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SEPARATION OF URANIUM ISOTOPES BY ELECTROMIGRATION IN FUSED URANIUM TETRACHLORIDE

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SEPARATION OF URANIUM ISOTOPES BY ELECTROMIGRATION IN FUSED URANIUM TETRACHLORIDE

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ABSTRACT

Separation of uranium isotopes by countercurrent electromigration in fused uranium tetrachloride has been demonstrated on a laboratory scale. A separation factor of 1.005 ± 0.001 was obtained between cathode and anode samples with an average current of 0.13 amperes for 116 hours; this value corresponds to an electromigration separation coefficient of 1.00036 ± 0.00007.

SEPARATION OF URANIUM ISOTOPES BY ELECTROMIGRATION IN FUSED URANIUM TETRACHLORIDE

Recent experiments have demonstrated that isotopes may be separated by countercurrent electromigration in fused salts (4,9,10). Results of a number of experiments have been correlated by a semiempirical theory developed by Klemm (8). Since no data were available on electromigration in tetrahalide salts, evaluation of the separation coefficient for uranium isotopes by direct measurement was desirable. The series of electromigration experiments by Klemm, et al., served as a guide for the experimental work, a combination of Klemm's procedures being selected for the experiment on uranium tetrachloride described in this report.

CONCLUSION

The single significant experimental result on electromigration of uranium isotopes in fused uranium tetrachloride is in agreement with the result calculated from Klemm's semiempirical correlation. The agreement is quite good in view of the experimental difficulties, the extrapolations of molecular weight and valence, and the assumptions as to the identity of the migrating ionic species which were necessary in order to apply Klemm's formula.

EXPERIMENTAL

Basic Theory of Operation

Concentration of isotopes by countercurrent electromigration depends upon the difference in mobility of isotopic ions in an electric field (2,11). The flow of cations toward the cathode is opposed by a counter flow of electrolyte at a rate just sufficient to balance the total flow of cations. Under these conditions, the more mobile isotopic ions move toward the cathode, while the slower moving species are carried back toward the anode by the counter flow. Thus, the cathode compartment is enriched and the anode compartment is depleted in light component, and a concentration gradient is developed by diffusion. The rate of concentration change at each electrode is inversely proportional to the uranium inventory in the electrode compartment.

In fused salt cells, reflux at the proper flow rate is achieved by allowing the cathode product to react with the gaseous anode product. In the present case, chlorine from the anode is made to flow over the cathode surface, regenerating uranium tetrachloride which then flows hydrostatically back toward the anode.

Thermal remixing of isotopic concentrates is suppressed by the use of a porous packing between the electrode compartments. The packed section of the cell is referred to as the separation tube.

Materials

The electrolyte was prepared from normal assay uranium tetrachloride containing 2 ± 0.5% volatile impurity and less than 0.01% metallic impurity. Most of the volatile impurities were removed at 375 ± 25°C. by sublimation into a vacuum trap. A further conditioning of the electrolyte was accomplished during the early stages of electrolysis by reaction with tank chlorine at atmospheric pressure. Some properties of the electrolyte (5) are as follows: melting point, 590 ± 1°C.; vapor pressure, 34 mm. Hg at 615°C. Commercial grade chlorine and argon were used without purification.

Equipment

Details of the fused quartz electromigration cell are shown in figure 1. The anode compartment was especially large to accommodate the initial charge of powdered electrolyte. The cathode compartment was designed to hold 1 to 3 grams of electrolyte, the small volume permitting a rapid change of isotopic concentration.

The separation tube was packed with quartz powder which had been sieved and cleaned. Fritted ends of the tube were prepared from 90-mesh powder and quartz wool, which were sintered in place. Permeability of the tube was such that a pressure differential of 2 psi. across it would cause an electrolyte flow of 2 cc./min.

Electrodes which would withstand attack by the electrolyte were prepared from carbon rods of high density, 2.7 ± 0.1 g./cc. These were degassed at 630°C. and stabilized with chlorine at atmospheric pressure.

Heaters on upper sections of the cell were provided for the periodic melting of electrolyte which had been sublimed or entrained by flowing chlorine. A timing device was used to activate the heaters for 1.5 minutes in each 90 minutes. This melt-down prevented plugging of outlet tubes b and c of figure 1 and also restored the inventory of electrolyte.

