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MOUND LABORATORY PROGRESS REPORT FOR JUNE, 1964

J. F. Eichelberger, G. R. Grove and L. V. Jones

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Progress Reports

MOUND LABORATORY PROGRESS REPORT FOR JUNE, 1964

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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-1203	MLM-1178
MLM-1196	MLM-1177
MLM-1192	MLM-1176
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SUMMARY

ALPHA AND NEUTRON SOURCE DEVELOPMENT

The neutron emission rate of plutonium-beryllium sources made with plutonium-239 is increasing due to the ingrowth of americium-241. The emission rate is being measured to determine if the growth rate can be predicted on the basis of calorimetric measurements.

ISOTOPE SEPARATION AND PURIFICATION

Helium-3 The tritium content in helium-3 was reduced approximately 50% to $3 \times 10^{-4}\%$ by passing the gas over cupric oxide at 700°C. A method of separating helium-3 and helium-4 that takes advantage of the superfluid properties of helium-4 was developed. In a series of 10 experimental runs, helium-3 was enriched from 0.08 atom % to more than 14 atom %.

Neon Isotopes Most of the neon-22 was removed from the intermediate material being used for enriching neon-21. The product has reached a concentration of about 19% neon-21.

Argon Isotopes At the top of the fourth stage in the thermal diffusion column system, a rate which will allow enrichment to 99% argon-36 will be determined.

Krypton Isotopes About 50 liters of krypton-78 and 80 enriched to about 10% were accumulated from the first stage runs in a two column system. A test run to enrich krypton-84 and 86 was started.

Xenon Isotope Separation and Purification In the program to enrich xenon-136 the product was withdrawn regularly from the five-stage system to establish conditions maintaining the concentration of xenon-131 below one percent.

A new longitudinally finned gas chromatographic column was used to reduce the krypton-85 in the xenon. Results were better than those with previous columns.

Thermal Diffusion Research A computer program was developed to calculate column transport coefficients as a function of pressure for a given temperature and column geometry from the McInteer and Reisfeld table of shape factors. Its uniqueness is the development of special interpolation techniques to obtain accurate shape factors from original data stored in the computer.

RADIOELEMENTS RESEARCH

Promethium-147 Half-life The half-life of promethium-147, which was prepared at the Hanford Laboratories, was measured. It was 2.6244 ± 0.006 years with an estimated absolute error limit of 0.0006 years. The power and average beta energy for promethium were determined to be 0.33267 watts per gram and 60.54 kev, respectively.

Actinium-227 Separation The contents of one of three actinium slugs have been processed through the ion-exchange column. The efficiency of the separation has not been calculated as yet.

Uranium-234 Separation and Purification Mound Laboratory is separating and purifying uranium-234 from aged plutonium-238 solutions by a combination of anion exchange and solvent extraction techniques. A sample containing nearly two grams of uranium-234 had previously been processed by an anion exchange procedure to separate the uranium from 99% of the plutonium. A hexone extraction reduced the plutonium level further and separated the uranium from the bulk of the inactive contaminants. The product from the hexone step contained 1.96 grams of uranium and 2.9 milligrams of plutonium.

A study of the denitration of acid solutions with sugars showed that dextrose was better than sucrose as a denitrating agent.

ADHESIVES RESEARCH

Three commercial systems, Humiseal 2A60[®] (a polyurethane system), DC 269[®] and RTV 615[®], both silicone systems, were evaluated as matrices for flexible conductive adhesives. All three were unsatisfactory.

The addition of nine percent low viscosity depolymerized rubber to a carbon black silicon formulation increased the peel strength of the formulation from 0.5 to 4.0 pounds per inch.

ALPHA AND NEUTRON SOURCE DEVELOPMENT

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 MEASUREMENTS

The neutron emission of plutonium-beryllium sources made with plutonium-239 is increasing due to the in-growth of americium-241 which results from the beta-decay of plutonium-241. The rate of increase is being measured with a long counter. Previously, the rate of increase was inferred from calorimetric measurements. In arriving at the rate of increase in the neutron emission from calorimetric measurements, it is necessary to know the ratio of the neutron yield from americium-241 alpha-particles to plutonium-239 alpha-particles. The only reported value for this ratio is $(74 \pm 2)/(60 \pm 2)$ or 1.23 ± 0.05 reported by Runnalls and Boucher.¹ Direct measurements with the long counter will check this figure, as well as determine whether or not the increase in emission is proportional to the increase in power output from the source.

Measurements with a long counter are made by comparison between the source whose emission rate is desired, and a second or "standard" source. Table 1 is a summary of some data obtained to date.

The predicted growth rates and those obtained by comparison with Pu-3 agreed well, but the growth rates obtained using HAM-1 disagreed with the other two. Based on the data above and assuming that any change in neutron emission for PuBe sources is proportional to the change in heat output as measured by calorimetry, the AmBe source is decreasing in neutron emission approximately 0.3 - 0.4% per year faster than expected from the decay of the americium-241 alone.² Additional measurements on the above and other sources will help determine whether the change in neutron emission can be accurately predicted from calorimetric measurements, and whether the ratio of 1.23 from Runnalls and Boucher is accurate.

