MOUND LABORATORY PROGRESS REPORT FOR OCTOBER, 1963

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The Mound Laboratory Progress Report, issued monthly, is intended to be a means of reporting items of current technical interest in research and development programs. To issue this report as soon as possible after the end of the month, editorial work is limited; and since this is an informal progress report, the results and data presented are preliminary and subject to change.
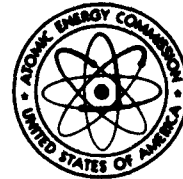
These reports are not intended to constitute publication in any sense of the word. Final results either will be submitted for publication in regular professional journals or will be published in the form of MLM topical reports.

The previous reports in this series are:

MLM-1176
MLM-1175
MLM-1170
MLM-1160
MLM-1157
MLM-1155

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SUMMARY

Adhesives and Plastics Research

Adhesives   Two new flexible, conductive polysulfide-epoxy adhesives were evaluated. Both formulations were filled with carbon black and silver. The specific resistivities of the cured formulations remained at approximately 0.1 ohm-centimeter during a test period of three months. When the samples were heated to 160°F for six hours, the resitivities increased irreversibly; therefore, these formulations would be unsatisfactory for use above 160°F.

The tensile strength for three conductive silicone adhesives was below the strength of comparable polyurethane adhesives.

Radioelements

Promethium Separation and Purification   Ion exchange separations of rare earth elements are being investigated for the purification of promethium. Neodymium, used as a substitute for promethium, was separated from samarium. Two methods, elution with either hydrochloric acid or alpha-hydroxy-isobutyrate seem promising.

Half-life of Polonium-208 and Polonium-209   During the past year, 18 power measurements were added to the half-life calculations for the calorimetric polonium-208/polonium-209 half-life sample. The most probable half-lives have increased from 1052.38 to 1053.50 days for polonium-208, and 13.05 to 16.11 years for polonium-209. The number of internal probable errors has also increased from 4.75 to 8.16, an unusually high value which is based on 100-year half-life. Power measurements will be continued, probably for an additional year, to confirm a band-spectra measurement indicating 15.5 ± 3 mass per cent polonium-209 in the sample.

Uranium-234 Separation and Purification   Uranium-234 is separated from aged plutonium-238 solutions by ion exchange and solvent extraction techniques. The ratio of mass 234/238 in the sample was determined by mass spectrography to be 63.5.

The determination of uranium in plutonium is being investigated by controlled potential coulometry and a spectrophotometric method in which the color is developed with 4-(2 pyridylazo) resorcinol (PAR). Quantitative results were obtained by controlled potential coulometry with five milligrams of uranium. Beer's law was followed from 0 to 300 micrograms of uranium complexed with PAR.

Half-life of Plutonium-238   In a five-month study the half-life of plutonium-238 was determined calorimetrically to be 87.5 ± 0.3 years, rather than the currently accepted value of 86.4 years.

Potassium Plutonium Sulfate Dihydrate   This compound is being studied as a potential primary calorimetric standard for plutonium. An equation was developed for $K_4Pu(SO_4)_4 \cdot 2H_2O$ solubility, which is affected by the formation of various sulfatoplutonate complexes. A 30-gram sample has been prepared and is being analyzed by mass spectrometry, alpha counting techniques, and calorimetry.

Isotope Separation

Carbon-13   A six-stage cascade system of six hot-wire columns and two concentric-tube columns for the separation of carbon-13 from netural methane is approaching steady state. The enrichment of gas from the middle of the sixth stage has increased to 66 per cent carbon-13 in the total carbon in 85 per cent methane.

Complete static thermal diffusion data have been obtained for carbon monoxide with various carbon isotopes; the column, 24 feet long with a 3/4-inch ID, contains a 1/16-inch hot wire at 500°C. The data were analyzed statistically to find ratios of the coefficients in the isotope transport equation.

Curves were drawn from a combination of theoretical tray requirements and height-equivalent-theoretical-plate (HETP) data. With these curves the actual required column length can be selected for any given recovery of carbon-13 from carbon monoxide feed. The time required for a column to reach steady-state operation can be reduced by one method with the use of a tapered column. A second method employs a straight column of the size required by reflux ratio considerations; a higher than normal boil-up is used, and the feed is introduced at progressively higher points in the column.

Xenon   An eight-column, four-stage, hot-wire thermal diffusion unit was used in an overlap arrangement between columns; fission xenon was used as feed to deplete the xenon-131 content. Xenon-131 was reduced to 1.7 per cent in the final product.

Krypton-85 is being separated from xenon by gas chromatography. In three experiments the ratios of xenon in the feed to xenon in the trap were 1701, 971, and 752.

Trennschaukel   A detailed investigation of Van der Waerden's Trennschaukel theory uncovered an error in the determination of the relaxation time. The necessary equations have been derived for an asymmetrical coefficient matrix and will be solved by a computer.

Collision Integrals   Collision integrals are being calculated for a generalized potential function of the following form:

$$(r) = Ae^{-ar} - Ce^{-cr} - B_1 r^{-6} - B_2 r^{-8} - B_3 r^{-10}$$

Low-temperature Thermal Diffusion Factor   The thermal diffusion factor is important for theoretical calculations because of its sensitive dependence on the intermolecular potential function. Because of the increasing quantum effects below room temperature, its value in this range is of special interest. An experiment to measure the thermal diffusion factor over the temperature range of 10-250°K is being performed using a two-bulb apparatus. The preliminary design for the two-bulb apparatus is complete. Corrections are being calculated for the final gas composition to compensate for the gas in the tube which connects the two bulbs. This factor was ignored in earlier work reported in the literature.

Alpha and Neutron Source Development

Neutron Sources   The neutron growth rate for a one-gram PuBe source was calculated to be 1.1 per cent per year with a standard error of 0.4 per cent per year. Two PuBe sources were newly fabricated, and 18 recanned PuBe sources were returned to their users.

Alpha Sources   Alpha source windows are destroyed by direct contact with appreciable amounts of polonium as a result of damage by recoil fragments from alpha decay. Four one-curie polonium alpha sources were fabricated on September 20, 1963. The windows were gold or stainless steel, and the distance of the window from the polonium deposit was varied. The sources were stored separately for periodic wipe checks for leakage. On October 15, 1963, all four sources were wipe free. The test will be continued through at least one polonium half-life.

Techniques are being developed for the fabrication of large area, high specific activity plated alpha sources. These sources will have a minimum activity of one curie per square centimeter; they must retain 95 per cent of their activity over one or two polonium half-lives.

Analytical

Low-level Tritium Counting   A vacuum system has been completed for the analysis of gas samples containing as little at 5×10^{-13} mole per cent tritium. The precision for an analysis (which requires four hours) of 10^{-11} mole per cent is ± 4 per cent.

Adhesive formulations are being developed for specialized applications. The cured formulation must be flexible at low temperatures, and it must retain its tensile strength at high temperatures. In addition, the properties of diallyl phthalate formulations are being evaluated to help produce superior plastic parts.

Adhesives

Two new flexible, conductive polysulfide-epoxy adhesives, CS-18 and CS-19 (Mound Laboratory designation), were formulated and evaluated. Table 1 lists their compositions and the composition of CS-17 previously described. All formulations were cured and held at room temperature. Measurement of specific resistivities began one day after gluing and continued at irregular intervals for three months. The specific resistivity of the CS-17 formulation remained essentially constant at about 0.1 ohm-centimeter during this period. The specific resistivity of CS-18 dropped from about 1.5 ohm-centimeter to 1.2 ohm-centimeter, and the resistivity of CS-19 dropped from 0.56 to 0.28 ohm-centimeter.

Table 1

COMPOSITION OF FLEXIBLE POLYSULFIDE-EPOXY CONDUCTIVE ADHESIVES

Component	CS-17	Component in Formulation (wt %) CS-18	CS-19
LP-3[a]	14.4	14.4	10.6
DMP-30[b]	0.7	0.7	1.1
Hysol 2038[c]	- -	3.6	- -
Epon 820[d]	7.2	- -	- -
DER 332[e]	- -	- -	8.0
Butyl glycidyl ether	- -	- -	2.7
Continex CF black[f]	6.7	6.7	6.7
J-2 silver powder[g]	71.0	71.0	71.0

[a] Polysulfide prepolymer (Thiokol)

[b] 2,4,6-Tri (dimethylaminomethyl) phenol (Rohm and Haas)

[c] Epoxy resin (Hysol Corp.)

