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Foreword

This report is issued semiannually by Mound Facility. Under the sponsorship of the DOE Division of Basic Energy Sciences, Mound Facility is responsible for producing materials for use in the physical sciences to further the progress of science and technology in the public interest. Additional research activities of related interest under the sponsorship of the Division of Military Application are also reported here.

This report is submitted by W. T. Cave, Director of Nuclear Operations, and R. E. Vallee, Manager of Technology Applications and Development, from contributions prepared by W. M. Rutherford, Science Fellow (Thermal Diffusion); W. L. Taylor, Science Fellow (Gas Dynamics and Cryogenics); G. L. Silver, Science Fellow (Separation Chemistry); L. J. Wittenberg, Leader, Metal Hydride Research; and from members of the Isotope Separation Section: W. R. Wilkes, Isotope Separation Manager; E. D. Michaels, Leader, Isotope Separation Engineering; W. J. Roos, Leader, Stable Isotopes Inventory; B. E. Jepson, Senior Research Specialist, Metal Isotope Separation Research and Development; and R. E. Eppley, Leader, Uranium Isotope Chemistry and Radioisotope Inventory.

These reports are not intended to constitute publication in any sense of the word. Final results will either be submitted for publication in regular professional journals or be published in the form of MLM topical reports.

Previous reports in this series are:

MLM-2168	MLM-2414
MLM-2198	MLM-2450
MLM-2241	MLM-2506
MLM-2296	MLM-2555
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During this period 0.875 STP liter 20% xenon-124, 0.720 STP liter 40% xenon-124, and 8.75 STP liters 80% xenon-136 were separated.

II. Low temperature research

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A study of the intermolecular potential functions for spherically symmetric para H_2 has shown that the second virial data, the differential scattering data, and the bound state energies determined from spectroscopic data cannot all be described by any one of the published potential functions. We are therefore modifying a Hartree-Fock Dispersion type potential in an attempt to describe all the data.

A low temperature, condensed gas calorimeter has been constructed to be used in conjunction with vapor pressure measurements to determine latent heats at absolute zero in the study of intermolecular potential functions.

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Sensors and associated electronics and hardware have been assembled for the construction of an accurate thermal conductivity gas analyzer. Sufficient temperature control has been achieved and standard gas mixtures have been obtained for calibration of the instrument. When the technique has been demonstrated on the bench, a low temperature trennschaukel will be instrumented for in situ determinations of the change in concentration of a gas mixture during thermal diffusion experiments. Systems to be studied are He-Ne and ^3He - ^4He from approximately 25-250 K. The bench demonstrator model will remain intact for use in analyzing gas mixtures from other experiments.

III. Separation chemistry

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A total of 10.9 mg of thorium-229 was separated from previously extracted and aged U_3O_8 and shipped to Isotope Sales at ORNL in FY-1979. The thorium-229 production facility has been placed on standby for FY-1980.

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Separation and purification of two uranium-234 products were completed. Product A20 contained 8.884 g of uranium-234 at an isotopic purity of 99.855% with 2.3 ppm plutonium-238, and product A21 contained 3.473 g of uranium-234 at an isotopic purity of 99.634% with 3.8 ppm plutonium-238. All of product A20 and 1.116 g of product A21 were shipped to Isotope Sales at ORNL.

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Additional experiments were conducted with a new liquid thermal diffusion column designed specifically for research. Improved methods were developed for obtaining and reducing separation data as a function of time, and these methods were applied to isotopic separation experiments involving chlorobenzene, 1-chloropropane, ethyl bromide and carbon disulfide. Column parameters were obtained as functions of hot-to-cold wall spacing in the range from 178 μm to 305 μm . Good agreement with theory was found at spacings equal to or greater than 200 μm . Some restriction to thermogravitational circulation was noted at 178 μm .

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Additional experiments were completed on calcium isotope separation by liquid phase thermal diffusion. Uniform solute concentrations were established by controlled solvent injection; however, significant separation of isotopes was found in only two out of eight samples. The separation was equivalent to a 5% shift in the abundance of calcium-48. Apparently the particular conditions chosen for the experiments led to unstable conditions and remixing of the column contents. A short column was constructed to evaluate isotope separation without solvent injection. Separations amounting to a 5% shift in calcium-48 abundance were observed.

