Bündel um so enger sind, je größer die Zahl der Atome im Molekülion ist, so daß von den üblichen Dubletts das ($^{12}C^1H_4 - {}^{16}O$) am stärksten gefälscht wird. Die Untersuchungen führten auch zu einer Erklärung der Unstimmigkeiten in der erwähnten Arbeit von Mattauch und Bieri[5], obwohl dort kein so deutlicher Gang aufgetreten war.

Maßnahmen zur Vermeidung des Fehlers

Zur Vermeidung des Fehlers wurde zunächst eine allgemeine Theorie der Justierung[17] aufgestellt, die eine systematische Justierung auf Doppelfokussierung ermöglicht.

Um die Feldstärkeabhängigkeit der vorderen Magnetfeldgrenze zu kompensieren, wird man außerdem die Apparatur bis einschließlich zur Magnetfeldblende gegen Magnetfeld und Platte einer Eichung entsprechend querverschieben müssen, wenn die Feldstärke geändert wird, damit die Justierung erhalten bleibt.

Nach Aufdeckung des systematischen Fehlers planten wir sogleich, durch Veränderung des Kraftlinienverlaufs im Ionenrohr die Bündel beim Radialfeldeintritt breiter zu machen als die dort zu denkende virtuelle Aperturblende, die durch den Kanal gegeben ist. Jordan[18] erreichte dies offenbar durch ein magnetisches Hilfsfeld zwischen Kanal und Präzisionsspalt.

Im Hinblick auf eine zuverlässige Konstanthaltung der Apertur planten wir ferner, den Kanal von 0,15 mm Breite auf eine Bohrung von 1 mm ϕ zu erweitern und die Aperturbegrenzung durch die Magnetfeldblende und eine enge Radialfeld-Austrittsblende vorzunehmen.

Wir rechnen damit, daß die beschriebene Fälschung der Resultate durch die angegebenen Maßnahmen vermieden wird.

Wir danken Herrn Dr. R. Bieri für wertvolle Ratschläge und Herrn H. Wende für seine Mitarbeit bei den Aufnahmen; beiden danken wir für die Hilfe beim Ausmessen der Platten am Mikroskop.

[17] F. Everling, erscheint demnächst.

[18] E. B. Jordan, Phys. Rev. **60**, 710 [1941].

The Isotope Effect of a Direct Electric Current through Liquid and Solid Metals

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The isotope separation effect of a direct electric current in a liquid metal is demonstrated by passing a current through mercury, which is enclosed in a capillary tube. The second part of the paper deals with an attempt of establishing an isotope effect when a direct current is passed through an uranium wire.

If a direct current is passed through liquid mercury enclosed in a capillary tube the light mercury isotopes are enriched at the positive end of the capillary. This effect was reported in an earlier paper[1] and it has since then also been demonstrated in gallium by Nief and Roth[2] and in potassium by Lundén, Reuterswärd and Lodding[3]. Klemm[4] has treated the effect theoretically. In the first part of the present paper another mercury experiment will be described. The second part deals with an attempt of establishing an isotope effect when a direct current is passed through an uranium wire.

The mercury experiment was done in a cell according to Fig. 1. The diaphragm tube, connecting the anode and the cathode compartments of the cell, was 170 mm long and had 1 mm inside diameter. The tube was filled with small glass spheres (0.09 – 0.12 mm diameter). The anode volume, above the diaphragm, contained 115 mg Hg, the diaphragm itself about 36 mg Hg per cm length and the cathode volume 18.230 mg Hg. Between the inner and the outer glass tubes a stream of

[1] E. Haeffner, Nature, Lond. **172**, 775 [1953].

[2] G. Nief and E. Roth, C. R. Acad. Sci., Paris **239**, 162 [1954].

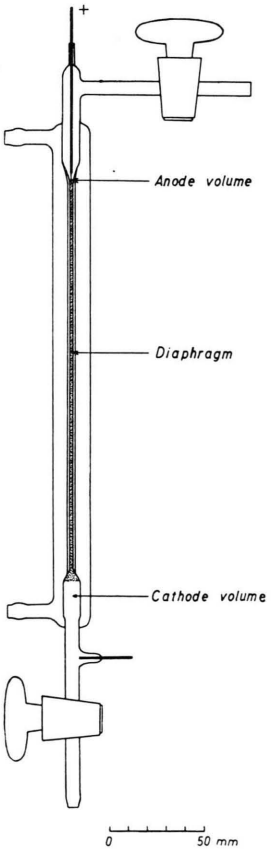
[3] A. Lundén, C. Reuterswärd u. A. Lodding, Z. Naturforschg. **10 a**, 924 [1955].