[d] Epoxy resin (Shell Corp.)

[e] Epoxy resin (Dow Chemical Co.)

[f] Conductive carbon black (Witco Chemical Corp.)

[g] Engelhard Industries

To determine the effect of heat on the specific resistivity of these formulations, samples which were conditioned for three months at room temperature were heated at 160°F for six hours and cooled to room temperature. Then their resistivities were determined. Large increases in specific resistivities were noted with all formulations. The resistivity for the CS-17 sample rose from 0.13 to 99.2 ohm-centimeters, for the CS-18 sample from 9.78 to 494 ohm-centimeters, and for the CS-19 sample from 0.28 to 54 ohm-centimeters.

These increases were irreversible: After the samples stood for two weeks at room temperature there was no decrease in resistivity. From these data it was evident that polysulfide-epoxy formulations of this type would be electrically unacceptable for use at or above 160°F.

Three conductive silicone adhesives J2-102, G3-102, and G3-602 were tested for tensile strength. The values obtained were 44, 105, and 171 psi, respectively. All values were below the values obtained for comparable polyurethane adhesives (300-400 psi).

Basic and applied research on a number of radioelements is being conducted to determine the physical properties, develop analytical techniques, and study the basic radiochemistry involved. Of particular interest are alpha emitters, their decay chains, their isotopes, and their chemical homologs.

Promethium Separation and Purification

The separation of promethium from a contaminated solution is being studied. A literature search was made for various methods of separating promethium from samarium and americium, which are likely to be the principle contaminants in solution. Two methods for removing each contaminant were selected. Americium may be separated from promethium by the hydrochloric acid method[1] or by the thiocyanate method.[2] Samarium may be separated from promethium by the lithium nitrate method[3] or by the alpha-hydroxy-isobutyrate method.[4] All four methods are based on ion exchange.

All of the methods suggested for the separation of promethium from its contaminants were originally studied using tracer quantities of americium, promethium, and samarium. Small columns (frequently 1 mm ID) and finely divided resin (200-400 mesh) were used. The samples were transferred to the columns by means of a drop of resin. Little work has been done with weighable amounts of elements using these methods, and few attempts have been made to separate milligram quantities of promethium. In a recent article,[5] F. Weigel (University of Munich) briefly described the separation of promethium from americium and samarium and the subsequent reduction of promethium to the metal. He chose the thiocyanate method to separate promethium and americium, and the alpha-hydroxy-isobutyrate method to separate promethium from samarium.

The hydrochloric acid method is based on the ability of a cation exchange resin to adsorb promethium from 12 normal hydrochloric acid, while americium is eluted with the same solvent. Trivalent elements, such as americium and presumably iron (III), which form chloro complexes, should be eluted from the resin leaving only the rare earth. Elements of lower valence would probably be separated along with the americium since lower valence cations should not be held as strongly as trivalent ions. By this method rare earths could also be separated from a large group of other cations, leaving the rare earth in a hydrochloric acid solution.

The thiocyanate method involves retention of the americium (as thiocyanate complex) or an anion exchange resin; promethium (and presumably other noncomplexed elements) are eluted through the column. Two molar NH_4SCN is suggested, although Weigel used eight molar NH_4SCN. This separation would be effective only for elements sufficiently complexed by thiocyanate to be retained on an anion exchange resin. The number of such elements is not large, and there is a problem of disposing of the NH_4SCN. This method does not have the potential of the hydrochloric acid method.

The alpha-hydroxy-isobutyrate method appeared promising for the separation of promethium; and since the literature had indicated its superiority over the lithium nitrate separation, the latter method will not be studied further. The hydrochloric acid method and alpha-hydroxy-isobutyrate method were investigated on a milligram scale. Neodymium was used as a substitute because of its probable similarity to promethium. Figure 1 shows a typical elution of neodymium from BioRad 50W-X8 resin with 12 normal hydrochloric acid.

[1]K. Street Jr., and G. T. Seaborg, *J. Am. Chem. Soc.*, **72**, 2790 (1950).

[2]J. P. Surls Jr., and G. R. Choppin, *J. Inorg. & Nucl. Chem.*, **4**, 62-73 (1957).

[3]Y. Marcus and F. Nelson, *J. Phys. Chem.*, **63**, 77 (1959).

[4]G. R. Choppin and R. J. Silva, *J. Inorg. & Nucl. Chem.*, **3**, 153-54 (1956);

H. L. Smith and D. C. Hoffmann, *J. Inorg. & Nucl. Chem.*, **3**, 243-47 (1956).

[5]F. Weigel, *Angew. Chem.*, **75**, 451 (1963).

Figure 1. *Elution of Neodymium and Zinc from BioRad 50W-X8.*

0.488 mmoles of Neodymium on column

Zn Elution

Nd Elution

12 N HCl	1:1 HCl
30% Nd	70% Nd

Amount Eluted (mmoles)

Number of 5ml Washes

9901

6
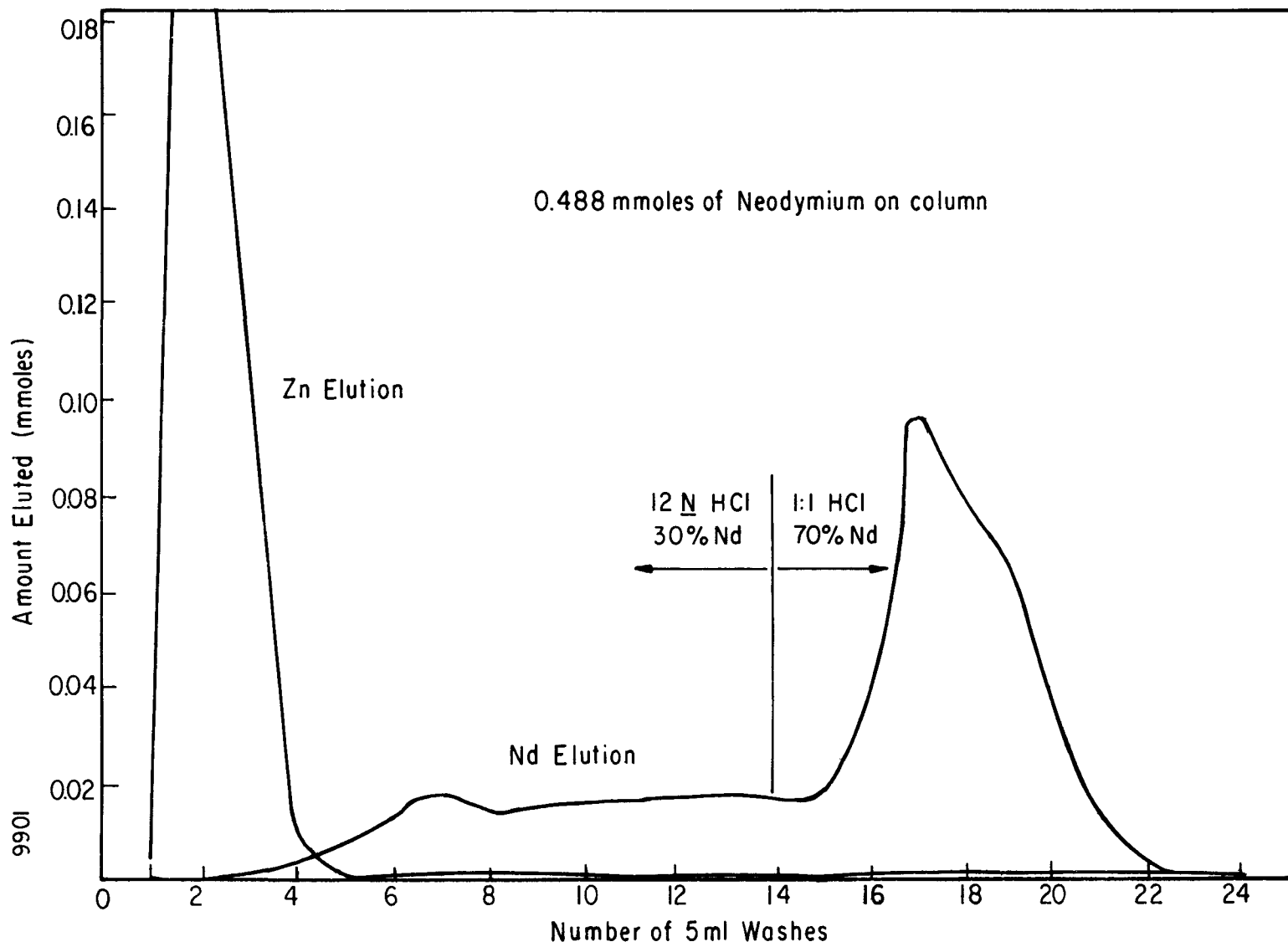
Neodymium is adsorbed by the resin, but it is eluted slowly, the elution does not occur in a sharp peak as desired. The rare earth content of each five-milliliter increment—as measured by EDTA titration—was plotted against the number of increments. The neodymium appears at the third five-milliliter wash, which is also the third column volume. The neodymium content of each wash increases until a relative steady state is reached, somewhat less than 0.02 millimoles per column volume. Then neodymium can be quickly removed from the column with 1:1 hydrochloric acid.