Table 1

Increase in Neutron Emission of PuBe Sources

Source with Unknown Rate of Increase	Source Used for Comparison		Predicted from Calo- rimetric Measurements ^c
	Pu-3 (PuBe) ^a	HAM-1 (AmBe) ^b	
M-977	2.03 ($\pm 0.14\%/yr$)	2.30 ($\pm 0.06\%/yr$)	2.01%/yr
M-591	1.31 ($\pm 0.08\%/yr$)	1.76 ($\pm 0.06\%/yr$)	1.31%/yr

^aThis source contains plutonium-239 with relatively little plutonium-241. Calorimetric measurements over a period of 2.5 years failed to show any increase in heat output. It is estimated that any increase in neutron emission for this source is less than 0.1% per year.

^bThe americium-241 in this source is essentially pure. The values in this column have been corrected for the decay of americium-241, or 0.15% per year.

^cValues of the plutonium-241 content at time zero were obtained from calorimetric measurements. Time zero is that time when the americium-241 content was zero.

¹O. J. C. Runnalls and R. R. Boucher, "Neutron Yields from Actinide-Beryllium Alloys", *Can. J. Chem.*, **34**, 949 (1956).

²MLM-1185, p. 19

Another PuBe source which has been used extensively is M-1045, the internal source for calibrating the long counter. It is of interest to know the extent to which this source can be used for an exact calibration of the equipment. Below is a summary of some data obtained for this source:

Change in neutron emission from comparisons between M-1045 and Pu-3	$2.05 \pm 0.06\%/yr$
Change in the absolute counting rates for M-1045 from 10-3-63 to 12-13-63 (6 data points)	$1.99 \pm 0.21\%/yr$
Change in absolute counting rate for M-1045 from 2-7-64 to 6-5-64 (8 data points)	$2.17 \pm 0.15\%/yr$
Change in neutron emission based on the isotopic composition of the Pu used in the source	$1.52\%/yr$

The discrepancy between the predicted and the measured rates of change indicated that either the isotopic composition of the plutonium used in this source was not known accurately, or that the neutron emission rate is increasing because of a slow uniform redistribution of the plutonium and beryllium. A redistribution is suggested for M-1045 and not for PuBe sources in general because of the relatively low specific neutron emission for this source. M-1045, as well as most other PuBe sources, was fabricated with sufficient amounts of plutonium and beryllium to give an atom ratio of 1:13. All PuBe sources are heated to form the intermetallic compound, $PuBe_{13}$.³ For the great majority of sources this compound is successfully formed as evidenced by a constant specific neutron emission of about 44×10^{-6} neutrons per alpha-particle. The completion of the intermetallic reaction becomes difficult for small sources, such as M-1045 with one gram of plutonium. The low specific emission for M-1045, 33×10^{-6} neutrons per alpha-particle, indicated that the reaction was not complete for this source.

The good agreement between the rate of increase of the neutron emission from comparison measurements and the rate of change of the absolute counting rate measurements indicated that the long counter in its present form is quite stable. This confirms data from March, 1962. The stability permits the use of an internal source as a comparison standard for an external source.

³J. L. Richmond and C. E. Wells, U. S. Patent 3,073,768, January 15, 1963.

ISOTOPE SEPARATION AND PURIFICATION

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

HELIUM-3 SEPARATION AND PURIFICATION

A unit was designed and built to reduce the tritium content of helium-3 to less than 2×10^{-10} mole percent. A one-inch OD chamber was loaded with approximately 100 grams of copper oxide. The ends were packed with glass wool to prevent the loss of the oxide powder.

The chamber containing the copper oxide powder was heated to approximately 700°C . Feed gas (~ 0.5 liter STP) was bled into the chamber and allowed to react with the copper oxide for approximately 10 minutes. The gas was then drawn into a small cold trap at liquid nitrogen temperature to freeze out the water vapor produced in the chamber. The test results were

Feed - 6.40×10^{-8} mole % tritium

Prod - 2.68×10^{-8} mole % tritium

The reduction in tritium content was not as large as expected.

Superfluid Experiments Helium-4 becomes superfluid below 2.17°K , but helium-3 does not. A method is being evaluated to separate helium-3 from helium-4 taking advantage of this difference in their physical properties. The method is a combination of "superfluid filtration" and "heat flush".

The experimental results depend a great deal on how the experiments were conducted. The experimental procedure is presented below:

1. The system is evacuated to less than 1 torr.
2. Liquid helium-4 is introduced into the cryostat and pumped on until a temperature well below the lambda temperature is reached ($\sim 1.4^{\circ}\text{K}$).
3. The feed gas is sampled and condensed in the copper tube cold finger (feed and product side of superleak).
4. The heaters on the dump side of the experimental system are turned on.
5. A light is used to heat the dump side of the superleak to initiate the transfer of the superfluid atoms through the superleak.
6. When the liquid helium has evaporated to the level of the heaters, the light is turned off and the liquid is allowed to rise in the dump side until no further increase in the liquid level is observed.
7. The warm-up is begun by shutting off the vacuum pump. When a temperature is reached above the lambda temperature, a heater is inserted into the liquid helium bath to boil off the remaining liquid helium.
8. The helium in the dump and product sides of the experimental apparatus is collected in separate cylinders and allowed to stand for 24 hours. Samples are taken of the two cylinders to determine the helium-3 enrichment.

The results of ten successive experimental runs are given in Table 2 and Figure 1. Since a different amount of power was supplied to the heater for varying times in each experiment, the same amount of helium-4 was not transferred through the superleak in each experiment. Thus, the increase in helium-4 concentration does not show an increase with each successive flush. When the product gas is diluted to equal pressure with new make-up gas in each succeeding run, the overall amount of helium-3 present in the product gas is increased with each experimental run.