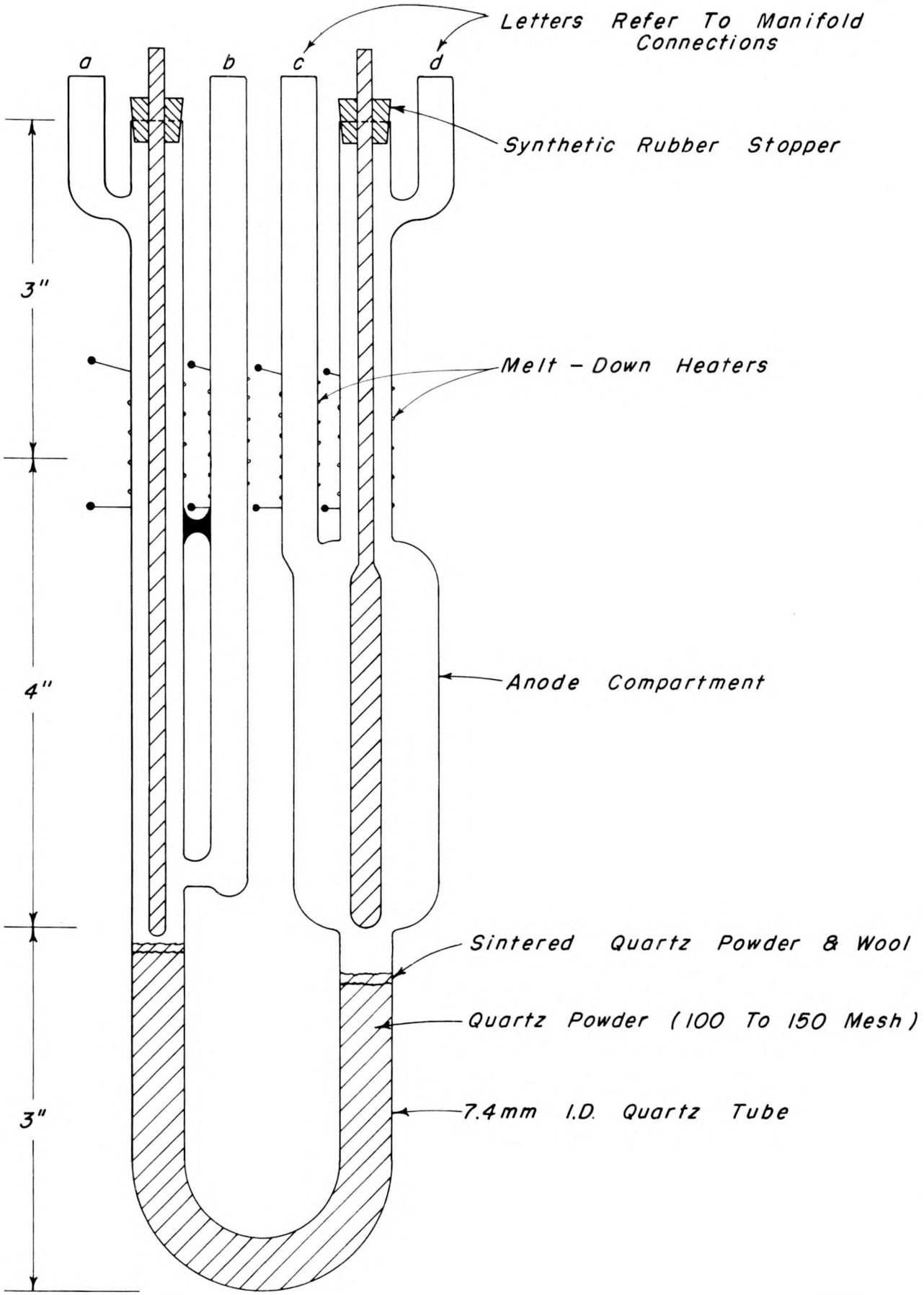
Gases entering and leaving the cell were controlled through a manifold which is schematically shown in figure 2. The flow of tank chlorine to the manifold was regulated by means of a microadjustable needle valve of nickel construction.

The cell temperature was manually controlled to ±5° by a Variac and tube furnace. Details of the furnace are shown in figure 3. Temperatures were measured by means of a thermocouple probe and potentiometer.