Figure 1 also shows the elution curve of zinc under identical conditions. Zinc is removed quickly. This behavior is characteristic of a divalent metal ion, and it may be typical of other divalent ions. Similar behavior is predicted for americium. The behavior of neodymium in this elution study is not entirely unexpected since, even on a tracer scale, the band of eluted promethium shows noticeable broadening.

It appears possible to separate neodymium from americium and some divalent cations by the hydrochloric acid method, although some of the neodymium was lost. Whether the behavior of promethium would be analogous to neodymium is questionable; however, the difference would probably not be great where americium is involved. The behavior of neodymium with other resin types (Dowex 50W-X8 and BioRad 50W-X4) was investigated and found to be similar to the behavior with BioRad 50W-X8.

Alpha-hydroxy-isobutyrate has been found superior to other acids, such as citric and lactic acids, for promethium-samarium separations, at least on a tracer scale. Preliminary experiments with this method have now been completed, and it appears that the method will be satisfactory for a promethium-samarium separation. A six-inch column with two milliliters of BioRad 50W-X4 resin was loaded with samarium and promethium. With 0.35 molar alpha-hydroxy-isobutyrate at pH 5 and pH 4 there was no separation. At pH 4, however, there was a broadening of the rare earth band, indicating that separation had begun. At pH 3.5, 0.5 molar alpha-hydroxy-isobutyrate gave a definite separation (Figure 2) on an eight-inch column washed with 10-milliliter volumes of eluant.

The rare earth content was found by EDTA titration. A significant difference occurred in behavior of the neodymium and samarium. The samarium eluted in a sharp band, while the neodymium eluted in a diffuse band. This order of elution agreed with that reported for separation on a tracer scale, but the separation factor was not as large. No mention is made in the literature of the integrity of the eluted bands. The diffuse band of neodymium was similar to the elution of this element from cation exchange resins with 12 normal hydrochloric acid, indicating that promethium may not be analogous to neodymium in the hydrochloric acid method. The difference may be greater than expected; the ionic radius of promethium is almost the mean of of the ionic radii of neodymium and samarium, but it is closer to samarium.

The elution of samarium from an eight-inch column at pH 3.5 is relatively efficient. The amounts eluted were 0.13 millimole of samarium and 0.26 millimole of neodymium. First, the elements were adsorbed onto two milliliters of resin from an ammonium acetate solution; then the resin was filtered and mechanically transferred to the column. The curve was similar to that shown in Figure 2. Separation of the samarium occurred between tenth and sixteenth washes. Hot alpha-hydroxy-isobutyrate was used as eluant until all the samarium eluted; then the elution continued with cold solution. Hydrochloric acid (1:1) quickly removed the neodymium from the resin.

For the samarium-promethium separation Weigel used Dowex 50W-X12 in a column equilibrated at 87°C. According to a journal article 50W-X4 is equally efficient at room temperature.[6] During his separation Weigel lost nearly 70 per cent of the promethium in the starting material.

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[6]H. L. Smith and D. C. Hoffmann, *J. Inorg. & Nucl. Chem.*, **3**, 243-47 (1956).
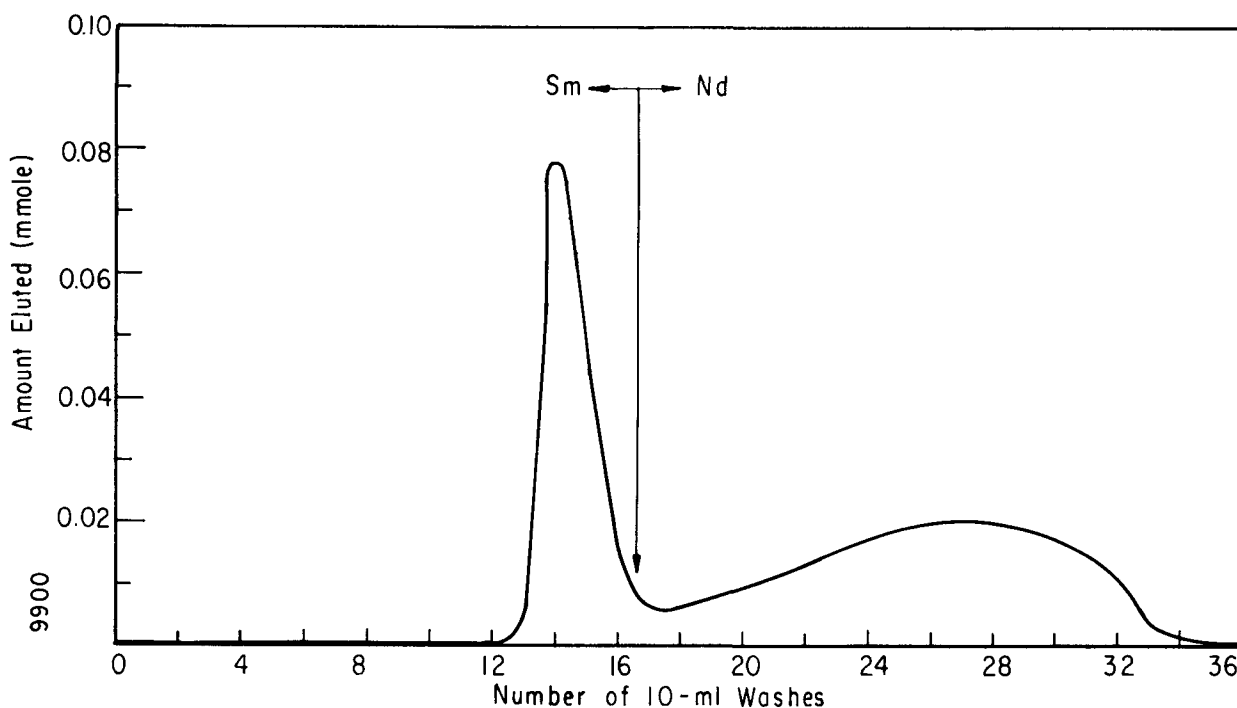
Figure 2. *Elution of Samarium and Neodymium With a 0.5 M
Alpha-hydroxy-isobutyrate at pH 3.5.*

Half-life of Polonium-208 and Polonium-209

During the past year eighteen power measurements were added to the half-life calculations of the polonium-208-polonium-209 half-life. sample.[7] Table 2 shows the calculations made from the latest measurements (Cf. MLM-1157). Two measurements with large deviations were dropped; thus, the sum of the deviations squared is smaller than before. The most probable half-lives have increased from 1052.38 to 1053.50 days for polonium-208 and from 13.05 to 16.11 years for polonium-209. It is more significant to calculate the increase in the number of probable errors from the most probable half-life of polonium-209 to a half-life of 100 years, the currently accepted value. The number of probable errors (internal) has increased from 4.75 to 8.16 as obtained by an equation reported earlier:[8]

$$ B = \frac{1}{P.E.S.O.} \sqrt{\Sigma di^2 \,(100 \text{ yrs}) - \Sigma di^2 \,(16.11 \text{ yrs})} $$

$$ = \frac{1}{0.8812} \sqrt{155.86 - 104.11} = 8.16 $$

An error of eight internal probable errors in calorimetry would set a precedent; therefore, the half-life of polonium-209 is less than 100 years and is probably no greater than 24 years (which is equivalent to three internal probable errors above 16 years).

[7]MLM-1157.
[8]MLM-1148.

