitution occur when direct current passes through mercury,[2,3] thallium,[4,5] potassium,[6] and indium.[7] In all these cases it has been found that the concentrations of the heavy isotopes increase near the cathode, and of the light ones near the anode. However, the work has not been carried out systematically, which makes comparison with theory difficult. It therefore appeared appropriate to measure some of the fundamental quantities connected with the effect.

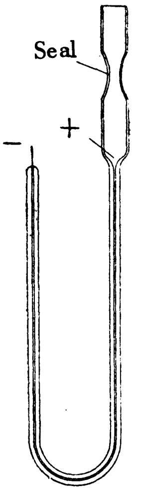

FIG. 1.

EXPERIMENTAL PART

All the experiments were carried out in glass capillary tubes (Fig. 1) 28 cm long and of inner diameter 0.05 cm. Before being filled with mercury, the capillary tubes were evacuated by a diffusion pump and heated to a temperature of 300°C; mercury was then distilled into them. The volume of the reservoir was much greater than that of the capillary, so that the composition of the mercury at the anode was always the same. The experiments were carried out with temperatures of (41 ± 2)°C and (− 10 ± 3)°C at the outer capillary wall. The temperature of (41 ± 2)°C was maintained by placing the capillary in a stirred-water bath. The temperature of (− 10 ± 3)°C was maintained in a kerosene bath cooled by a copper rod with one end in liquid nitrogen. After a certain, definite time the current was turned off and the capillary quickly cut into pieces. The mercury in each piece was analyzed with a mass spectrometer. The method used to make the mass spectrometer measurements has been described before in detail.[8]

Fig. 2 shows how the variation of the concentrations of Hg^{198} and Hg^{204} with the time of current flow. The quantity plotted along the Y axis is $\Delta a/a_0$, where $\Delta a = a_0 - a$ and a_0, a are the ratios of the concentration of Hg^{198} to the concentration of Hg^{204} in normal mercury and that found near the cathode. The duration of current flow is plotted on the X axis. From the figure it is evident that the curves tend to saturate as the time increases, and for a fixed voltage the change in concentration is less at − 10°C than it is at 41°C.

The curves of Fig. 3 show how the concentration varies along the length of the capillary. The value of $\Delta a/a_0$ from various parts of the capillary is plotted along the ordinate. Comparison of the curves shows that their curvature decreases as equilibrium is approached.

Fig. 4 shows how $\Delta a/a_0$ at the cathode depends on the voltage applied between the electrodes. The voltage across the electrodes is plotted along the X axis. The bath temperature was 41°C, the current was on for 1500 to 1800 hours.

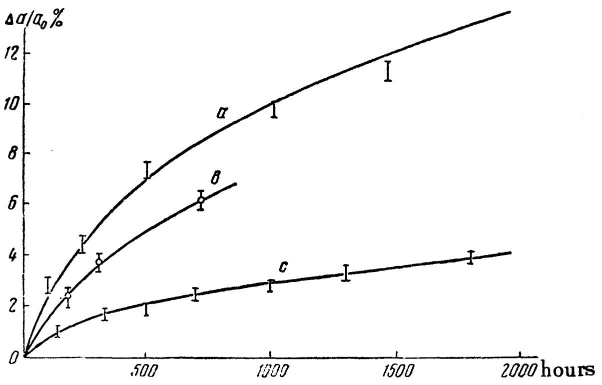

FIG. 2. Variation in the concentrations of Hg^{198} and Hg^{204} with duration of current flow. Curves a and c: bath temperature 41 ± 2°C, applied voltage 6 and 2 volts respectively; curve b: bath temperature — 10 ± 3°C, applied voltage 6.