[4] A. Klemm, Z. Naturforschg. **9 a**, 1031 [1954].

water at a temperature of $47.0 \pm 0.5^\circ$ C was passed. The current through the cell was kept constant at 4.3 amp. The voltage across the tungsten electrodes was then 5.8 V. The experiment lasted 42 days. Immediately after the current was shut off the diaphragm was divided in parts of about 10 mm each. The ratio Hg^{198}/Hg^{204} in the mercury contained in the anode and cathode volumes and six of the diaphragm samples has been measured with a mass spectrometer. The measurements were carried out by Dr. H. v. Ubisch and Mr. S. E. Sälg in the mass spectrometer group of our laboratory. The result is given in Table 1 and Fig. 2.

The distance of the samples from the anode, given in Table 1 and Fig. 2, is the distance from the top end of the diaphragm to the middle of the analysed diaphragm sample. The isotope analysis was done with a reproduceability of 0.2% in the figures given.

It is interesting to note the very steep isotope concentration gradient in the diaphragm near the anode. The maximum enrichment of Hg^{198} to Hg^{204} is reached in sample nr 2 and corresponds to a separation factor of 1.093. The low enrichment in the anode mercury can to some extent be due to a weak contact between this and the rest of the mercury in the diaphragm.



← Fig. 1. Mercury cell.

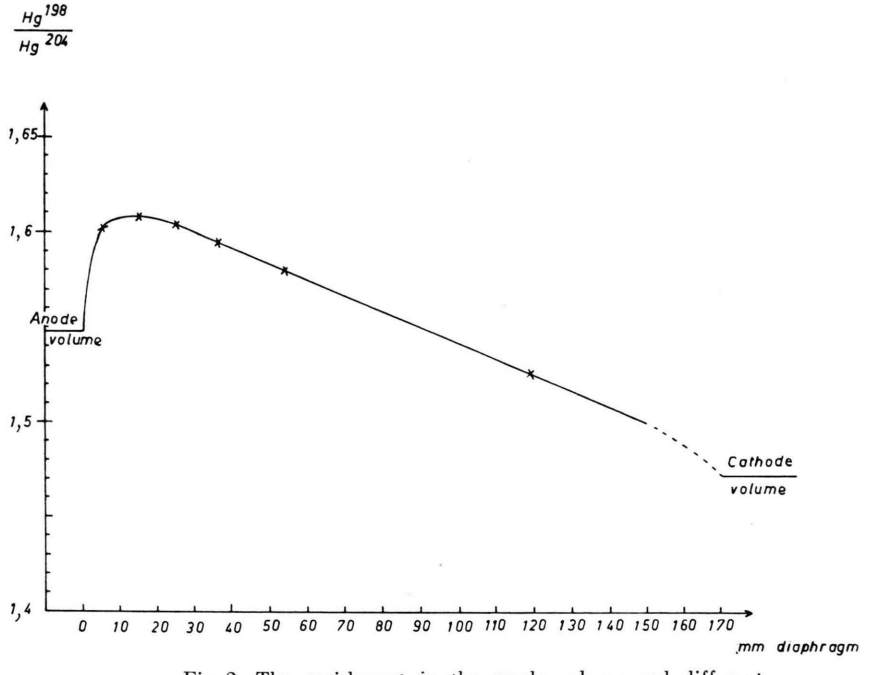


Fig. 2. The enrichment in the anode volume and different samples along the diaphragm.

Sample	Distance from anode, mm	Hg^{198}/Hg^{204}
Anode volume	—	1.548
nr 1	5	1.603
„ 2	15	1.608
„ 3	25	1.604
„ 4	36	1.595
„ 5	54	1.580
„ 6	119	1.526
Cathode volume	170	1.472

Table 1.