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Table 2

HALF-LIVES OF POLONIUM-208 AND POLONIUM-209: 65 DATA POINTS
TAKEN BETWEEN OCTOBER 7, 1953, AND AUGUST 30, 1963
(CALORIMETER 60)

Assumed Half-Life of Po^{209} (yrs)	Most Probable Half-life of Po^{208} (days)	Most Probable Initial Power of Po^{208} (μw)	Most Probable Initial Power of Po^{209} (μw)	Sum of Deviations Squared [$(\mu w)^2$]	Probable Error in T 1/2 (Po^{208}) (days)
100.00	1057.598	21,484.20	153.25	155.864	0.1487
25.68	1055.496	21,434.86	204.56	114.571	0.1019
17.37	1053.910	-	-	104.505	-
16.47	1053.624	21,384.17	256.76	104.257	0.0954
16.11[a]	1053.497	21,380.54	260.49	104.108	-
14.00	1052.588	-	-	105.755	-

[a]Most Probable half-life of Polonium-209 (for which the P. E. S. O.,probable error per observation, is 0.8812 μ/watts).

If the gravimetric mass purity of 77 ± 2 per cent polonium-208 in the sample is correct,[9] the sample must contain something besides polonium-208 and polonium-209, because 23 per cent for polonium-209 is equivalent to a half-life of 133 years.

If the band-spectra measurement of 15.5 ± 3 mass per cent polonium-209 is correct,[10] the half-life of polonium-209 would have to be 100 years. The present calorimeter results call for 4.8 mass per cent polonium-209. Probably the 23 ± 2 per cent as determined gravimetrically is composed of two components, a nonradioactive component of 15.5 per cent as measured by band-spectra, and a radioactive component of five per cent as determined calorimetrically. The power measurements will be continued, probably for an additional year, until the band-spectra results are negated or confirmed. At that time, the sample will be opened and studied by other techniques, such as chemistry, alpha pulse height analysis, mass spectrometer analysis, and possibly by gravimetric analysis.

Uranium-234 Separation and Purification

Uranium-234 is being separated from aged plutonium-238 solutions by a combination of ion exchange and solvent extraction techniques. The aqueous strip from a hexone extraction was evaporated from about 600 milliliters to less than ten milliliters (MLM-1160, p. 17). During the evaporation a small amount of precipitate appeared, but when dilute nitric acid was added, a large flocculent precipitate formed. The major portion of this precipitate was insoluble in one-normal nitric acid.

Results of mass spectrographic analysis of a sample of a previously purified product are given in Table 3. The 234/238 ratio of 63.5 was determined from the average of ten scans. The values for masses 235 and 236 are from a single scan and thus are subject to greater error. However, since these values are low, the value of 98 per cent isotopically pure uranium-234 is accurate. Thus, it is feasible to obtain high isotopic purity uranium-234 samples from aged plutonium-238.

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[9]MLM-683.
[10]MLM-735.

Table 3

MASS SPECTROGRAPHIC ANALYSIS

Mass	Voltage Reading (v)	Amount Calculated (a/o)
234	23.25	97.98
235	0.078	0.33
236	0.036	0.15
238	0.366	1.54
	23.730	100.00

$234/238 = 23.25/0.366 = 63.5$

The determination of uranium in plutonium is being investigated by controlled potential coulometry and by a spectrophotometric method in which the color is developed with 4-(2-pyridylazo) resorcinol (PAR). Quantitative results were obtained by controlled potential coulometry with five milligrams of uranium. Beer's law was followed from 0 to 300 micrograms of uranium complexed with PAR in the spectrophotometric method.

Half-life of Plutonium-238

Two samples of plutonium-238 were prepared in May 1962 for calorimetric half-life studies. The samples, assayed in Calorimeters 39 and 90, had gross half-lives ranging from 88.2 to 89.0 years with internal probable errors as low as 0.1 year. After a correction was made for radioactive impurities, as determined by mass spectrometer, the half-life of plutonium-238 ranged from 87.1 to 87.9 years. The most probable value is 87.5 years ± 0.3 year (absolute probable error). This value indicates that the currently accepted value of 86.4 years is probably incorrect.

Potassium Plutonium Sulfate Dihydrate

Potassium plutonium sulfate dihydrate [$K_4Pu(SO_4)_4 \cdot 2H_2O$] is being studied as a potential calorimetric standard for plutonium. These investigations include solubility studies, stability studies, and determination of the plutonium-238 half-life by the specific activity method (Cf. above). The nearly complete solubility studies indicate that the solubility of $K_4Pu(SO_4)_4 \cdot 2H_2O$ is described by the following equation:

$$K_{sp} = \frac{[K]^4 \, \gamma^4 \, [Pu^*] \, [HSO_4{}^-]^4 \, \beta^4}{1 + K_1 [HSO_4{}^-] \, \beta + K_1 K_2 \, [HSO_4{}^-]^2 \, \beta^2 + K_1 K_2 K_3 \, [HSO_4{}^-]^3 \, \beta^3}$$

where K_1, K_2, and K_3 are successive stability constants of the sulfatoplutonate complexes; [Pu^*] is the plutonium concentration; γ is the fraction of potassium that is not complexed with $SO_4{}^{-2}$; and β is the fraction of total sulfate that exists as bisulfate.

Experimental results indicate that, at two molar $HSO_4{}^-$ concentration, the most predominant sulfatoplutonate complex is $Pu(SO_4)_3{}^{-2}$. Studies are planned at higher sulfate concentrations to determine if other sulfatoplutonate complexes exist.

The acidity study reported previously was performed using hydrochloric acid. Although for chloride concentrations up to two molar the plutonium-chloride complexation should be small, this work will be repeated using perchloric acid, which forms no known complex with plutonium. This study will also be extended to lower and higher acid concentrations. At lower acid concentrations the fraction of free sulfate will be increased, and the solubility should be decreased. At higher acid concentrations the formation of sulfatoplutonate acids should cause the compound to be more soluble.

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The half-life of plutonium-238 will be determined by the specific activity method using purified potassium plutonium sulfate. The compound is stoichiometric, and the isotopic ratio can be determined by mass spectrometry. Therefore, a known amount of plutonium-238 can be weighed into a vessel and analyzed for alpha activity by calorimetry or alpha counting techniques. From the specific activity, mass analysis, and stoichiometry of $K_4Pu(SO_4)_4 \cdot 2H_2O$, the half-life can be calculated.

Thirty grams of potassium plutonium sulfate have been prepared and recrystallized twice. The compound is now being analyzed for isotopic ratio, plutonium, sulfate, and impurities. Three grams of the compound will be weighed into each of ten calorimeter cans and calorimetered. The half-life will be calculated from these data.

A portion of the material from the half-life study will be placed in storage and analyzed periodically over a period of six months in order to verify the stoichiometric stability of the compound. The plutonium-239 derivative is also being prepared for a similar study. If these compounds are stable, potassium plutonium sulfate will be recommended as a primary standard for plutonium.

Processes are being developed for separating and purifying the isotopes of a number of elements including hydrogen, the noble gases, carbon, and uranium. Potential sources of supply of these materials are being evaluated.

Carbon-13

Measurement of Carbon Monoxide Transport Coefficients   Complete static thermal diffusion separation data have been obtained for carbon monoxide with various carbon isotopes; the column, 24 feet long with a 3/4-inch ID, contained a 1/16-inch hot wire at 500°C. The data were analyzed statistically to find ratios of the coefficients in the isotope transport equation:

$$r = Hc \ (1-c) - (K_c + K_D) \ \frac{dc}{dz}$$

where r is the isotope transport rate, c is the fraction of the desired isotope, and dc/dz is the isotope concentration gradient along the column. The coefficients H and K_c are functions of pressure:

$$H = H' \ p^2$$

$$K_c = K_c' \ p^4$$

For a static column at equilibrium:

$$\frac{L p^2}{\ln q} = \frac{K_D}{\ln q} + \frac{K_c'}{H'} \ p^4$$

where L is the length of the column (or column section) and q is the separation factor. Thus, the quantity $Lp^2/\ln q$ is a linear function of p^4.