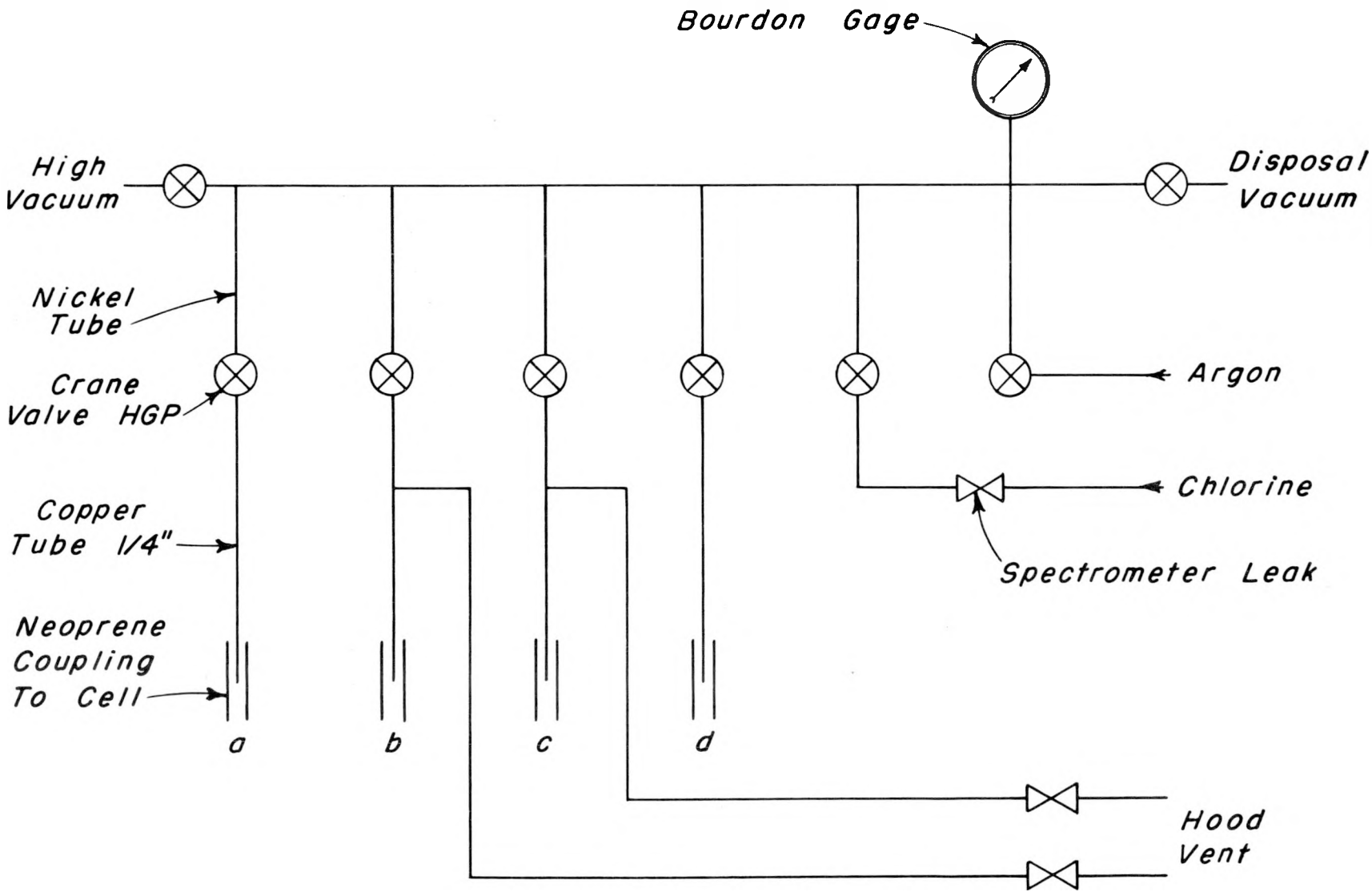
Electrolytic power was supplied from a full-wave vacuum tube rectifier equipped with an accurate milliammeter.