Even though these initial experiments were of an exploratory nature, helium gas containing about 0.08 atom % helium-3 has successfully been enriched to over 14 % helium-3.

Table 2

EXPERIMENTAL DATA HELIUM-3 SEPARATION

Run	Make Up Feed (% He ³) ^a	Feed Gas (% He ³)	Prod. Gas (% He ³)	Dump Gas (% He ³)	Sep. Fact.	Begin Press. (mm Hg)	End Press. (mm Hg)	Power Used (mw)	Time Power Used (min)
1	0.08	0.08	0.81	0.00	10.1	500	~ 200	35.0	10
2	0.09	0.14	1.42	0.00	10.1	500		35.0	10
3	0.07	0.17	2.20	0.00	12.9	570		35.0	5
4	0.08	0.29	2.41	0.00	8.3	500	395	151.7	10
5	0.08	0.30	3.05	0.16	7.8	500	53	71.9	10
6	0.04	0.42	4.11	0.00	9.8	500	59	57.8	10
								94.4	20
7	0.04	0.46	1.21	0.00	2.6	500	65	109.7	15
8	0.08	0.47	3.56	0.00	7.5	500	69	94.4	120
9	0.03	0.59	8.59	0.00	14.6	500	33	94.3	26
								129.2	93
								154.2	30
10	0.05	0.63	14.51	0.00	23.0	500	20	129.2	45
								154.2	55
								180.1	50

^aAll concentrations given in atomic %.

Figure 1. Concentration of He³ as a Function of Experimental Runs

NEON ISOTOPE SEPARATION

Neon-21 Separation In the two-column cascade for the enrichment of neon-21 approximately 18 liters of neon-22 have been removed, resulting in a neon-21 concentration of 19 percent in the reservoir. After an additional liter has been removed and the neon-22 has been withdrawn, the resulting intermediate feed will be used in batch processing.

ARGON ISOTOPE SEPARATION

The calcium purification system described previously is keeping impurities at about 0.3 percent at the top of the fourth (last) stage of the argon thermal diffusion column system. Argon enriched in argon-36 is being removed from the fourth stage top to determine the maximum flow rate of argon-36 at an isotopic concentration of 99.0%.

The excess argon-36 which had accumulated in the system during the equilibration period was removed. The system required about two weeks before the profile began to equilibrate and the composition would reflect more accurately the product rate. The product composition at a continuous flow of about 2.5 ml/hr was as follows:

Total Argon	99.72%
Argon-36	98.61%
Argon-38	1.24%
Argon-40	0.14%

The argon-36 concentration is presently increasing slowly at this draw-off rate.

KRYPTON ISOTOPE SEPARATION

Run 23 of the first stage krypton-78 and 80 enrichment was completed. More than 50 liters of product at a krypton-78 and 80 concentration of over 10 percent were accumulated.

Piping revisions were made on the krypton system to permit enrichment and controlled withdrawal of the heavy isotopes, krypton-84 and 86, as shown in Figure 2. Raffinate gas from the first stage krypton-78 and 80 enrichment, which contains 76% krypton-84 and 86, is being used as feed for this experimental work. The product will be drawn off at point 11G in Figure 2 at the rate of about 10 ml per hour. A krypton-84 and 86 average concentration of 99% will be maintained.

Figure 3 shows the theoretical flow curve of product flow (σ) as a function of product concentration (C) when the initial concentration (C_i) is 0.76. These data were calculated using McInteer and Reisfeld shape factors for the Lennard-Jones 12-6 potential.

XENON ISOTOPE SEPARATION AND PURIFICATION

Thermal Diffusion After about six weeks of operation, the five-stage swing system separated the 458 ml of xenon. The xenon-131 concentration was 0.47%. The curves in Figure 4 show the concentration changes in xenon-136 and xenon-131 as a function of time.

With a new charge of gas, equilibration was started to bring the swing volume gas to less than 1% xenon-131. This was the initial step in an attempt to determine the maximum flow rate of product gas containing less than 1% xenon-131.

Figure 2. Piping Diagram of Krypton Thermal Diffusion System

Figure 3. Product Flow as a Function of Krypton-84 Plus -86 Concentration for a Two Stage Thermal Diffusion Column System (column pressure - 310 torr; wire temperature - 850°C; feed concentration - 76% $Kr^{84} + Kr^{86}$)

Figure 4. Xenon 5 Stage Swing Equilibrium Product Concentration in Xe¹³¹ and Xe¹³⁶ at Stage 5 Bottom (column pressure - 170 torr; wire temperature - 850°C)

The product was withdrawn at the rate of 12 ml per day; the xenon-131 concentration was 0.7%. The withdrawal rate will be increased to maintain a product concentration of 1.0% xenon-131.

Experimental Chromatograph Studies are continuing to reduce the krypton-85 content in fission product xenon. A new chromatographic column was built containing eight internal fins that run the length of the column. Four fins are 1/8 x 7/16-inch, and four fins are 1/8 x 5/16-inch. The column is 1.25 inches in diameter and 7.5 inches long. These fins create parallel, multiple columns which are interconnected to provide uniform pressure and material equilibrium through lateral diffusion. Also, the fins help maintain a uniform temperature across the column. This type of column was used by Wright⁴ who claimed a 400 percent improvement in efficiency over conventional columns.

Three runs were made using this column. The krypton-85 in the feed was more than 6,000 times the krypton-85 in the xenon trap in each run, as shown in Table 3. A product containing about 2×10^{-9} mole % krypton-85 was obtained from the last run, using a feed gas with about 1.6×10^{-5} mole % krypton-85.