The Uranium Experiment

Experimental

An uranium wire was prepared in the workshop of the laboratory by alternatingly heating and rolling a piece of uranium rod. The diameter of the wire prepared was 1 mm with a tolerance of 0.1 mm.

A length of 347 mm of this wire was inserted in a 'Pyrex' glass tube as shown in Fig. 3. The apparatus was filled with argon which then was purified by its circulating through the heated uranium turnings in

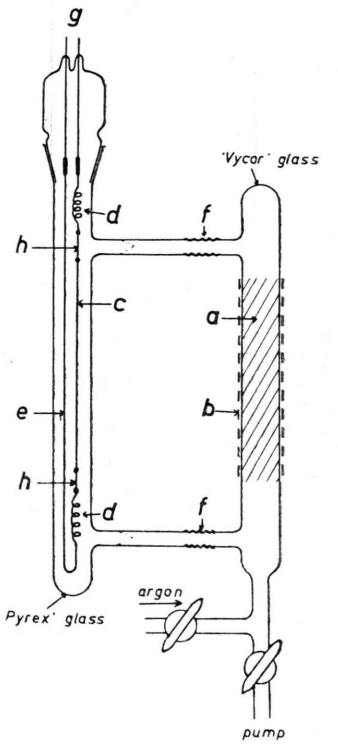


Fig. 3. Glass apparatus for containing the uranium wire and purifying the argon gas.

a) uranium turnings, b) heating coil, c) uranium wire, d) copper springs, e) copper support, f) graded seal between 'Vycor' and 'Pyrex' glass, g) tungsten terminals, h) platinum wire connections.

an attached 'Vycor' tube. After a sufficient time elapse the wire tube was sealed off and the terminals connected to a direct current source. The current through the wire was 16.8 amp. and the voltage across the end points was 5.6 V. Because of the varying diameter the wire had a temperature varying between 750° C and 870° C as determined with an optical pyrometer. The current was shut off after 171 days and the wire was divided in 35 pieces. 13 of these samples were treated in the following way.

The piece of wire was dissolved in nitric acid and the uranium extracted from the solution with diethylether. From the ether solution the uranium was reextracted into a water phase and then precipitated as uranium peroxide at p_H 2.5 with hydrogen peroxide. By heating in a furnace at 800° C the uranium peroxide was transformed to U_3O_8. A part of this was carefully weighed and then dissolved in nitric acid. The solution was diluted in a volumetric flask to 25 ml and 100 λ of this solution was placed on a platinum disk. Above the solution on the disk vapors of ammonia was blown which dissolved in the water and caused the uranium to precipitate on the disk as ammoniumdiuranate. The water was evaporated and the disk was heated for 3 minutes at 800° C.

By this technique it was possible to get a thin, even layer of uranium oxide, with carefully known weight, on the platinum disk. Three sources were prepared in this way from each sample. It was thus possible to determine the specific α-activity of the uranium, and this was done in an α-scintillation counter. The result is given in Fig. 4 where the specific activities of the samples are plotted along the wire, at the midpoints of the pieces of wire analysed. The errors in the measurements are calculated to be ± 6 pulses per minute and mg U as shown below.

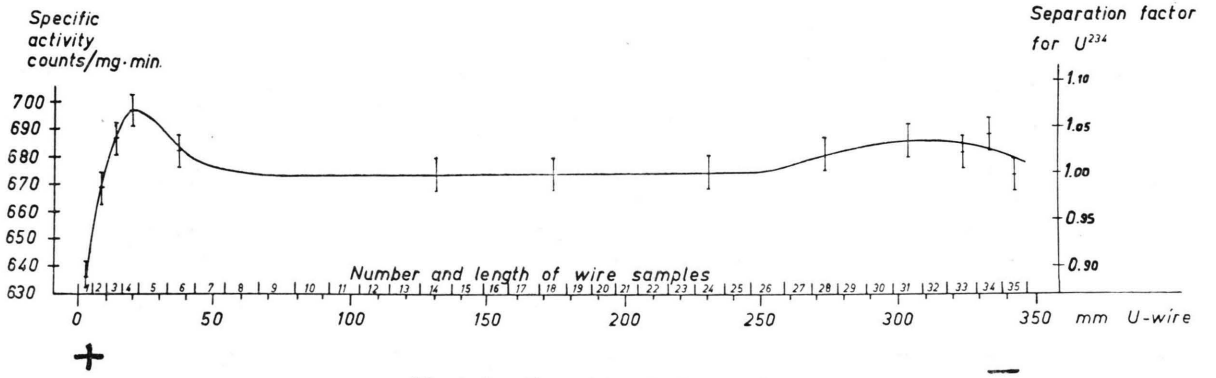


Fig. 4. Specific activity of wire samples.