The experimental static data for 17 points at pressures ranging from 150 to 550 torr were expressed in the linear form indicated above. A least squares fit to the data gave the following results:

TRANSPORT COEFFICIENT RATIOS FOR THE SEPARATION OF MASS 29 AND MASS 28 CARBON MONOXIDE

	K_D/H'	K_c'/H'
Experimental Ratio	23.55	1431
Calculated Ratio	21.05	1073

Also given in the table are ratios calculated using the thermal diffusion column shape factors of McInteer and Reisfeld.[11] The calculated values of the transport coefficients depend on the intermolecular potential function used in the calculation of the physical properties of carbon monoxide. Published values of these parameters are in conflict; hence, there is some uncertainty in the calculated values tabulated above.

Measurements of the separation factor as a function of flow rate for carbon monoxide isotopes were completed for pressures of 260 and 404 torr and are in progress for a pressure of 500 torr.

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[11]B. B. McInteer and M. J. Reisfeld, LAMS 2517, February 1961.

Carbon Monoxide Distillation The data reported previously on theoretical tray requirements for various carbon-13 concentrations and recoveries were combined with the height-equivalent-theoretical-plate (HETP) data for Podbielniak Heli-Pak 2917 to give the curves shown in Figure 3. These curves permit selection of actual column length required for any given recovery of carbon-13 from the carbon monoxide feed and for any given $C^{13}O$ concentration in the bottom product. For example, a column 38 feet long can produce 1.0 gram per day of carbon-13 as 90 per cent $C^{13}O$ with recovery of 60 per cent of the carbon-13 from the feed gas.

A long period of time is required from start-up until steady-state operation is reached. An inventory increase of carbon-13 in the column is required before draw-off can begin. The time required for the system to come to steady-state can be reduced by using a tapered column which narrows toward the product end or by using a series of several columns with progressively smaller diameters.

Another approach is the use of a straight column of the size required by reflux ratio considerations; with this system a higher than normal throughput is used, and the feed is introduced at progressively higher points in the column. This method is feasible since during the time when the bottom concentration is less than desired, fewer than the maximum number of theoretical trays are required.

Also, optimum feed location is near the bottom soon after start-up when the bottom concentration has increased only slightly from natural abundance and moves upward as the column approaches steady state. These various alternatives are being studied.

Xenon

Thermal Diffusion An eight-column, four-stage, hot-wire thermal diffusion unit was used in an overlap arrangement between columns; fission xenon was used as feed to deplete the xenon-131 content. After steady-state conditions were reached, the xenon product from the last stage was reduced to 1.7 per cent xenon-131. at a flow rate of three milliliters per hour. The xenon-136 concentration was 73 per cent.

This system is being modified to a "swing" arrangement between columns. The "swing pump" will be located at the end of the last stage. The gross "swing" volume will be 100 milliliters, resulting in a net transfer of 30 milliliters. The "swing pump" will operate on a ten-minute cycle initially.

A pilot model of the column to be used in the 24-column xenon tube bundle thermal diffusion system has been constructed. A series of tests will be made with this column to evaluate design and performance.

Experimental Chromatography Chromatography is being used as one method for separating krypton from xenon. Three additional experiments were conducted using a column filled with coconut charcoal adsorbent (50/60 mesh). The column was 2.54 centimeters in diameter and 19 centimeters long. Precooled helium was used as a carrier gas. The results are presented in Table 4.

Table 4

CHROMATOGRAPHIC SEPARATION OF KRYPTON-85 FROM XENON

Experiment	Kr^{85} in Feed (mole %)	Xe in Trap (mole %)	Kr^{85} in Trap (mole %)	Xe Feed/ Xe Trap	Xe Recovery (%)	Time for Xe Peak (min)
12[a]	2.13×10^{-5}	1.36×10^{-8}	1.25×10^{-4}	1701	80	111
13[b]	2.33×10^{-5}	2.40×10^{-8}	1.32×10^{-4}	971	84	159
14[b]	2.31×10^{-5}	3.07×10^{-8}	1.31×10^{-4}	752	83	156

[a]The column temperature was held at $193^\circ K$ until completion of the Kr^{85} peak; then it was allowed to rise to $243^\circ K$.

[b]The column was held at $193^\circ K$ until the Kr^{85} peak passed on the recorder and returned to about 5% of peak height; then it was allowed to rise to $243^\circ K$.
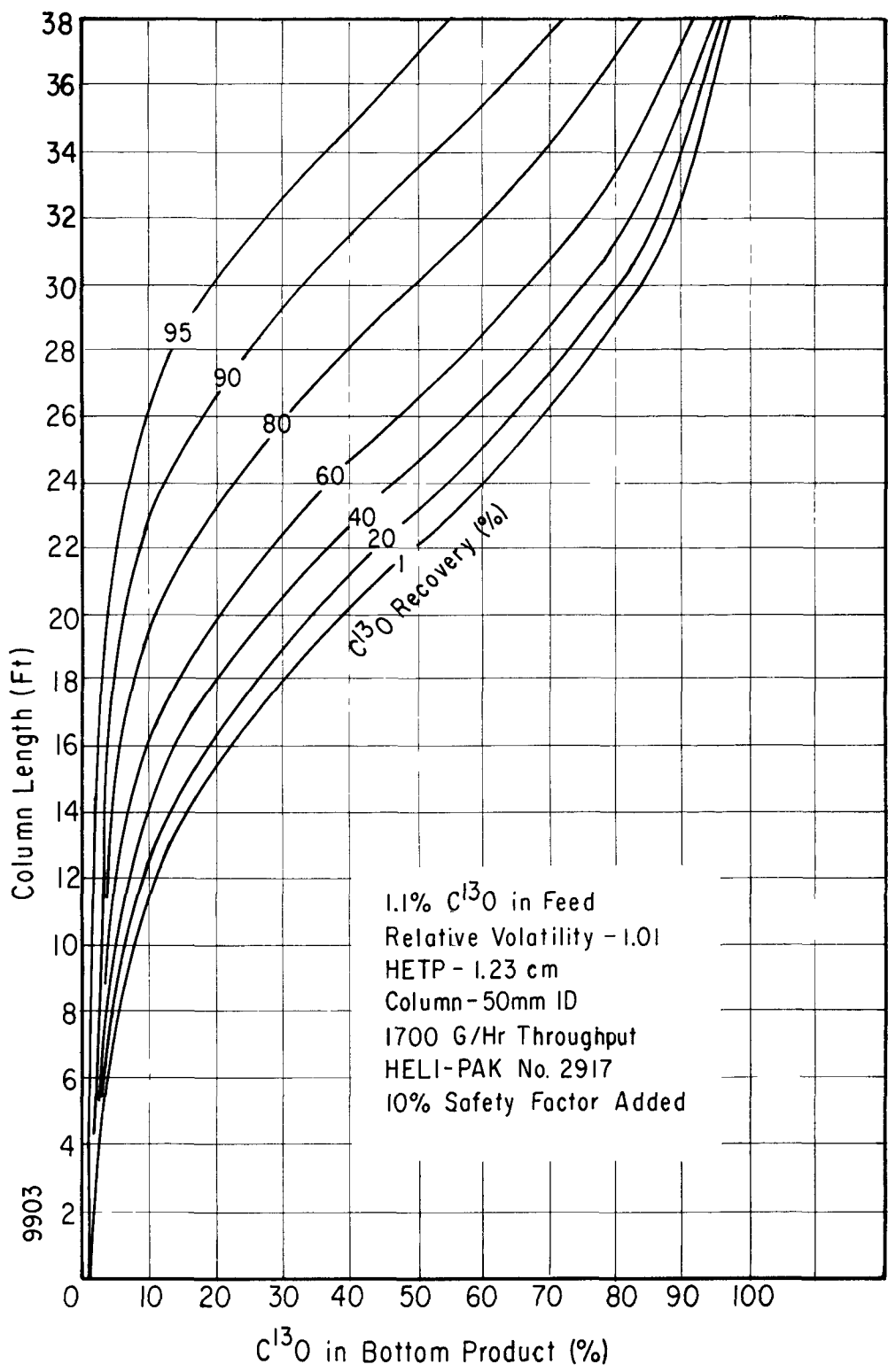
Figure 3. *Distillation Column Length for Separation of $C^{13}O$ From $C^{12}O$.*

The conditions of Experiments 13 and 14 were similar to those of previously reported experiments [MLM-1175]. The earlier experiments had an average ratio of 1822 for xenon in the feed to xenon in the trap, whereas the average of the present two experiments was 862. Also, the earlier experiments had higher recoveries. Additional runs will be made to confirm these results.