The recovery in the xenon trap was increased to 99.8%. Previous columns had recoveries about 80 to 85%.

All these runs were made at 193°K until the krypton-85 peaked, then the column was warmed to 243°K. Since the xenon peak was not discernable, the krypton and xenon traps were switched when the krypton peak became asymptotic to the base line.

⁴J. L. Wright, "Advanced Column Design for Large Scale Gas Chromatography", *J. Gas Chromatography*, 1:11, 10 (November, 1963).

Table 3

**CHROMATOGRAPHIC SEPARATIONS USING A FINNED
COLUMN - INTERNAL FINS PARALLEL TO AXIS**

Run	Cleanup, Conc. Kr-85 in Feed Conc. Kr-85 in Xe Trap	Krypton Retention Time (min.)	Elapsed Time When Traps Were Switched (min.)	Recovery in Xe Trap (%)
1	6190	13	27	99.8
2	8560	13	32	99.8
3	10400	13	32	99.8

THERMAL DIFFUSION RESEARCH

Calculation of Thermal Diffusion Column Transport Coefficients The net transport of the desired isotope toward the positive end of a gaseous thermal diffusion column is given by

$$T = H' p^2 c (1-c) - (K'_c p^4 + K_d) \frac{dc}{dz}$$

where c is the fraction of the desired isotope, z is the distance along the column, and p is the pressure. The coefficients H' , K'_c , and K_d are complicated functions of the column geometry, the hot and cold wall temperatures, and the physical properties of the gas mixture. For the Lennard-Jones potential these coefficients are given by

$$H' = \left(\frac{2\pi}{6!} \right) \left(\frac{\alpha_o \rho_o^2 g}{\eta_o} \right) r_c^4 h(\gamma, \theta, T^*)$$

$$K'_c = \left(\frac{2\pi}{9!} \right) \left(\frac{\rho_o^3 g^2}{\eta^2 D_o} \right) r_c^8 k_c(\gamma, \theta, T^*)$$

$$K_d = 2\pi (\rho_o D_o) r_c^2 k_d(\gamma, \theta, T^*)$$

where D_o is the diffusivity, η_o is the viscosity, α_o is the thermal diffusion factor, and ρ_o is the density, all at the cold wall temperature and at one atmosphere pressure. The quantities h , k_c , and k_d are shape factor integrals. The shape factors depend only on the radius ratio, γ , the temperature ratio, θ , and the reduced temperature at the cold wall, T^* . The shape factors for the Lennard-Jones potential have been evaluated and tabulated by McInteer and Reisfeld.⁵

Accurate interpolation between values of the McInteer and Reisfeld tables is difficult in certain regions. At a radius ratio of one, singularities exist in all three shape factors. In addition, there is a singularity in h at $T^* = 0.92$ where the thermal diffusion factor at the cold wall temperature is equal to zero. Accuracy of interpolation in the neighborhood of these singularities is poor.

⁵B. B. McInteer and M. J. Reisfeld, LAMS 2517, (1961).

The difficulty with the radius ratio interpolation can be handled by factoring the primary radius ratio dependence out of the tabulated shape factors. The column transport coefficients are then given in terms of the new shape factors h' , k'_c and k'_d by

$$H' = \left(\frac{2\pi}{6!} \right) \left(\frac{\alpha_o \rho_o^2 g}{\eta_o} \right) \left(\frac{y+1}{y} \right) \left(\frac{y-1}{y} \right)^3 r_c^4 h' (y, \theta, T^*)$$

$$K'_c = \left(\frac{2\pi}{9!} \right) \left(\frac{\rho_o^3 g^2}{\eta_o^2 D_o} \right) \left(\frac{y+1}{y} \right) \left(\frac{y-1}{y} \right)^7 r_c^8 k'_c (y, \theta, T^*)$$

$$K'_d = 2\pi (\rho_o D_o) \left(\frac{y+1}{y} \right) \left(\frac{y-1}{y} \right) r_c^2 k'_d (y, \theta, T^*)$$

The new shape factors vary slowly with radius ratio, and interpolation is reliable. A complete set of these shape factors was calculated from the McInteer and Reisfeld shape factors.

The terms h or h' can be interpolated accurately by recognizing that the product hk_T^* where k_T^* is the thermal diffusion ratio, is positive and well-behaved in the region around T^* equal to 0.93. Values of hk_T^* can be interpolated on T^* and the result divided by the appropriate value of k_T^* to obtain h .

The complete calculation of the column transport coefficients has been programmed in FORTRAN for the IBM 1620 computer. The program includes calculation of the transport properties of the gas at the cold wall temperature, if desired. Three point, unequal-interval interpolation in three dimensions is used to calculate shape factors from internally stored table values. The stored tables are modified as described above. They cover the complete range of the McInteer and Reisfeld tables, but only about one-third of the number of points are included. Typical interpolation accuracy is 0.5% in the region between table values of the independent variables.

Center Wire Heating by Alternating Current The last experiment in this series for determining the effect of alternating current on the thermal diffusion of neon-20 and neon-22 isotopes was conducted using a mercury trap with alternating current. The only difference other than the use of alternating current between this run and previous similar runs was that the wire was heated to operating temperature in approximately 20 seconds. The data obtained are shown in Table 4.