Procedure

The equipment assembly was placed in operation as follows. Manifold and cell were leak tested, then degassed for 24 hours at a pressure of 10^{-5} mm. Hg and a furnace temperature of 650°. During the next 12-hour period an

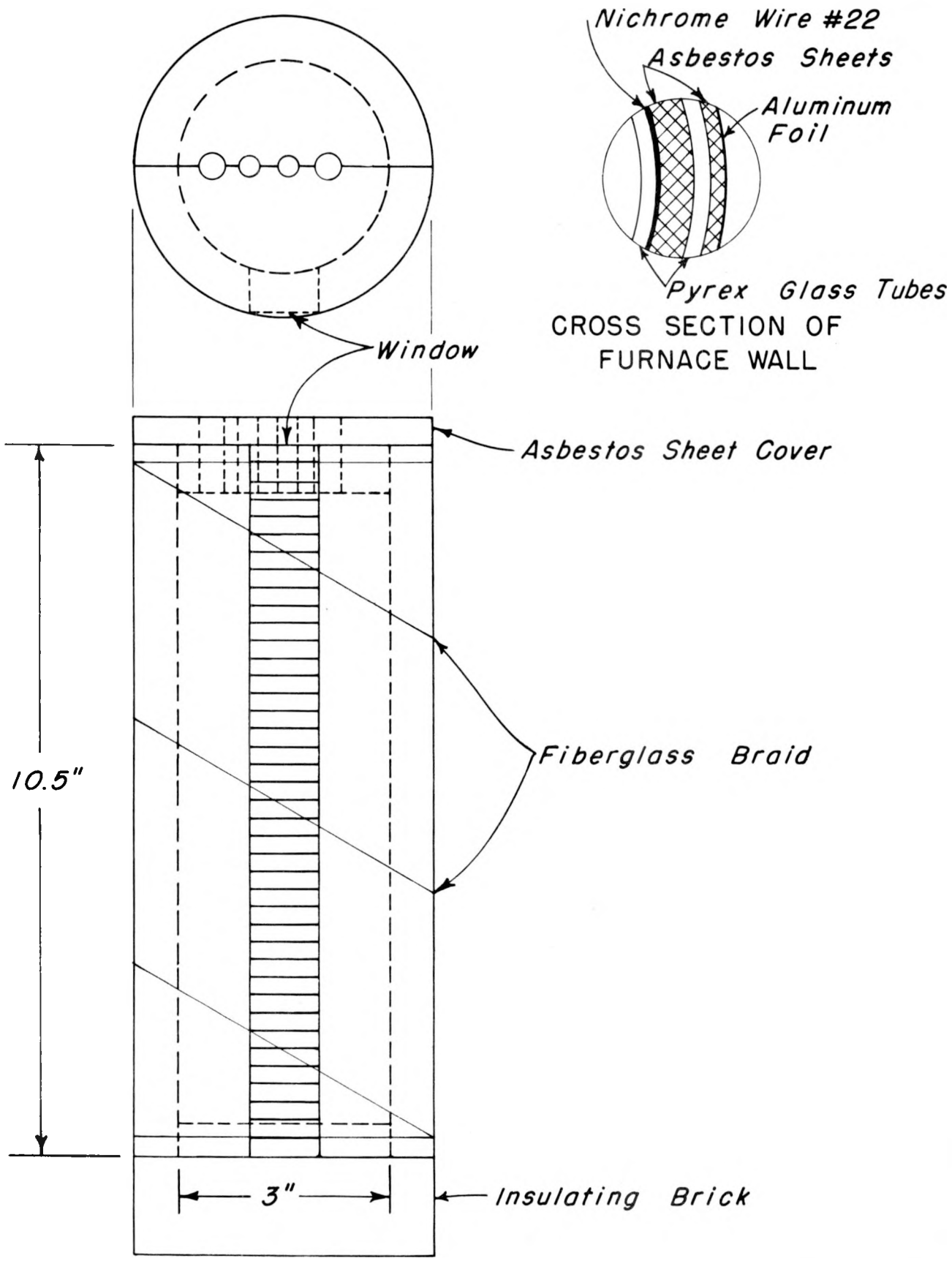


ELECTROMIGRATION CELL
FIGURE 1



SCHEMATIC ASSEMBLY OF MANIFOLD

FIGURE 2



TUBE FURNACE
FIGURE 3

atmosphere of chlorine was flushed in and out of the system, following which the temperature was lowered to 450°. A flow of chlorine, 10 to 20 cc./min., was used to protect the cell during removal of the anode and transfer of 35 ± 5 g. of powdered electrolyte into the anode compartment. The electrolyte was melted at 590 ± 1° and the temperature was set at 615°. Molten electrolyte was forced through the separation tube into the cathode using a pressure differential of 2 psi.