Trennschaukel

A "Trennschaukel," or swing separator, is being constructed to measure the thermal diffusion factor in the temperature range extending from -50°C to 1000°C. A detailed investigation of Van der Waerden's "Trennschaukel" theory has uncovered an error in the determination of the relaxation time. The theory expresses the transport in the n tubes and in the bellows by a set of $n+2$ linear differential equations with a solution of the form

$$u_j = C_1 e^{-\mu_1 t} \sin \lambda_1 j + C_3 e^{-\mu_3 t} \sin \lambda_3 j + \ldots$$

This may be expressed as an *eigenvalue* problem for the characteristic values $\mu_1, \mu_3, \ldots \mu_{\frac{1}{2}(n+1)}$. Van der Waerden assumes that the coefficient matrix is symmetric and , hence, that the *eigenvectors* are orthogonal. This assumption allows him to solve for the undetermined coefficients $C_1, C_3 \ldots C_{\frac{1}{2}n+1}$ in a relatively simple manner. The leading coefficient C_1 is used to evaluate the relaxation time of the system. Actually, the coefficient matrix is not symmetric, and the problem must be solved in a different manner. Fortunately, the system may be solved rigorously. The necessary equations have been derived and a numerical solution will be carried out by a Gauss-Jordan reduction on a computer.

Collision Integrals

Collision integrals are being calculated for a generalized potential function of the form

$$\phi(r) = A e^{-ar} - C e^{-cr} - B_1 r^{-6} - B_2 r^{-8} - B_3 r^{-10}$$

Margenau,[12] who originally proposed this function from theoretical considerations, calculated six of the parameters for the He-He interaction (he neglected the last term). Using Margenau's parameter, Yntema and Schneider[13] found that this potential gave values for the second virial coefficient of helium which were 27 per cent lower than their experimental values. In recent years, accurate calculations of both the short range and long range forces in He-He interaction have been made. This information is being reviewed in preparation for recalculating the above parameters.

During the past month an attempt was made to calculate the parameters in the following manner. At large separation distances, dispersion forces are predominant, and $\phi(r)$ is equal to the last three terms in the above function. Fontana[14] calculated B_1, B_2 and B_3 for this case, and his values were used without modification. The remaining four parameters were calculated from the equations:

$$\phi(r_o) = U, \quad \text{where } U > 0$$

$$\frac{d\phi}{dr} r_a = U', \quad \text{where } U' > 0$$

$$\phi(r_o) = -E, \quad \text{where } E > 0$$

$$\frac{d\phi}{dr} r_a = 0$$

[12]H. Margenau, *Phys. Rev.*, **56**, 1000 (1939).
[13]J. L. Yntema and N. G. Schneider, *J. Chem. Phys.*, **18**, 640 (1950).
[14]P. R. Fontana, *Phys. Rev.*, **123**, 1865 (1961).

The first two equations fit ϕ to a known value of the potential in the repulsive region. Amdur's scattering data were used to obtain this known value, i.e., U and U'.[15] The last two equations specify that ϕ must have a minimum value $(-E)$ at $r - r_a$. The values of E and r_a obtained by Mason[16] for the exp-six potential were used in this work. This procedure is inadequate. From a computational viewpoint, the reason for the failure of the procedure is understandable.

In Figure 4 the function ϕ', where $\phi' = \phi + Ce^{-cr}$, is shown. The parameters A and U used to plot this curve were obtained by fitting the exponential term to Amdur's data. Also shown in Figure 4 is the location of the minimum point which was used in these calculations. The effect of subtracting the term Ce^{-cr} (C and c are positive by definition) from ϕ is to move the minimum of ϕ' in the direction shown by the arrow. Using these values for A, a, B_1, B_2, and B_3, it is impossible to fit ϕ to the minimum point that was used.

There are two possible methods of modifying this procedure. The first method would be to use a different value for the minimum point. There are some theoretical calculations which indicate that the minimum point is deeper and occurs at a smaller r than the value used in these calculations. The second method is to modify B_1, B_2 and B_3. Yntema and Schneider used this procedure. Both methods are being studied.

The calculations of the collision integrals for the potential function proposed by Yntema, Schneider, and Fontana have been completed. The increments in the radius used in the numerical integration above the boundary curve have been made smaller to test the accuracy of the original calculation. The testing has been carried out from a small radius up to the maximum in the boundary curve. Thus far, a smaller increment has had no greater effect than the fourth decimal place of the original computation. An error analysis will be made.
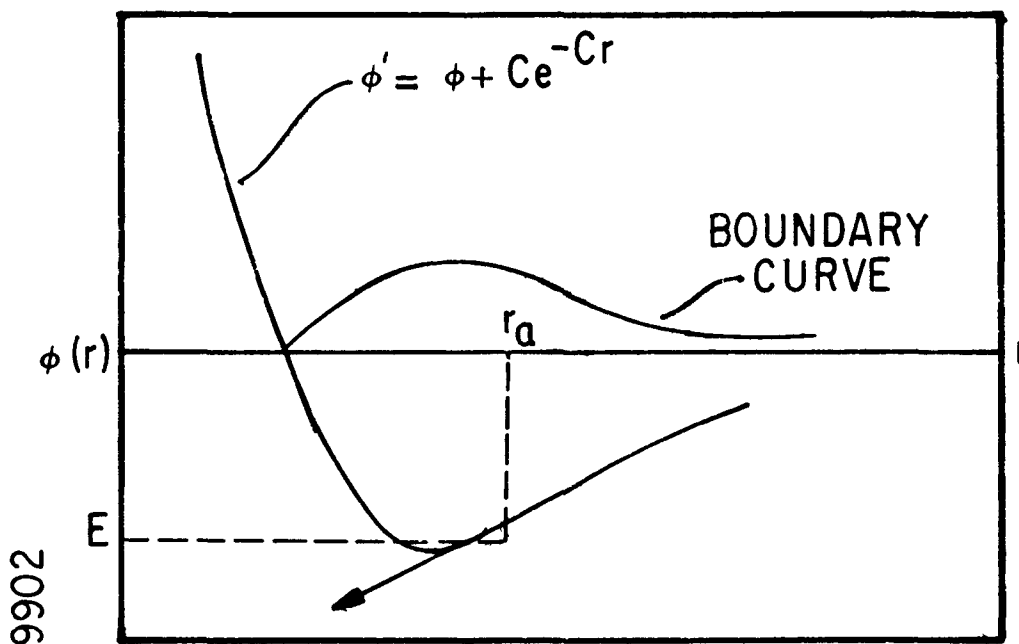

Figure 4. *The Plot of ϕ'.*

[15]I. Amdur and L. L. Harkness, *J. Chem. Phys.*, **22**, 664 (1954); I. Amdur et al., *J. Chem. Phys.*, **34**, 1525 (1961).

[16]E. A. Mason and W. E. Rice, *J. Chem. Phys.*, **22**, 522 (1954).

The thermal diffusion factor is important for theoretical calculations because of its sensitive dependence on the intermolecular potential function. Because of the increasing quantum effects below room temperature, its value in this range is of special interest. An experiment to measure the thermal diffusion factor over the temperature range of 10° to 250°K is being performed using a two-bulb apparatus.

Watson, Howard, Miller, and Shiffrin[17] reported the determination of the coefficients of thermal diffusion for isotopic mixtures of helium and neon over the temperature range of 136° to 312°K. These measurements agree with classic extrapolations of results appearing in previous papers for higher temperatures; therefore, no significant quantum effects occur in this temperature range.

The values for relaxation time for the two-bulb experiment are shown in Table 5. A correction to the final concentration is also required to account for the changing concentration of the gas in the interconnecting tube. This correction is discussed later.

A design has been completed for the two-bulb apparatus and is shown in Figure 5. The cryostat is pictured as having a pumping manifold, although in actual practice, most operations will be carried out at temperatures above the normal boiling point of the liquid used for the bath. An experimental determination with this equipment proceeds as follows. The isotopic mixture of helium having a known composition is loaded into the apparatus at room temperature to a given pressure through the loading tube (15). The modified Hoke valve (13) is closed, and the bath is filled. After a short time, the transfer gas is evacuated from around the two bulbs and the experiment is begun. The temperature in each bulb is controlled to the desired temperature by means of a proportional controller. This type of controller has been used successfully to control room temperature baths to less than 0.001°C. The temperature sensing element in each bridge circuit is a platinum resistance thermometer consisting of 47 gauge (0.002-in. diameter) wire wound spirally onto mica forms. These wound forms are shown as (8) and (11) in Figure 5. The heaters are formed from single strand cotton insulated Tophet A wire wound in a bifilar fashion into grooves on the outside of each bulb.