Table 4

USE OF ALTERNATING CURRENT FOR NEON ISOTOPE SEPARATION
IN THERMAL DIFFUSION COLUMN WITH MERCURY TRAP

Sample	Concentration (Mole %)									
	1-B	1-T	2-B	2-T	3-B	3-T	4-B	4-T	5-B	5-T
Total Neon	99.96	99.92							98.77	95.24
Neon-20	50.29	55.18	0.94	99.52	0.94	99.48	0.91	99.49	0.84	99.52
Neon-21	0.23	0.22	0.09	0.04	0.09	0.05	0.07	0.07	0.07	0.07
Neon-22	49.48	44.60	98.97	0.45	98.98	0.47	99.02	0.44	99.08	0.41
Hydrogen	0.00	0.04							0.00	4.69
Water	0.03	0.02							0.02	0.04
Nitrogen	0.01	0.01							1.21	0.03
Time of Sample	0 hrs.		24 hrs.		28 hrs.		33 hrs.		46 hrs.	
Separation Factor	--	--	23,200		22,300		24,600		28,600	

The mass spectrographic error in the 0.3% neon range is approximately $\pm 40\%$ while in the 98-100% neon range the error is $\pm 0.25\%$. When the results using alternating current were compared to the results obtained using direct current, little difference could be observed between the two methods of heating a thermal diffusion column center wire under the conditions of this experiment.

Thermal Pump A "thermal pump" is presently being developed for use in transferring rare gases. The pump contains a series of small volumes, each separated by electrically controlled valves. The cylinders are arranged such that they can be alternately heated and cooled; then with suitable control on the valves gas can be pumped in steps by means of PVT expansion through the series of heating vessels. Advantages of this kind of pump include no moving parts, no leakage, and a high upper limit on pressure to which gas may be pumped.

Cooling water jackets were installed around the heating vessels of the pump to rapidly cool the vessels. A loaded cylinder pressure of 88 psig was attained in 28 cycles under the following conditions:

Feed Pressure:	20 psig
Time Cycle:	15 minutes
Heater Cycle:	1.5 minutes
Refeed Time:	0.5 minutes
Cooling Time:	8.5 minutes

Gas Compressibility Measurements An apparatus for measuring the compressibility factor of the rare gas isotopes was designed as shown in Figure 5. It consists primarily of two high pressure chambers connected by an expansion valve. A precise pressure measuring device for determining the pressure in the chambers at any given time, and a precise temperature controller and thermometer were built into the system.

Figure 5. Apparatus for Measuring Compressibility Factor

1. Dead weight pressure gage
2. Diaphragm differential pressure indicator
3. Manual oil injector
4. Visual high pressure manometer
5. Burnett pressure chamber no. 1
6. Burnett pressure chamber no. 2
7. Temperature control and measurement
8. Constant temperature bath

To make a measurement the evacuated Chamber I is filled with gas to 10,000 psi. The expansion valve is closed during the filling, and Chamber II is evacuated. The constant temperature bath is set to the predetermined temperature and the controller is adjusted to maintain that temperature. When thermal equilibrium is reached, the supply valve is closed and the initial pressure is measured. The expansion valve is then opened, and the compressed gas is expanded. Again, after thermal equilibrium is reached, the expansion valve is closed carefully, and the pressure after expansion is measured. This procedure is continued until the pressure in Chamber I has dropped to about one atmosphere.

From a ratio of the pressures measured, the compressibility factor of the gas is determined for that temperature and pressure range. This method requires high quality pressure and temperature measurements and minimum number of small correction factors.

RADIOELEMENTS RESEARCH

In support of other programs at Mound Laboratory basic and applied research on a number of radioelements is being conducted to determine 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.

CALORIMETRY

Half-life of Promethium-147 Promethium-147 with a half-life of 2.6 years, is a fission product of interest as a heat source for thermoelectric generators. The specific power (watts/cc) is about the same as for 28-year strontium-90 in equilibrium with yttrium-90. The maximum beta energy of promethium-147 is only 0.225 Mev, whereas the maximum beta energies of strontium-90 and yttrium-90 is 0.54 and 2.27 Mev, respectively. Thus, the advantage of promethium-147 is the ease with which the bremsstrahlung rays can be shielded.

As a part of the evaluation of promethium-147, the half-life of the isotope was redetermined. Two purified promethium oxide (Pm_2O_3) sources of 990 and 860 curies, respectively, were prepared at the Hanford Laboratories (HAPO) for a calorimetric determination of the power in watts per gram.⁶ The samples were sent to Mound Laboratory for an independent check of the calorimetric measurements. Since it was possible to keep the samples for a month or more, it was decided to measure the half-life of each sample.

Sample 1 was measured daily in Calorimeter 90 from April 8 to May 11, 1964. Sample 2 was measured daily in Calorimeter 91⁷ from April 8 to May 28, 1964. Each calorimeter has an automatic sample loader which is hermetically sealed to the calorimeter by a Lucite enclosure.⁸ The heater currents were maintained by constant current controllers.⁹ Bridge potential outputs were recorded after shunting one arm of the bridge to suppress most of the unbalance.¹⁰ Neither system was modified during the half-life determinations.

The results are given in Table 5. The half-life of each sample was calculated for three time intervals. No significant deviation of half-life as a function of time was observed, although the half-life during the first 19 days in each case was about two probable errors less than for the entire span. A plot of the deviations against time for each sample indicated no observable trends from 13 days to the final measurements. On this basis, perhaps the best half-lives to report are listed in Rows 3 and 6 in Table 5. It seems safer, however, to report the weighted grand mean which includes all measurements. Thus, the half-life of Sample 1 of 2.6218 ± 0.0017 years combined with the half-life of Sample 2 of 2.6247 ± 0.0006 years gives a weighted mean half-life of 2.6244 ± 0.0006 years, the error being the probable error by external consistency.