Electrolysis was started with a low current which was increased as conditions in the cell permitted. Intermittent electrolysis was started when the rapid formation of bubbles in the separation tube diminished. Gases from the anode were initially vented to the hood and tank chlorine, 1 cc./min. excess, was circulated to the cathode. This procedure served to purify or stabilize the electrolyte. The electromigration run was begun when resistance of the cell had dropped to approximately 500 ohms. At this point the gas circulation system was isolated and sufficient chlorine was added to maintain 1 psig. pressure. As conductance of the cell improved, the current was increased from 80 to 200 ± 20 milliamperes. Electrical equivalents used in the cell were computed from periodic reading of the milliammeter.

One short term run was made using the foregoing procedure, and, after adding more electrolyte, a second longer run was made. During the latter run a chlorine bleed was added to the circulating gas so that the vented excess was approximately 1 cc./min. This latter procedure eliminated the formation of semisolids at the cathode.

Upon conclusion of the runs the cathode was removed and the catholyte withdrawn into a tared sample tube which also served as a pipette. The changes in isotope concentrations were determined by mass spectrometer measurements.

RESULTS AND DISCUSSION

A number of experimental difficulties limited the length of experimental runs and probably reduced the accuracy of results. In the first run a hot spot developed in the separation tube near the cathode, and the run was stopped in order to avoid isotope remixing losses. The second run was terminated when a plug occurred in the outlet of the anode compartment causing an additional 1 gram of electrolyte to be forced into the cathode compartment. In each run the electrolyte developed a color gradient observable across the separation tube. The cathode end was darker and emitted fewer bubbles. These bubbles were assumed to be either chlorine or silicon tetrachloride; available thermodynamic data do not exclude the possibility of formation of the latter by reaction of the electrolyte with quartz. Chlorine might have been formed by the disproportionation of higher uranium chlorides produced at the electrolyte surfaces.

Experimental data and calculated results are summarized in table I. Changes in isotope concentration are tabulated as separation, R_t/R_o, where R_o is the initial ratio of light to heavy isotopes and R_t is the same ratio at time t. The analytical result of run 2 is statistically more significant

than that of run 1 due to the larger isotopic separation. The true value of the electromigration separation coefficient, i.e., the ratio of mobilities, is estimated to lie between 1.0002 and 1.0008. Methods used in calculating the separation coefficients are described in appendix A.

TABLE I

SUMMARY OF ELECTROMIGRATION RUNS

Run No.	Time, hrs.	Average Current, amp.	Catholyte Weight, g.	Diffusion Distance, $\sqrt{\pi D' t}$, cm.	Separation, R_t/R_o	Separation Coefficient
1	34	0.16	1.5	4.2	1.002 ± 0.002	1.00028 ± 0.00028
2	116	0.13	2.5	7.7	1.005 ± 0.001	1.00036 ± 0.00007
Estimated for ionic species U^{+4} and Cl^-						1.00045 (a)
Estimated for ionic species UCl^+_3 and Cl^-						1.00024 (a)

[a]See appendix A.

Agreement between the experimentally determined values of the coefficient and those estimated from Klemm's relationship in appendix A is remarkably close in view of the experimental difficulties and the extrapolations by molecular weight and valence which were necessary.

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Experimental work was completed December, 1954.

Appendix A

Electromigration Separation Coefficients

The electromigration separation coefficient is defined as the ratio of the mobilities or velocities of migration of the two isotopic ions being separated. Using Klemm's nomenclature, the coefficient is w_1/w_2, where the subscripts refer to the light and heavy isotopic ions respectively. The following relation has been derived by Klemm (6,8) to permit the experimental evaluation of the coefficient.

$$\left[\frac{w_1}{w_2} - 1\right] = \frac{\Delta N_1}{N_1 N_2} \frac{Fqn}{It} \qquad (1)$$

where N_1 and N_2 are the mole fractions of the light and heavy isotopes in the starting material, F is the Faraday equivalent, q is the valence of the migrating ion, I is the current in amperes, t is the time in seconds, n is the total number of moles concentrated in the catholyte, and ΔN_1 is the change in N_1 accomplished in the catholyte by electromigration.

In the present experiment, it was assumed for simplicity that the fused uranium tetrachloride was ionized to form U^{+4} ions, though it is doubtful if dissociation really proceeds this far. For uranium of normal assay, $N_1 = 0.007205$ and $N_2 = 0.992747$. The factor ΔN_1 can be expressed in terms of the ratios R_t and R_o which are measured by the mass spectrometer as follows:

$$\Delta N_1 = \frac{R_t - R_o}{(R_t + 1)(R_o + 1)}$$

$$= \frac{\left[\frac{R_t}{R_o} - 1\right]}{\left[\frac{R_t}{R_o} + \frac{1}{R_o}\right](R_o + 1)} .$$

This quantity had the value 1.43×10^{-5} and 3.58×10^{-5} for runs 1 and 2 respectively.