After the control temperature of each bulb is reached, the valve between the cold bulb and the interconnecting tube (9) is opened, and the system is allowed to equilibrate. Then this valve is closed, and the modified Hoke valve is opened; the contents of the hot bulb and the interconnecting tube are transferred to a gas burette with a Toeppler pump. The gas burette enables a check on leakage between the two bulbs. When the hot volume and the tube have been evacuated, the upper valve is closed, and the lower valve is opened. This process is repeated until the amount of gas in the cold bulb is sufficient for an accurate mass spectrometer analysis.

The two valves have indium seats to enable adequate operation at reduced temperatures. Both can be operated from outside the cryostat without disturbing the heat balance of the system. The lower valve is driven through the two gears (1) and (2). Since the screw thread which advances the bonnet (3) has 16 threads per inch and the gear ratio is 1:6.25, each revolution of the drive shaft will result in a 0.010-inch axial travel of the valve stem. This may prove useful if it becomes necessary to study the effect of valve opening on the performance of the apparatus.

During the operation of the experiment, the plate (12) serves as the heat leak for the hot bulb and the ring between the outer chamber, and the cold bulb serves as the heat leak for the cold bulb. The calculated energy flow along these two paths and along the interconnecting tube and the enclosed gas column are given in Table 6 for various bulb and bath temperatures.

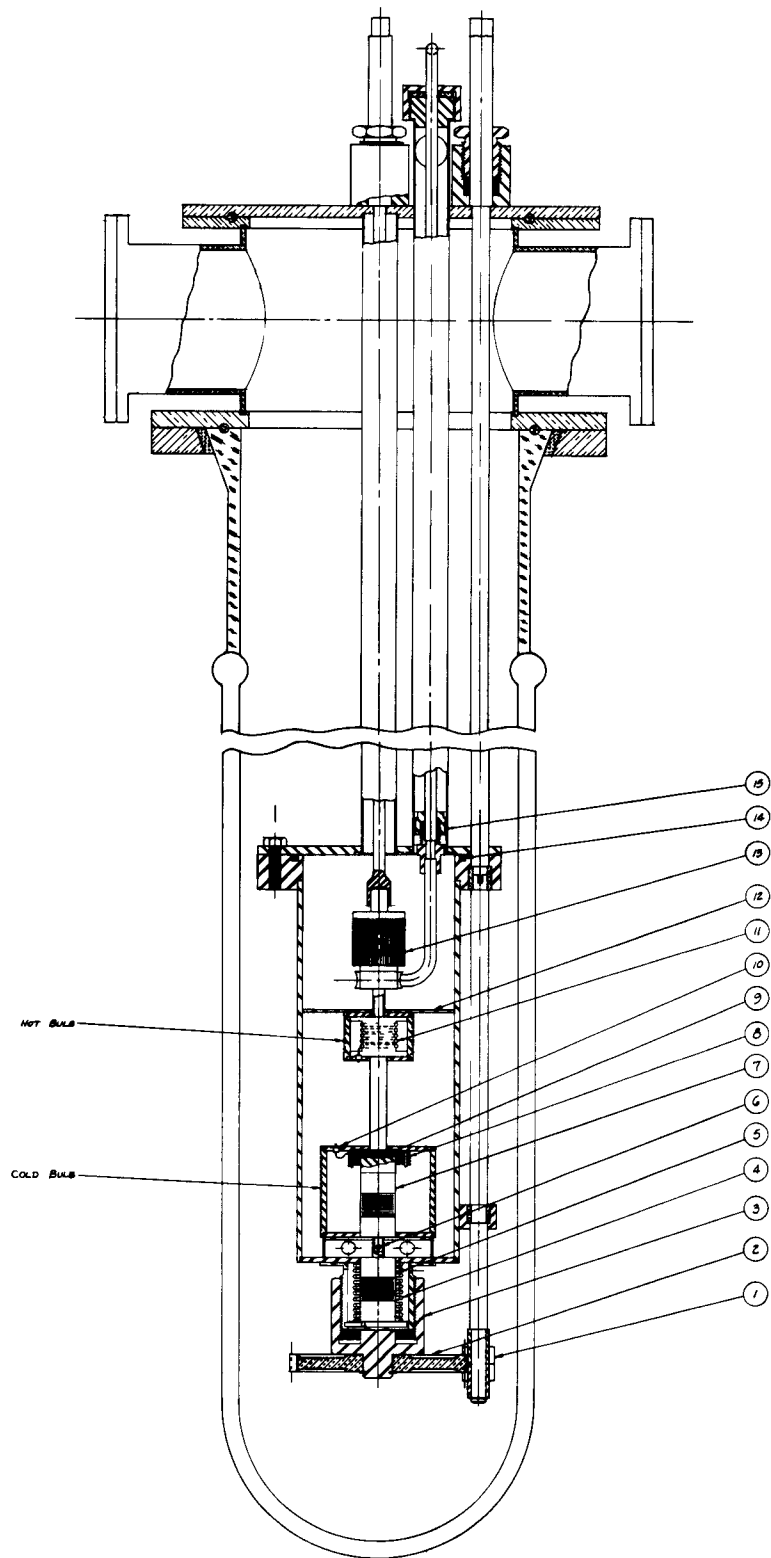[17]Watson et al., *Z. Naturforsch.*, **18**, 242 (1963).

HOT BULB

COLD BULB

15
14
13
12
11
10
9
8
7
6
5
4
3
2
1

Figure 5

Table 5

TWO-BULB THERMAL DIFFUSION EXPERIMENT

Temperatures		Volume (cc)		Tube Dimensions		Thermal Diffusion Coefficient x 10^2	Self-Diffusion Coefficient at 760 mm Hg	Separation Factor	Concentration in Cold Bulb		Relaxation Time per Pass [a]
Cold Bulb (°K)	Hot Bulb (°K)	Cold Bulb	Hot Bulb	Length (cm)	Dia. (cm)				Light Isotope	Heavy Isotope	
97.5	102.5	75	15	20	0.6477	5.95	0.275	1.00298	49.614	50.385	59m 16s
95.0	105.0	75	15	15	0.6477	5.95	0.275	1.00597	49.247	50.752	44m 12s
92.5	107.5	75	15	20	0.6477	5.95	0.275	1.00898	48.876	51.123	53m 29s
				15							41m 57s
90.0	110.0	75	15	15	0.6477	5.95	0.275	1.0120	48.505	51.494	39m 46s
9	11	75	15	15	0.6477	-1.1	0.0087	0.99779	50.274	49.725	1h 17m 23s
8	12	75	15	20	0.6477	-1.1	0.0087	0.99555	50.561	49.438	2h 7m 38s
7	13	75	15	15	0.6477	-1.1	0.0087	0.99321	50.854	49.145	2h 5m 41s
197.5	202.5	75	15	20	0.6477	5.4	0.7657	1.00135	49.814	50.185	43m 39s
195.0	205.0	75	15	15	0.6477	5.4	0.7657	1.00270	49.648	50.351	33m 25s
192.5	207.5	75	15	20	0.6477	5.4	0.7657	1.00406	49.482	50.517	41m 31s
190.0	210.0	75	15	15	0.6477	5.4	0.7657	1.00542	49.317	50.682	31m 45s

[a] h = hours; m = minutes; s = seconds

Table 6

HEAT TRANSFER IN TWO-BULB APPARATUS

Bath Temp. (°K)	Cold Bulb Temp. (°K)	Hot Bulb Temp. (°K)	Heat Transfer Along Path[a] (watts)				
			A	B	C	D	E
77	90	110	0.026	0.002	7.700	3.427	0.066
77	190	210	0.038	0.003	41.654	40.580	0.553
4	7	13	0.0006	0.0001	0.165	0.061	0.0008

[a]Paths are:
A - Tube connecting bulbs
B - Gas column between bulbs
C - Plate between hot bulb and container
D - Ring between cold bulb and container
E - Valve stem between cold bulb and container