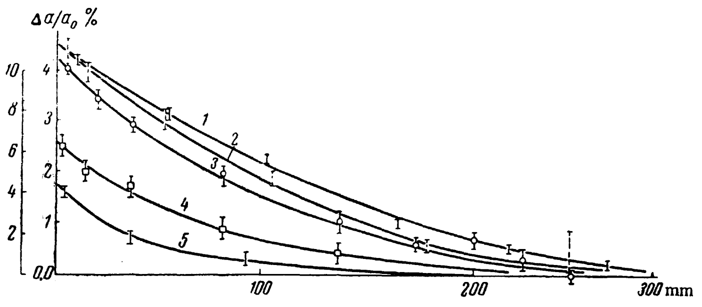

FIG. 3. The concentration of the mercury isotopes as a function of distance along the capillary. 1 — time t of current flow 1800 hrs, applied voltage U = 5.15 volts; 2 — t = 1460 hrs., U = 2.14 volts; 3 — t = 1800 hrs., U = 2 volts; 4 — t = 700 hrs., U = 2 volts; 5 — t = 340 hrs., U = 2 volts. The right-hand scale refers to curves 2 — 5, the left hand one to curve 1. Temperature 41°C.

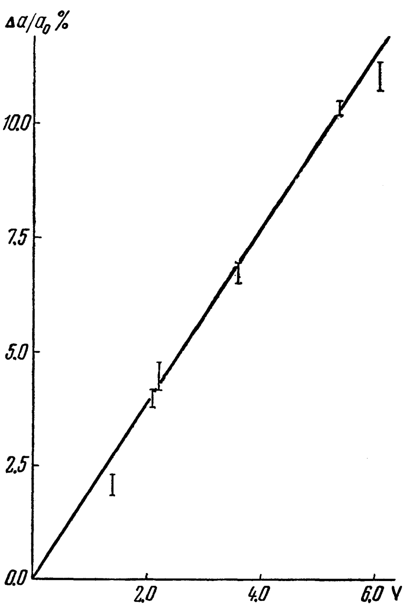

FIG. 4.

CALCULATION OF CONCENTRATION DISTRIBUTION

Bresler and Pikus[9] considered quantitatively the isotope separation induced by direct current. They studied a mixture of two isotopes and took the electric field to be constant along the length of the column. The electric field displaces both kinds of ions in the same direction; there is a backward hydrodynamic flow of the liquid as a whole because it is incompressible, and a backward diffusion flow because of the gradient in isotope concentration which is set up. The equations for the ion current show that the ions can be separated because they have different mobilities.

The boundary conditions used in the calculation above correspond to zero flux of matter at both ends of the capillary, a condition which did not obtain in our experiments. We therefore give a solution for different boundary conditions.

It is shown in Ref. 9 that if the diffusion coefficients of the two isotopes differ little, the equation for the concentration c can be put in the form [Eq. (6) of Ref. 9]

$$\frac{d}{d\varkappa}\left[\frac{\partial y}{\partial \varkappa} + y^2\right] = \frac{\partial y}{\partial \tau} \tag{1}$$

where $\varkappa = x/b$ is a dimensionless length, $\tau = tD/b^2$ is dimensionless time, $1/b = \Delta\mu E/D$, $\Delta\mu = \mu_2 - \mu_1$ is the difference between the mobilities of the second and first isotopes, D is the diffusion coefficient, E the applied voltage, and $y = \frac{1}{2} - c$.

The condition that there be no flux of matter at the cathode can be written

$$[\partial y / \partial \varkappa + y^2 - 1/4]_{\varkappa=0} = 0. \tag{2}$$

The second boundary condition, that the concentration be constant at the anode, is

$$y\,|_{\varkappa=L} = {}^1\!/_2 - c_0 = \alpha = \text{const}. \tag{3}$$

The initial condition is:

$$y(\varkappa, \tau)\,|_{\tau=0} = \alpha.$$

Introducing, after Bresler and Pikus, a new variable $\varphi = \varphi^* \exp\left[-\int z(\tau)\,d\tau\right]$, we obtain Fourier's equation:

$$\partial^2\varphi / \partial\varkappa^2 = \partial\varphi / \partial\tau, \tag{1a}$$

with y and φ being related through the equation

$$\varphi = \exp\left[\int_0^{\varkappa} y d\varkappa\right]. \tag{5}$$

The initial and boundary conditions then take the form

$$[\partial^2\varphi / \partial\varkappa^2 - {}^1/_4\varphi]_{\varkappa=0} = 0; \tag{2a}$$

$$[\partial\varphi / \partial\varkappa - \alpha\varphi]_{\varkappa=L} = 0; \tag{3a}$$

$$\varphi(\varkappa, \tau)\,|_{\tau=0} = \exp[\alpha\varkappa]. \tag{4a}$$

Upon taking Laplace transforms we obtain

$$\bar{\varphi}'' = p\bar{\varphi} - \exp[\alpha\varkappa]; \tag{1b}$$

$$[\bar{\varphi}'' - {}^1/_4\bar{\varphi}]_{\varkappa=0} = 0; \tag{2b}$$

$$[\bar{\varphi}' - \alpha\bar{\varphi}]_{\varkappa=L} = 0. \tag{3b}$$

A solution of (1b) satisfying (2b) and (3b) is

$$\bar{\varphi} = \frac{\alpha^2 - 1/4}{(p - 1/4)(\alpha^2 - p)}\,\frac{\sqrt{p}\cosh\sqrt{p}(\varkappa - I) + \alpha\sinh\sqrt{p}(\varkappa - I)}{\sqrt{p}\cosh\sqrt{p}\,L - \alpha\sinh\sqrt{p}\,L} + \frac{\exp[\alpha\varkappa]}{p - \alpha^2}. \tag{6}$$

Upon applying the inverse transform, we find that

$$\varphi = \frac{\cosh[(\varkappa - I)/2] + 2\alpha\sinh[(\varkappa - I)/2]\,e^{\tau/4}}{\cosh(L/2) - 2\alpha\sinh(L/2)} + \sum_{n=1}^{n=\infty} A_n \sin\lambda_n\varkappa \exp\{-\lambda_n^2\tau\}, \tag{7}$$

where

$$A_n = \left(\frac{L}{2} - \frac{\sin 2\lambda_n L}{4\lambda_n}\right)^{-1} \frac{\lambda_n(1/4 - \alpha^2)}{(\alpha^2 + \lambda_n^2)(\lambda_n^2 + 1/4)}, \tag{8}$$

and the λ_n are determined through the equations

$$\alpha\tan\lambda_n L = \lambda_n. \tag{9}$$

From (5) we can then conclude that the concentration is distributed according to the following equation:

$$c = \frac{1}{2}\left[1 - \frac{\sinh[(\varkappa - \varkappa_0)/2] + 2\cosh(\varkappa_0/2)\,e^{-\tau/4}\sum\limits_{n=0}^{n=\infty} A_n\lambda_n\cos\lambda_n\varkappa\exp\{-\lambda_n^2\tau\}}{\cosh[(\varkappa - \varkappa_0)/2] + \cosh(\varkappa_0/2)\,e^{-\tau/4}\sum\limits_{n=0}^{n=\infty} A_n\sin\lambda_n\varkappa\exp\{-\lambda_n^2\tau\}}\right], \tag{10}$$

κ_0 being determined by the condition that the concentration be a constant at $\kappa = L$:

$$\alpha = {}^1/_2\tanh[(L - \varkappa_0)/2]. \tag{11}$$

Equation (10) can conveniently be used for values of time causing the series to converge rapidly. A formula convenient for small times can be obtained by expanding the right hand side of (6) in powers of $\exp(-\sqrt{p})$ and using the inverse Laplace transformation on only the first few terms. However, formula (10) does not present any real computational difficulties for times down to 100 hrs.