In the calculation of the electromigration separation coefficient from these data, it is necessary to make a correction for the diffusion of the separated material back into the separation tube. This diffusion tends to decrease the apparent number of moles of material concentrated in the catholyte. Klemm (7) calculated that this diffusion effect extended into the separation tube a distance $\sqrt{\pi D' t}$ cm., where D' represents a coefficient of combined diffusive and convective mixing. The concentration gradient over this distance is approximately linear. For the present calculation it was assumed that the value of D' for the uranium (IV) ions was the same

as that measured by Klemm (1) for thallous ions in molten thallous chloride, 4.6 x 10-5 sq. cm./sec. The total number of moles of isotope concentrate obtained in the experimental runs, n, was calculated as follows. For run 1,

$$n = (1.5 + \frac{0.587\sqrt{\pi D't}}{2})/380 = 0.0072 ,$$

since for this run the catholyte weighed 1.5 g., the separation tube contained 0.587 g. electrolyte per centimeter, and the average enrichment in the portion subject to back diffusion was half as much as the catholyte enrichment.

For run 2, a further correction was necessary to allow for the surging of 1 g. of electrolyte into the cathode compartment from the separation tube:

$$n = \left[2.5 + (0.587\sqrt{\pi D't} - 1)\left(\frac{0.587\sqrt{\pi D't} - 1}{2 \times 0.587\sqrt{\pi D't}}\right)\right] \Big/ 380 = 0.0102$$

The latter terms adjust the length and concentration gradient in the separation tube for the loss of 1 g. of electrolyte concentrate.

These values were substituted in equation 1 to obtain the values of the electromigration separation coefficient shown in table I.

The coefficients may be compared with one calculated from Klemm's semi-empirical relationship:

$$\frac{\Delta w}{\bar{w}} \simeq \frac{w_1 - w_2}{w_2} = 0.15 \frac{2.1m^-}{2.1\, m^- + m^+}\left[\frac{m_2^+ - m_1^+}{m^+}\right] \qquad (2)$$

The constants in this equation were evaluated from separation data on the molten chlorides of lithium, zinc, cadmium and thallium (8), m^+ and m^- being the gram atomic weights of the cationic and anionic species respectively. The value of $\Delta w/\bar{w}$ for the species U^{+4} and Cl^- is 4.515×10^{-4}; if the species UCl_3^+ and Cl^- are assumed, the coefficient has the value 2.36×10^{-4}.

In Klemm's treatment, the cationic velocities are measured with respect to the anions. In Westhaver's corresponding theory for aqueous electrolytes 2 ,11), cationic velocities are measured with reference to the solvent, water. Thus, Westhaver obtains an expression similar to equation 1 with the total current, I, replaced by I t^+, where t^+ is the transport number of the positive ion. In a fused salt, if velocities w^- and w^+ are measured with respect to bulk electrolyte, then relations of equation 3 are obtained:

$$\frac{w^+}{w^+ + 4\, w^-} = t^+; \quad \bar{w} = \frac{N_1W_1 + N_2W_2}{N_1 + N_2} \simeq W_2 \text{ since } N_2 >> N_1$$

$$\left(\frac{\Delta w}{w_2}\right)_{Klemm} \simeq \left(\frac{\Delta w}{\bar{w}}\right)_{Klemm} = \frac{\Delta w^+}{w^+ + 4w^-} = \frac{\Delta w^+}{w^+}\, t^+ \qquad (3)$$

Thus, the expression for $\frac{\Delta w^+}{w^+}$ in a fused salt would be identical to Westhaver's for aqueous solution, as expected. Unfortunately, a value for t^+ in fused uranium tetrachloride is not available. Klemm assumed in several of his papers that t^+ is unity for cations in fused salts, though recent work on lead chloride by Duke and Laity (3) indicates that a value of t^+ below unity should be used .

It is the value of $\frac{\Delta w^+}{w^+}$, rather than $(\frac{\Delta w}{w})_{Klemm}$, which is used in Westhaver's cascade theory (11).

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