This design for a two-bulb apparatus requires a correction to the final composition listed in Table 5 because the gas in the interconnecting tube was neglected in that calculation. This correction is similar in principle to the calculations for the one-bulb experiment reported previously. A similar correction must be made in the analysis of the data. The starting point is the modified diffusion equation as given by Jones and Furry.[19]

$$\nabla c_1 = \alpha c_1 c_2 \nabla \ln T$$

With cylindrical symmetry, a constant temperature gradient along the tube, and $c_2 = 1 - c_1$, the following equation is obtained:

$$\frac{dc_1}{dz} = \frac{\alpha c_1 c_2 \tau}{T} = \frac{\alpha c_1 (1-c_1) \tau}{T}$$

where:

c_1 = concentration of light isotope
c_2 = concentration of heavy isotope
α = thermal diffusion coefficient (assumed to be a constant)
τ = constant thermal gradient along tube

Since $T = T_c + \tau z$, where T_c is the temperature of the cold bulb, the variables in the above equation can be separated and integrated between definite limits according to the boundary conditions:

$$c_1 = c_c \qquad at \qquad z = 0$$

$$c_1 = c_x \qquad at \qquad z = x$$

Thus,

$$\left[\ln \left(\frac{c_1}{1-c_1} \right) \right]_{c_c}^{c_x} = \alpha \tau \left[\frac{1}{\tau} \ln (T_c + \tau z) \right]_0^x$$

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[19]R. C. Jones and W. H. Furry, *Revs. Mod. Phys.*, **18**, 151 (1946).

or

$$\frac{c_x}{1 - c_x} = \frac{c_c}{1 - c_c} \left(\frac{T_c + \tau x}{T_c} \right) \alpha$$

This expression becomes:

$$c_x = \frac{1}{1 + \left(\dfrac{1 - c_c}{c_c} \right) \left(\dfrac{T_c}{T_c + \tau x} \right) \alpha}$$

To evaluate this equation, either c_c or α can be considered as an integration constant which can be evaluated using the material balance equation for the light isotope as given by:

$$\frac{V_h}{1 + \left(\dfrac{1 - c_c}{c_c} \right) \left(\dfrac{T_c}{T_h} \right) \alpha} + c_c V_c + A \int_0^L \frac{dz}{1 + \left(\dfrac{1 - c_c}{c_c} \right) \left(\dfrac{T_c}{T_c + \tau z} \right) \alpha} = c_c' V_c$$

where:
A = Cross sectional area of interconnecting tube
V_h = Volume of hot bulb
V_c = Volume of cold bulb
c_c' = Concentration of light isotope in cold bulb
   just before previous expansion
T_h = Hot bulb temperature

In the present case of preliminary design, α is assumed to be known, and an iteration on c_c is performed until the left side of the above equation is as close to the right side as desired. In the reduction of the actual data, c_c will be known, and the iteration will be performed on α. Since this equation requires a numerical integration, it has been programmed for a computer. However, only one case has been completed. This result along with the approximate results for various temperatures using the apparatus dimensions as shown in Figure 5 are given in Table 7. The one case that includes the correction has been evaluated so that the two sides of the material balance equation are within 0.1 per cent of each other for each expansion Comparing this result with the corresponding approximate result shows that the latter gives a composition change which is 50 per cent too great. This calculation will be completed for all approximate cases listed in Table 7.

24

Table 7

TWO-BULB THERMAL DIFFUSION EXPERIMENT

Mean Temperature (°K)	Temperature Difference (°K)	Hot Bulb Volume (cc)	Cold Bulb Volume (cc)	Tube Diameter (cm)	Tube Length (cm)	No. of Expansions	Final Composition(%)		Pressure[a]		Total Relaxation Time[b]
							Light Isotope	Heavy Isotope	Initial (mm Hg)	Final (mm Hg)	
10	6	16.81	100	0.9017	5	20	51.709	48.290	1296	40.54	34m 17s
	4						51.123	48.876			44m 51s
	2						50.546	49.453			57m 8s
200	20	16.81	100	0.9017	5	20	48.634	51.365	1296	40.54	14m 37s
	15						48.965	51.034			15m 2s
	10						49.297	50.702			15m 26s
	5						49.629	50.370			15m 52s
100	20	16.81	100	0.9017	5	20	47.012	52.988	1296	40.54	18m 11s
	15						47.753	52.246			19m 15s
	10						48.493	51.506			20m 21s
	10 (corrected)						48.995	51.004			
	5						49.228	50.771			21m 30s

[a]Pressures are for room temperature (300°K)

[b]m - Minutes
s - Seconds

Mound Laboratory is responsible for producing alpha and neutron sources, manufactured from polonium-210 and plutonium-239, which cannot be produced by American industry at the present time. The techniques of fabricating these unusual sources are being developed and publicized.

Neutron Sources

The neutron growth rate of plutonium-beryllium sources is being determined from calorimetric measurements. The neutron growth rate was 1.1 per cent per year with a standard error of 0.4 per cent per year on a source (M-246) loaned to Mound Laboratory by General Electric (HAPO) for recanning and comparison studies between Mound Laboratory and Hanford precision long counters.

One newly fabricated PuBe neutron source was shipped. Eighteen recanned PuBe neutron sources were returned to their users. One newly fabricated PuBe source awaits shipment.

New sources are being made by crushing scrap $PuBe_{13}$ alloy into the inner container. A special set of inner can holding dies and hardened tool steel crushing and compacting punches has been made for this purpose. The loose $PuBe_{13}$ alloy can be compacted to a bulk density of 3.7 g/cc. Some of the otherwise nonrecoverable scrap alloy is being reused by this method.

Alpha Sources

Alpha source windows are destroyed by direct contact with appreciable amounts of polonium as a result of damage by recoil fragments from alpha decay. Therefore, the standard alpha source design incorporates a 0.015-inch space between the window and the polonium to prevent the damage. For large area, high intensity sources, however, the spacing is impractical.

Four one-curie polonium alpha sources were fabricated on September 20, 1963, as follows:

1. Standard construction: A 0.00013-inch thick stainless steel window was spaced 0.015 inch from the polonium deposit.
2. Modified standard construction: A base plate was shouldered so that the lower gold gasket was recessed. The 0.00013-inch thick stainless steel window was placed in contact with the polonium.
3. Standard construction: The window was made of three layers of beaten gold foil; otherwise the source was the same as No. 1.
4. Modified standard construction: The window was made of three layers of beaten gold foil; otherwise the source was the same as No. 2.

The sources were stored separately for periodic wipe checks for leakage. On October 15, 1963, all four sources were wipe free. The test will be continued through at least one polonium half-life.

Attempts to make wipe-free plated window polonium alpha sources with specific activities of more than five millicuries per centimeter have been discontinued. Tests with various plating techniques, base materials treatments, and attempts to roll or swage an initial layer of beaten gold leaf before plating the rest of the window were unsuccessful. Either a wipe-free window was not obtained, or it became contaminated within a short time.

Applications do exist, however, for large area, high specific activity alpha sources which are not necessarily wipe-free but which will retain most of the polonium. Techniques are being developed for fabricating sources with a minimum activity of one curie per square centimeter; the sources must retain 95 per cent of their activity over one or two half-lives. Polonium has been deposited on substrate followed by gold electroplating. On copper and nickel substrates, the polonium was plated successfully; however, the polonium layer cracked and peeled from the substrate during the gold-plating. Two sources electroplated on gold substrates appear to be satisfactory. Test sources will be scrubbed periodically to remove any loose activity; then they will be calorimetered to determine any loss of activity.

ANALYTICAL

Methods of analyzing elements and compounds are being developed to support other programs at Mound Laboratory. These methods include instrumental techniques and classical wet methods.

Low-level Tritium Counting

A vacuum system has been completed for the analysis of gas samples containing ultra-low levels of tritium. The natural background on a one-liter counting tube, counted in the four-inch thick lead shield was approximately 450 counts per minute; thus the detectable tritium concentration is limited to 5 x 10^{-13} mole per cent. Work is being continued to lower the background.

The system operates at a vacuum of 10^{-5} millimeters, thus giving a background from residual gas in the system of 0.02 counts per minute; this background is negligible with the present system. Samples ranging from 1 x 10^{-9} to 5 x 10^{-13} mole per cent have been analyzed on the new system. An analysis requires about four hours. The precision for an analysis of 10^{-11} mole per cent is ± 4 per cent. For samples of lower tritium content, the precision decreases as determined by the counting statistics.