DISCUSSION OF THE RESULTS

Equations (8) – (11) can be used to find the quantity L and the difference $\Delta\mu = DL/\ell E$ in ion mobilities from the experimental datax (ℓ is the length of the column). In the case that $\lambda_n^2 \gg 1$, $\alpha \ll 1$ and $\kappa_0/2 \ll 1$, which applies to all our experiments, the concentration at the cathode as a function of the time for which the current was on is given by the relation

$$\Delta c = \frac{L}{4}\left[1 - \sum_{n=0}^{n=\infty} \frac{8}{\pi^2(2n+1)^2}\exp\left[-\frac{\pi^2 D(2n+1)^2}{4l^2}t\right]\right] \tag{12}$$

The sum of the concentration changes in both isotopes, Δc is proportional to L, which agrees well with the experimental data shown in Fig. 4.

In order to find L, the mixture of mercury isotopes was considered to consist of two parts: the lighter one included the isotopes Hg^{196}, Hg^{198}, Hg^{199}, and Hg^{200} and was 50.14% of the whole, while the heavier part consisted of all the other isotopes. In this case, the changes in the concentrations of each component are the sum of the changes Δc_i in each isotope, and can be obtained from the mass spectrometer measurements, taking the Δc_i to be linear functions of the molecular weight of the isotope.

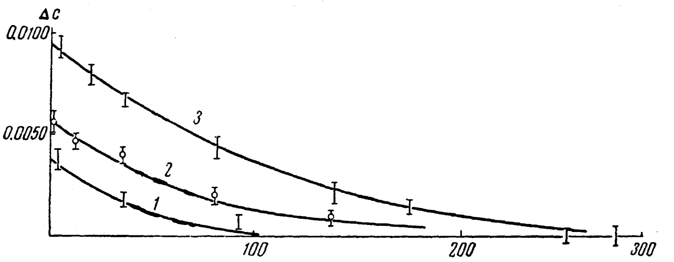

FIG. 5. Distribution of isotope concentration along the mercury column. 1 — t = 340; 2 — t = 700; 3 — t = 1800 hrs.

A value of L was calculated from each experimental value of $\Delta a/a_0$ whown in Fig. 2, and the average taken. The averages so obtained are: $L = 0.24 \pm 0.02$ for 6 volts and 41° C and $L = 0.08 \pm 0.007$ for 2 volts at the same bath temperature.

Using the Einstein relation $\mu = D\epsilon_0/kT$, where ϵ_0 is the charge on an electron, we obtain the relative difference in isotope mobilities as $\Delta\mu/\mu = (1.3 \pm 0.1) \times 10^{-3}$ when the temperature of the mercury column is 115° C, and $\Delta\mu/\mu = (1.1 \pm 0.1) \times 10^{-3}$ at 45° C, the temperatures inside the capillary being obtained by calculation. The average values of L so found were used to obtain $\Delta a/a_0$ as a function of time. The results are shown in Fig. 2 (curves a and c).

Using the calculated values of L the concentration along the mercury column was computed for a potential difference of 2 volts and for three values of time: t = 340, 700, and 1800 hours. The results are shown in Fig. 5, which also shows the experimental data. The sum of the changes in the concentrations of the light and heavy components is plotted on the Y axis, while the X axis shows the length of the capillary in millimeters. From Figs. 2 and 5 it is clear that the agreement between experiment and the results of the calculations is good.

For our experiments, the characteristic time

$$t_0 = \frac{4b^2}{D\,[1 + (2\lambda_n)^2]} = \frac{4l^2}{\pi^2 D}, \tag{13}$$

turns out to be about 5000 hours. From (13) it follows that t_0 does not depend on the magnitude of the applied electric field, and, what is more important, decreases as the square of the length of the isotope column, so that in order to decrease the time required for the experiment, one should use shorter capillaries.