The probable error associated with a half-life which has been determined in just a small fraction of one half-life (5% in this case) requires some discussion. If the system is purely statistical, i.e., there are no spurious heating effects or slow drifts in the measuring equipment, this probable error is just as reliable as one of the same value obtained over several half-lives. However, if there is a spurious effect, such as an unknown radioactive isotope, the constants have not been determined from the primary data. If these constants were determined by a double exponential solution, the probable errors would be increased to a reliable value, and the increase in probable error would be much larger for the half-life determined in the shorter time. Therefore, if there is a spurious effect in the present half-life determination, the probable error could be much too small.

⁶E. J. Wheelwright, D. M. Fleming, and F. P. Roberts, "Calorimetric Determination of the Decay Energy of Promethium-147" HW-77344, April 30, 1963.

⁷MLM-1185

⁸MLM-1192

⁹MLM-1183

¹⁰MLM-1179

At Hanford, the sample material was checked by emission spectroscopy, mass spectrograph, optical spectrometry, and radiochemical analyses.¹⁰ No impurities were detected which could significantly affect the half-life. Our deviations also indicate no trends. It has been our experience under similar conditions that a small segment of the total data gives a half-life such that plus or minus ten probable errors has always encompassed the half-life obtained with all the data. Unless a new precedent has been set, the true half-life of promethium-147 is 2.6244 ± 0.0060 years. The half-life from this work is in unusually good agreement with the grand mean of the literature values, as can be seen from Table 6. The seven values with probable errors have a weighted grand mean and probable error by external consistency¹¹ of 2.624 ± 0.019 years. A test for consistency given by Birge gives an h_x of 1.21 where the individual values are consistent if $h_x < 1.83$.

Table 5

PROMETHIUM-147 HALF-LIFE RESULTS

Time Span (days)	No. of Observations	Initial Power April 8, 1964 (microwatts)	Probable Error per Observation (microwatts)	Half-Life (years)	Probable Error in Half-Life (years)
<u>Sample No. 1, Calorimeter 90</u>					
0-33	24	339,110.8	7.6	2.6218	0.0017
0-19	15	339,114.8	8.7	2.6161	0.0039
13-33	14	339,110.8	4.4	2.6225	0.0021
<u>Sample No. 2, Calorimeter 91</u>					
0-47	35	289,608.0	3.7	2.6247	0.0006
0-19	15	289,611.4	3.4	2.6193	0.0019
13-47	25	289,603.5	3.3	2.6265	0.0009

Table 6

LITERATURE VALUES FOR THE HALF-LIFE OF PROMETHIUM-147

Half-Life and Probable Error (years)	Reference
2.66 ± 0.014	R. P. Schuman, M. E. Jones, and A. C. Mewherter, <i>J. Inorg. and Nuc. Chem.</i> , 3, p. 160-3, 1956.
2.64 ± 0.014	W. F. Merritt, P. J. Campion, and R. C. Hawkins, <i>Canadian Journal of Physics</i> , 35, p. 16-20, 1957.
2.50 ± 0.02	E. J. Wyatt, S. A. Reynolds, T. H. Handley, W. S. Lyon, and H. A. Parker, <i>Nuclear Science and Eng.</i> , 11, p. 74-75, 1961.
2.7 ± 0.07	J. P. Cali and L. F. Lowe, <i>Nucleonics</i> , 17, p. 86-88, October 1959.
2.67 ± 0.02	F. P. Roberts, E. J. Wheelwright, and W. Y. Matsumoto, <i>HW-77296</i> , 1963.

Table continued on next page

¹¹R. T. Birge, *Phys. Rev.*, 40, 207 (1932).

Table 6 (continued)

Half-Life and Probable Error (years)	Reference
2.52 ± 0.05	E. A. Melaika, M. J. Parker, J. A. Petruska, and R. H. Tomlinson, <i>Canad. J. Chem.</i> , 33, 830, 1955.
2.54 ± 0.034	Argonne National Laboratory, Ann. Rept. ANL-6125, p. 9, 1960.
G.M. (2.624 ± 0.019)	Weighted grand mean with probable error by external consistency.
2.6244 ± 0.0006	This report.

A private communication with E. J. Wheelwright at Hanford revealed that the weight of promethium-147 in each sample as of January 14, 1963, the date of purification, was 1.4103 and 1.2063 grams. The initial power of each sample in Table 5 (April 8, 1964) was adjusted to this date using a half-life of 2.6244 years. The result is 0.46953 and 0.40099 watts. These wattages compare quite well with calorimetry values obtained at Hanford of 0.46724 and 0.40207 watts, which were adjusted to the same data from measurements made on February 20, 1963, and April 5, 1963, respectively. Using Mound wattages and Hanford weights gives decay powers of 0.33293 and 0.33241 watts per gram. The average is 0.33267 watts per gram. The total calorimeter error in this figure from all sources does not exceed 0.1%. These errors are 0.07% decay error, assuming a spread of 0.006 years in the half-life, 0.01% from bremsstrahlung losses as indicated later, and 0.01% error in the calorimeter. The average beta energy can be obtained by multiplying the watts per gram by the following conversion factors: $f_1 = 146.96 \text{ g-mole}^{-1}$, $f_2 = 1/(6.0228 \times 10^{23}) \text{ mole-atom}^{-1}$, $f_3 = 1/(1.60207 \times 10^{-18}) \text{ kev-joule}^{-1}$, $f_4 = 2.6244/0.693147 \text{ years}$ and $f_5 = 365.22 \times 86400 \text{ sec-year}^{-1}$. Thus,

$$\bar{\beta} = 0.33267 f_1 f_2 f_3 f_4 f_5 = 60.54 \text{ kev}$$

This average energy is a factor of 0.2691 less than the peak energy of 225 kev and indicates that the beta energy distribution follows Fermi statistics although Hovi and Niemela¹² obtained 64.1 kev from the Fermi theory using a half-life of 2.64 years.