Determination of errors

The following symbols are used:

I = measured α-activity (pulses/min.),
A = specific α-activity (pulses/min. mg),
m = uranium weight (mg),
V = volume of volumetric flask (ml),
v = volume of micropipette (ml),
F = conversion factor U to U_3O_8,
μ = the momentary efficiency of the α-detector at each measurement,
μ_0 = the nominal efficiency of the α-detector, determined as the mean value of 18 measurements of a standard source,
n = number of micropipette volumes.

The specific α-activity can then be written

$$A = (I V/m\, n\, v)\, F(\mu_0/\mu).$$

After differentiating

$$\frac{\Delta A}{A} = \frac{\Delta (I V/m\, n\, v)}{I V/m\, n\, v} + \frac{\Delta F}{F} + \frac{\Delta (\mu_0/\mu)}{\mu_0/\mu}.$$

The first term on the right side can be interpreted as the error of preparing the sources starting from uranium oxide. The second term is the error associated with the chemical procedure of preparing oxide from the metal samples and the last term is the error of the α-measurements owing to the instability of the α-counter.

The first term was determined in the following way. U_3O_8 was prepared by heating nuclear pure UO_4 at 800° C for one hour. From this oxide 10 carefully weighed samples were taken. These were dissolved in nitric acid and each solution diluted in a volumetric flask to 25 ml. Three sources were prepared from each solution in the same way as previously described. The sources were measured in an α-scintillation counter to about 10.000 pulses. The counter was controlled by measuring a standard source between the other sources. The mean value of the three sources prepared from each sample is given in table 2. It was found a maximum deviation of 5 (0.77%) and a standard deviation of ± 2.5 (0.38%).

The term $\Delta F/F$ has not been determined in connection with this work but the procedure of obtaining pure U_3O_8 has been throughly investigated elsewhere[5] and $\Delta F/F$ is here not supposed to exceed ± 0.1%.

[5] J. J. Katz and E. Rabinowitch, The Chemistry of Uranium, New York 1951.

Sample No.	Uranium mgs	Spec. activity c/mg. min
1	0.1533	652
2	0.1574	648
3	0.1621	652
4	0.1763	652
5	0.1743	657
6	0.1520	653
7	0.1596	653
8	0.1557	655
9	0.1730	657
10	0.1754	652
		Mean: 653

Table 2.

The stability of the α-counter was controlled with a standard source which was measured 18 times between counting the wire sources. The mean value of these standard determinations was 102.9 pulses per minute. Each determination was made with a statistical error of 0.5% in the result. The maximum deviation was 0.7% and the standard deviation ± 0.4%.

The total error $\Delta A/A$ can then be reported to be ± 0.9% or ± 6 pulses per minute and mg U.

Discussion

Natural uranium consists of three isotopes all of which are α-active with half-lives given in Table 3[6].

Isotope	Spec. activity (pure isotope, counts/min. mg)	Half life, years	Abundance in natural uranium %
U^{234}	$1.370 \pm 0.009 \cdot 10^7$	$2.475 \cdot 10^5$	0.00579
U^{235}	$4.74 \pm 0.10 \cdot 10^3$	$7.3 \cdot 10^8$	0.719
U^{238}	738.8 ± 1.6	$4.51 \pm 0.01 \cdot 10^9$	99.28
Natural U	1501 ± 3	$2.221 \pm 0.004 \cdot 10^9$	

Table 3.