For the stationary case, as $t \to \infty$, the distribution of concentration assumes the form

$$c = \frac{1}{2}\left[1 - \tanh\frac{x - x_0}{2}\right]. \tag{14}$$

It follows that the ratio of concentrations at the cathode is

$$\frac{c}{1-c} = \frac{c_0}{1-c_0}\exp\left[\frac{\Delta\mu}{\mu}\frac{\varepsilon_0}{kT}El\right]. \tag{15}$$

In Ref. 10, thermodynamic arguments about the separation of isotopes in a dc electric field led to a similar equation, with $\Delta\mu/\mu$ being replaced by the relative difference in molar volumes of the isotopes, $\Delta V/V$, which leads to a difference in their specific charges. The difference in the mobility of the ions can be explained, as suggested by Bresler and Pikus, by a difference in their effective radii due to the different amplitudes of thermal motion in the two isotopes, and reduces essentially to a difference in molar volumes.

It is important to notice that, as follows both from Fig. 2 and Refs. 7 and 5, the isotope separation effect increases with increasing temperature. Hence we must presume that $\Delta V/V$ increases with temperature faster than the first power of T. However, it does not seem possible to explain such a temperature behavior. One must conclude, presumably, that the difference in molar volumes is not the only effect which plays an important role in the conentration changes induced by the flow of direct current.

The data available in the literature allow one to calculate $\Delta\mu/\mu$ for mercury, gallium, potassium, and indium. The results of the calculation are presented in the table, together with the results obtained in the present experiments. In the table, β is defined to be $\Delta\mu/\mu \times m/\Delta m$. It is the relative difference in mobilities per unit relative difference in the isotope masses. The temperature shown is that of the bath, except for the experiments on potassium and those on mercury reported here. For these, the temperature of the column of isotopes itself is shown. The calculation of $\Delta\mu/\mu$ for mercury and gallium, using the data of Refs. 2 and 4, was carried out by Bresler and Pikus,[9] without taking into account the smoothing of the concentrations produced by diffusion. The same method was used to obtain $\Delta\mu/\mu$ for mercury from the results of Ref. 3; the boundary conditions in the other experiments were such that relation (12) could be used. From the table it is evident that the various values of $\Delta\mu/\mu$ for mercury are all of the same order of magnitude. The lack of complete agreement is presumably due to approximations in the calculations on the results of Haeffner,[2] and of Haeffner, Sjöborg and Lindhe.[3] In these calculations, it is difficult to take proper account of the volume of mercury at the end of the capillary opposite from the reservoir.

Material	$\Delta\mu/\mu$	β	T, °C	Literature
Hg	$1.1 \cdot 10^{-3}$	$0,73 \cdot 10^{-1}$	45	Present work
	$1.3 \cdot 10^{-3}$	$0.86 \cdot 10^{-1}$	115	
Hg	$0.7 \cdot 10^{-3}$	$0,5 \cdot 10^{-1}$	15	[2]
Hg	$2.0 \cdot 10^{-3}$	$1.3 \cdot 10^{-1}$	47	[3]
Ga	$3,6 \cdot 10^{-3}$	$1.3 \cdot 10^{-1}$	48	[4]
Ga	$1,4 \cdot 10^{-3}$	$0.5 \cdot 10^{-1}$	52	[5]
	$3,6 \cdot 10^{-3}$	$1.3 \cdot 10^{-1}$	287	
K	$0,5 \cdot 10^{-3}$	$0.1 \cdot 10^{-1}$	158	[6]
In	$0.14 \cdot 10^{-3}$	$0.8 \cdot 10^{-2}$	210	[7]
	$0.9 \cdot 10^{-3}$	$5 \cdot 10^{-2}$	530	

In conclusion we note (15) implies that when saturation has been reached, it is not necessary to know the coefficient of self diffusion in order to calculate $\Delta\mu/\mu$ (and hence L). If the size of the effect at saturation is known, the diffusion coefficient can then be obtained by comparing the experimental time dependence of Δc with (12).

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