CaCl_2 solutions were found to be compatible with titanium at 180°C, and $\text{Ca}(\text{SCN})_2$ solutions were found to be too unstable for use in a process.

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The helium-argon total scattering cross section experiments have been successfully concluded. The neon-argon experimental cross sections were corrected for apparatus resolution and compared with theoretical values; results of the current data analysis are presented; further analyses are in progress. The rotatable, triply-pumped detector housing has been successfully leak tested and is ready for installation.

MUTUAL DIFFUSION

The study of diffusion coefficients, D_{12} , of krypton-noble gas systems has been completed over the presently attainable temperature range. Attention has since shifted to the systems helium-neon, argon, xenon, and argon-xenon. D_{12} values have been determined at seven different temperatures for argon-xenon mixtures, covering a temperature range of 344-1106 K; five values of D_{12} have been measured for helium-xenon from 351-1217 K. As part of this study and also at the request of Prof. R. A. Aziz of the University of Waterloo, we have made a very careful study of the diffusion coefficient of helium-argon at approximately 1300 K. The result of these high temperature experiments, plus some indirect information (interpolations and extrapolations) found in the literature, is the conclusion that the high temperature D_{12} data of Hogervorst [W. Hogervorst, *Physica*, 51, 59 (1971)] for helium-argon are too low by as much as 10% at 1400 K.

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I. Isotope separation

Argon

T. F. Walburg

Production of 1.3 STP liters of 95% argon-38 was completed. This rare middle isotope (0.063% natural abundance) poses one of the more difficult separations for a thermal diffusion cascade separation.

Now that additional argon-38 is available in sufficient quantity to establish the profile for a second, six-column enrichment cascade, it should be possible to produce this material on a more frequent basis. Also the 13-column cascade which produces intermediate enrichment feed (~7 to 10% argon-38) for the six-column system has benefited significantly from operating modifications. The modifications have currently resulted in a 50% increase in production rate. Production of 99.5% argon-36 continued with about 9.0 STP liters taken off the system.

Carbon

T. F. Walburg and G. E. Stuber

Approximately 280 g of 90% carbon-13 and 240 g of 98% carbon-13 as barium carbonate were produced by conversion from enriched carbon dioxide during the second half of the year. The new agitator for the large-scale barium carbonate reactor has arrived, and the larger conversion system should be in operation soon.

The reduction of enriched carbon monoxide produced 200 g of 99% and 130 g of 90% elemental carbon-13. The microprocessor used to control the elemental carbon conversion system has been disconnected to

allow some hardware modifications and the installation of new operating software. Mechanical control devices have been installed to allow continued operation of the conversion system until the microprocessor modifications have been completed.

Helium

T. F. Walburg

Approximately 5100 STP liters of 99.9% helium-3 was produced during this period. The helium product loading system was upgraded with the installation of a high-pressure compressor to facilitate loading customer orders up to 2000 psi.

Krypton

T. F. Walburg

Production of 70% krypton-82 was emphasized, with approximately 12.5 STP liters processed on the 10-column cascade. A second thermal diffusion cascade was brought into use to prepare enriched feed for the 10-column system. This 19-column system may soon be processing product-grade material from natural abundance feed. This would be the first time this separation has been accomplished in a single cascade.

Another 19-column thermal diffusion cascade was used to prepare enriched krypton-78 with approximately 3.0 STP liters of 50% material produced during this period. The system is currently being switched over for production of 90% krypton-78.

During this period approximately 10 STP liters of 90% krypton-84 was also processed.

Neon

W. J. Roos

During this period, filling of a single large order for neon-21 required the entire inventory of that isotope. Preparations are currently being made to enrich a new batch of neon-21 to >90%. A six-column thermal diffusion system is available for this purpose; it will be put into operation following necessary modifications and leak checking. Production of enriched material is expected to begin within 3-6 months. Collection of enriched neon-20 and neon-22 as by-products will be resumed.