As the isotopes U^{234} and U^{235} have shorter half-lives than U^{238}, it is clear, that an increase in abundance of the lighter isotopes means an increase of the specific activity of the uranium. The wire samples were all treated in the same way and measured under the same conditions, i. e. in the same geometry and the same α-counter. The increase in specific activity at the ends of the uranium wire is thus

[6] E. H. Fleming jr., AECD-3395.

indicating an enrichment of U^{234} and U^{235} in both ends of the wire or at least in the more pronounced maximum near the positive terminal. The separation factor for the isotopes U^{234} and U^{238}, given in Fig. 4, is calculated with the approximation that the whole increase of spec. activity is assigned to U^{234}. In another experiment (wire length 10 cm), carried out in the same way, the analysis showed the same characteristic increase of the specific activity at both ends of the wire. It is also possible to calculate the enrichment of U^{235} from the spec. α-activities if a linear dependence of the enrichment with the isotope mass difference is assumed. It seems better however not to say anything about the U^{235} content until an analysis can be done with a more direct method as fission counting or mass-spectrometry.

If the found effect is real, the enrichment near the positive terminal is the expected effect according to the mercury experiments; the enrichment at the negative end can be explained as due to uranium migration in the vapor phase from the positive end, where a decrease in weight and spec. activity is noticed in the first sample.

Acknowledgement

The experiments were done at the Department of Technical Electrochemistry at the Royal Institute of Technology, Stockholm, and we thank the director of this department, Professor Gösta Angel, for his kindness to place laboratory facilities at our disposal.

Der Isotopieeffekt bei der elektrolytischen Wanderung von Li-Ionen in geschmolzenem Lithiumnitrat

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Durch Elektrolyse von geschmolzenem Lithiumnitrat wurde an der Anode ^7Li im Verhältnis zu ^6Li angereichert. Die relative Differenz der elektrolytischen Wanderungsgeschwindigkeiten dieser beiden Isotope ergab sich zu 0,77%. Der Masseneffekt beträgt also

$$\mu = -(0{,}050 \pm 0{,}013) \quad (95\% \text{ Wahrscheinlichkeit}).$$

Der Masseneffekt ist größer als derjenige, welcher bei der Wanderung der K-Ionen in geschmolzenem Kaliumnitrat gefunden wurde[1]. Der Grund dafür wird diskutiert.

Hoover und Holloway[2] haben gezeigt, daß man die Li-Isotope durch elektrolytische Überführung in geschmolzenem Lithiumnitrat anreichern kann. Sie haben jedoch keine Bestimmung des Masseneffektes durchgeführt. Wir haben deshalb ihren Versuch mit einigen für die μ-Bestimmung geeigneten Modifikationen wiederholt.

Bei unseren Versuchen wurde das schwere Li-Isotop im geschmolzenen Lithiumnitrat (Schmelzpunkt 255°, Leitfähigkeit $\varkappa = 1{,}1\ \Omega^{-1}\text{cm}^{-1}$ bei 300° C[3]) an der Anode angereichert. Die Versuchsanordnung war derjenigen des Kaliumnitrat-Versuches[1] sehr ähnlich (vgl. Abb. 1). Das Elektrolysiergefäß bestand aus Supremaxglas, das von geschmolzenem Lithiumnitrat wenig angegriffen wird, da es einen kleinen Na-Gehalt besitzt[4]. Als Diaphragma im Trennrohr diente Quarzpulver. Die Anode bestand aus einem in ein Glasrohr eingeschmolzenen Platindraht[5] (Graphit[6], Aluminium, rostfreier Stahl, Tantal, Wolfram und Palladium, welche ebenfalls als Anodenmaterial in Betracht zu ziehen waren, erwiesen sich als ungeeignet). Als Kathode

[1] A. Lundén, C. Reuterswärd u. N. Sjöberg, Z. Naturforschg. **10a**, 279 [1955].

[2] J. I. Hoover u. C. E. Holloway, NRL 3897 (1951).

[3] Landolt-Börnstein, Physikalisch-Chemische Tabellen (5. Aufl.) H. W. II, 1063.

[4] G. Schulze, Z. Elektrochem. **17**, 509 [1911]; Ann. Phys., Lpz. (4) **37**, 435 [1912]. — B. Siede, Glas u. App. **18**, 163 [1937]; Chem. Abstr. **32**, 2699 [1938].

[5] A. Bogorodski, J. russ. phys.-chem. Ges. **37**, 703 [1905]; Zentralblatt 1905: 2,954.

[6] I. Z. Moltkehansen, Handbuch der technischen Elektrochemie (hrsg. von V. Engelhardt) III, 90.