Radiation levels from Sample 2 were taken at various distances and through various thicknesses of lead. The power at the time was 0.2783 watts. The same measurements were also taken with a strontium-90 source of 0.0511 watts. All the radiation levels were scaled to a one-watt level, and the results are presented in Table 7. Also, the ratios of the strontium-90 to the promethium-147 radiation levels are listed. In air this ratio ranges from 31 to 49. With a half-inch of lead at three inches strontium-90 is 2500 times more hazardous than promethium-147. The strontium-90 sample was assayed in Calorimeter 58 with a cylinder of lead of 3/8-inch wall thickness surrounding the sample. The lead was removed and the sample measured again. The power was 0.66% higher with the lead. It was estimated from Table 7 that 3/8-inch of lead stops 87% of the bremsstrahlung rays from the strontium-90 sample. This would mean that $0.66 \times 1.13 = 0.75\%$ of the total beta energy leaves the sample as bremsstrahlung rays. Since the radiation level at three inches in air is about 49 times less from promethium-147, only $0.75149/49 = 0.015\%$ of the beta energy is lost. The half-life measurements were made with 1/4-inch of aluminum around the sample which stops about 40% of the radiation. The error in the power measurements due to bremsstrahlung ray losses from the calorimeter would be $0.015 \times 0.6 = 0.01\%$.

¹²V. Hovi and L. Niemela, *Ann. Acad. Sci. Fenn.*, A VI No. 103, (1962).

In conclusion, the half-life of promethium-147 is 2.6244 ± 0.0006 years (probable error) with an estimated absolute limit of 0.006 years. Using the Hanford values for the weight of promethium, the specific power and average beta energy are $0.33267 \text{ watts-gm}^{-1}$ and $60.54 \text{ kev-dis}^{-1}$, respectively. The loss of total power by bremsstrahlung rays is 0.015% from the samples and 0.01% from the calorimeters.

Table 7

**RADIATION LEVELS FROM PROMETHIUM-147 AND STRONTIUM-90
SOURCES* IN ROENTGENS PER HOUR PER WATT**

Conditions	Promethium-147	Strontium-90	Ratio
3 ft. (air)	0.032	1.0	31
3 ft. (1/16-in. lead)	0.001	0.49	490
3 ft. (1/2-in. lead)	- -	0.11	- -
18 in. (air)	0.12	3.9	32
18 in. (1/16-in. lead)	0.0043	1.5	350
18 in. (1/2-in. lead)	- -	0.43	- -
3 in. (air)	4.7	230	49
3 in. (1/16-in. lead)	0.072	72	1000
3 in. (1/2-in. lead)	0.009	23	2500

*Strontium-90, 0.0511 watts, 0.875 in. O.D. with 0.31 in. stainless steel for self-absorption.

Promethium-147, 0.2783 watts, 0.75 in. O.D. with 0.25 in. aluminum for self-absorption.

ACTINIUM-227 SEPARATION

One actinium slug was opened. The contents were dissolved in dilute HCl, loaded on an ion-exchange column of Dowex (AG) 50 W-X8[®] resin, and eluted with 2 M HCl, 2 M HNO₃, 4 M HNO₃, and 0.5 M NH₄OH (at pH 4) respectively. The eluted solution was separated into several fractions, the number of portions dependent upon the elutrient being used. Samples from fractions in which the actinium-227 and the thorium-227 were expected were removed from the cave and prepared for analysis. Results of the analyses have not yet been obtained, and therefore the degree of separation of the actinium from the daughter products is not yet known.

During the elution a large quantity of gas (probably helium and radon) was formed in the resin, reducing the elution rate from about 20 drops per minute to 3 drops per minute. Most of the gas bubbles were formed in the column during the HCl elution before the "short-lived" isotopes had been removed. Vacuum was used to speed this part of the elution by removing the gas which prevented normal flow.

URANIUM-234 SEPARATION AND PURIFICATION

Uranium-234 is being separated from aged plutonium-238 solutions by a combination of anion exchange and solvent extraction techniques. A sample containing nearly two grams of uranium-234 was processed previously by an anion exchange procedure to separate the bulk of the plutonium. The sample was extracted with hexone to reduce the plutonium level and to separate the uranium from the bulk of the inactive contaminants. A method of denitrating acid solutions with sugars was investigated.

Cold work was continued on the possibility of selective separation of plutonium from uranium by back-extraction from a tributyl phosphate (TBP) solution with the reducing agent, hydroxylamine hydrochloride. Earlier work

with this system showed that the HNO_3 normality was a critical factor. Experimentally, 86 milligrams of uranium were extracted into 20% TBP in a kerosene base (Amsco). The organic phase was then contacted with various normalities of nitric acid and molarities of hydroxylamine hydrochloride. Equal volumes of organic and aqueous phases were shaken for six minutes. The uranium was analyzed by the modified PAN method. Results indicated that 4.5% of the uranium was stripped by 4 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ /2 N HNO_3 , and 5.2% by 2 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ /4 N HNO_3 .