Enrichment of neon-20 which is slightly below product specification (99.95% neon-20) is continuing in a four-column thermal diffusion system.

Oxygen-16

W. R. Deal and G. E. Stuber

The new oxygen-16 electrolysis system was put into operation during the fourth quarter of 1979. Most of the initial problems associated with the start-up of the system have been solved. Approximately 11 kg of oxygen-16 gas has been produced. A spare part inventory is being procured.

Improvements to the original cold trap design are being made. These improvements will permit operation of the system with less operator attention.

Oxygen-17/18

G. E. Stuber

The system used to electrolyze water enriched in oxygen-17 or oxygen-18 produced 120 g of 50% oxygen-17 and 394 g of 95% oxygen-18 gas. The cold trap installed in the hydrogen line has decreased the loss of feed water from approximately 10% to 7%.

Changes in the operation procedures are expected to result in additional improvements in the yield of future conversion runs.

Xenon

W. J. Roos

During this period the following approximate quantities of materials were produced: 0.875 STP liter 20% xenon-124; 0.720 STP liter 40% xenon-124; and 8.75 STP liters 80% xenon-136.

II. Low temperature research

Hydrogen intermolecular potential functions

G. T. McConville

Hydrogen occurs in two nuclear spin states, ortho and para hydrogen. At low temperatures para has a total momentum quantum number of $J=0$ and is spherically symmetric, while ortho has a quantum number of $J=1$ and has a quadrupole moment. To determine

the potential for the general angular dependent case, we are first characterizing the para or $J=0$ case by studying its intermolecular potential function.

We have compared potentials to three types of data for para H_2 : second virial coefficients; total and differential scattering cross sections; and bound state energies for the $(H_2)_2$ di-molecule. The potentials we have studied are: Exp-6 with Mason-Rice parameters [1], beam potential of Farrar and Lee [2], and Hartree-Fock Dispersion forms proposed by Ahlrich, et al [3], Bauer, et al [4], and Silvera and Goldman [5]. The shapes of these potentials are shown in Figures II-1 and II-2. They differ considerably. The Exp-6 parameters were determined from high temperature second virial and transport property data. The Silvera and Goldman form was determined from beam and solid state data. The others were determined from beam data only.

We show first the fit to the high temperature second virial for para H_2 , in Figure II-3. The Exp-6, as expected, fits the data, while none of the beam potentials do. At low temperatures the difference between the para H_2 and normal H_2 (75% ortho) can be seen. In Figure II-4, it can be seen that the Exp-6 and the Bauer potentials are too high; Ahlrich is low at all temperatures. Silvera and Goldman produce a good, low temperature fit but a poorer, high temperature fit.

The energy levels for $(H_2)_2$ bound states depend on the shape of the attractive well of the potential. There are two bound states: one for angular momentum $L=0$, and one for $L=1$. The energy difference between these levels was observed

spectroscopically by McKeller and Welsh [6]. The $L=0$ state is the only one occurring in para H_2 . The calculated energies are compared to the experimental differences in Table II-1. The bound state energies are determined by the negative energy necessary to produce a wave function meeting the boundary condition that it goes to zero at large distances. The wave functions are generated through a numerical integration of the Schrodinger equation. It can be seen from the table that only the Evett and Margenau value lies within the experimental range. This is surprising because the Evett and Margenau potential was calculated in 1953 and contains incorrect dispersion parameters. None of the potentials produces experimental virials and bound state energies simultaneously.

The potentials of Ahlrich, Bauer, and Farrar and Lee were produced from beam measurements. Preliminary calculations of non-velocity-averaged, differential scattering cross sections show that the three potentials are not reconcilable to the data of Farrar and Lee. Calculations of the total cross sections to compare with the work of Bauer are in progress.

The problem is to find a potential function that will represent the three different types of data. The Hartree-Fock Dispersion form of the potential can make use of theoretically determined parameters.