The reaction of sucrose with nitric acid was reported¹³ as a replacement for the formaldehyde denitration process in nuclear waste processing. In this process the sucrose is hydrolyzed to glucose and fructose, which are oxidized and decarboxylated in a series of steps. The final products of the reaction are water and oxides of carbon and nitrogen. With multivalent metal ions present as catalysts and 12 hours heating at 85-95°C, one mole of sucrose reacted with 20 moles of HNO_3 .

A reaction pot with a reflux condenser was set up to test the sucrose denitration. When sucrose solution was slowly added to hot HNO_3 , a vigorous reaction occurred immediately with the evolution of large amounts of brown fumes. After 12 hours heating at 90° to 105°, a sample was taken and titrated, and the volume was measured (there was some loss by evaporation). As a qualitative measure of the completeness of the reaction, samples were evaporated to dryness. In all sucrose experiments, a black residue was left after evaporation, indicating incomplete reaction. Ferric, aluminum, uranyl, cerous, zinc or thorium ions were not effective in catalyzing the complete decomposition of sucrose. The results are shown in the top half of Table 8.

Table 8

DENITRATION WITH SUCROSE AND DEXTROSE

Sugar (moles)	HNO ₃		Acid Lost (moles)	Efficiency ^a
	(moles)	(normality)		
DENITRATION WITH SUCROSE				
0.110	2.04	5.07	1.12	10
0.073	2.04	5.81	0.94	13
0.146	4.08	5.81	1.69	12
0.200	3.92	12.27	2.48	12
0.166	3.92	12.46	2.04	12
0.400	3.92	10.90	2.80	7
DENITRATION WITH DEXTROSE				
0.028	3.00	11.49	0.52	19
0.028	2.46	9.93	0.41	15
0.028	2.04	8.68	0.36	13
0.028	1.66	7.37	0.28	10

^aEfficiency = moles of acid destroyed/mole of sugar

¹³Chemical and Engineering News, 42, 50 (Jan. 27, 1964).

Dextrose was found to be effective as a denitrating agent, and did not leave the black residue upon evaporation as sucrose did. The results of experiments using dextrose and 100 mg of platinum ion as a catalyst are reported in the bottom half of Table 8. Smaller amounts of dextrose were added to the cold HNO_3 solutions, then warmed to reaction temperature. The efficiency (moles of acid destroyed/mole sugar) was generally higher than for sucrose, but decreased as the acidity decreased.

ADHESIVES RESEARCH

Adhesives are being developed for use with explosives and for other specialized applications. The adhesives must have satisfactory working and curing characteristics; they must retain flexibility at low temperatures and adequate tensile strength at elevated temperatures.

Three commercial curing systems, Humiseal 2A60[®] (Columbia Technical Corporation) a two part polyurethane potting material, DC 269[®] (Dow Corning) a contact silicone adhesive, and RTV 615[®] (General Electric) a silicone potting material, were evaluated as matrices for flexible conductive adhesives. All three were unsatisfactory.

The peel strength of a carbon black-filled silicone adhesive Q90092[®] (Dow Corning Corporation) was increased from 0.5 to 2.5 pounds per inch by the addition of nine percent by weight of low viscosity depolymerized rubber (DPR, Inc.) to the mixture.

The peel strength of a silver-filled silicone formulation can be increased by first coating the adherends with a silicone primer. A commercial silicone primer, SS-4004[®] (General Electric) was mixed with 60 weight % J-2 silver powder (Engelhard Industries) and spread thinly on peel test strips. The solvent was removed by heating at 70°C for five hours. The adherends were cooled and bonded with a conductive silicone formulation composed of 70 weight % J-2 silver powder in Q-90092 adhesive. The specimens were cured at 70°C for five hours. After aging at room temperature for one week, the peel strength was five pounds per inch. The peel strength of this formulation without priming was only 0.5 pound per inch.

A method for determining the shrinkage of adhesives during cure was developed which continuously measures the change in density of a curing adhesive. A tared, thin-walled, elastic container is partially filled with the catalysed resin system (about 150 g). The container is deaerated under vacuum and sealed under tension. The weight of the system and the time of initial mixing are recorded. The container is suspended in a water bath at room temperature by means of a fine wire connected to the calibrated "A" load cell of an Instron Testing machine. As the volume of water displaced by the mixture decreases, the weight recorded on the Instron chart will increase proportionately.

The resin systems are held suspended until no further changes are observed on the chart. The total shrinkage is calculated as follows:

$$\% \text{ Shrinkage} = \frac{\frac{\text{Apparent weight gain in grams}}{\text{density of water}}}{\frac{\text{Total weight of mixture}}{\text{Original density}}} \times 100$$

The original density is obtained by plotting the apparent change in weight back to the time of initial mixing. Table 9 lists the shrinkage of the three adhesive systems.

Table 9

% SHRINKAGE OF ADHESIVES DURING CURE

Components	Actual Wt. Sample (grams)	Apparent Wt. Gain (grams)	Initial Density (g/cc)	Cure Time (hrs)	Shrinkage (%)
Epon 828- [®] Versamid	157.6	3.55	1.093	60	2.46
Oxiron- [®] Anhydride	152.51	5.20	1.166	120	3.98
Polysulfide- Lead Peroxide	151.64	2.98	1.0584	22	2.07