The form introduced by Scoles is:

$$Q(r) = Ae^{-\alpha r} - \left(\frac{C_6}{r^6} + \frac{C_8}{r^8} + \frac{C_{10}}{r^{10}} \right) f(r)$$

$$f(r) = \exp\left(-\left(D\frac{r_m}{r} - 1\right)^2\right) \quad r < r_m$$

$$f(r) = 1 \quad r \geq r_m$$

FIGURE II-1 - Attractive portion of five H_2 potentials: — Exp-6 (Mason-Rice); ---Ahlrich, et al; ---Silvera and Goldman; -.-Bauer, et al;Farrar and Lee.

FIGURE II-2 - Repulsive portions of five H_2 potentials: Legend same as Figure II-1.

FIGURE II-3 - High temperature second virial coefficients for H_2 . Experimental: $\bullet$, normal H_2 (difference from para H_2 within experimental uncertainty $\pm$). Theoretical: legend same as Figure 1.

FIGURE II-4 - Low temperature second virial coefficients for H_2 . Experimental: $\bullet$, para H_2 (spherically symmetric); $\blacktriangle$, normal H_2 (75% ortho-25% para). Theoretical curves (legend same as Figure II-1) are to be compared with the $\bullet$ para H_2 data.

Table II-1 - BOUND STATES FOR $(H_2)_2$ (ENERGY IN KELVINS)

Experimental		L=0 = L=1	
McKellar & Welsh (1974)		2.259 - 2.316	
Calculated	L=0	L=1	ΔL
Gordon & Cashion ⁷ (1965)			
L-J	3.656	1.426	2.230
Exp-6 (Mason-Rice)	3.762	1.525	2.237
Exp-6 (Evet-Marganau) ⁸	4.555	2.291	2.264
McKellar & Welsh (1974)			
Beam (Farrar & Lee) ¹			1.971
McConville (this work)			
Exp-6 (Mason-Rice)	3.759	1.522	2.237
Beam (Farrar & Lee) ¹	2.885	0.905	1.980
Beam (Ahlrich, et al) ²	4.812	2.450	2.362
Beam (Bauer, et al) ³	5.018	2.720	2.213
Silvera & Goldman ⁴	3.968	1.755	2.325

The values of A and α are obtained from self-consistent Hartree-Fock calculations for the $(H_2)_2$ system; the C_{2n} are obtained from Rayleigh-Schrodinger perturbation calculations. For the potential of Ahlrich [3], $A = 3.9788 \times 10^6 K$, and $\alpha = 3.349A^{-1}$ from the self-consistent field Hartree-Fock calculations of W. Meyer [9]. New values for C_6 , C_8 , and C_{10} of 12.2, 213, and 4700, respectively, in atomic units have been calculated in a second paper by Meyer [10]. Ahlrich used a value of 1.28 for D which he assumed to be a universal parameter for spherical systems. We have found [9] that $D = 1.24$ is necessary to obtain an accurate potential for helium. The difference between $D = 1.28$ and $D = 1.24$ using Ahlrich's other parameters for H_2 is shown in Figure II-5. D represents a parameter measuring the effect of electronic overlap of the two molecules and is the most difficult to obtain from theory. The effect of changing D on the experimental properties is under study. It is possible that a different value of D is required for each multiple term in the dispersion expansion.

A low temperature differential calorimeter has been designed and constructed with the assistance of a University of Cincinnati Co-op student, Janice Fair. The measurement of vapor pressure and heat capacity on the same gas samples can produce a precise value of the latent heat of vaporization at $T=0$. This quantity is one of the two solid state parameters used to obtain a self-consistent potential function for all three phases: solid, liquid and gas. The calorimeter and associated 3He refrigerator are shown in the next three figures. The cryostat, shown in Figure II-6, has two recirculating 3He refrigerators which were designed and built by W. R. Wilkes [11]. The platform on top of the cryostat (top of Figure II-6) holds the bellows for a pneumatically driven heat switch. In Figure II-7 the 1.5 K 3He refrigerator is in the copper tube on the feedthrough flange at the center of the figure. The 0.3 K 3He pot is the cylinder supported by 1/8-in. diameter stainless rods from the electrical feedthrough flange. The calorimeter itself is shown in Figure II-8. The twin calorimeter cans

FIGURE II-5 - Hartree-Fock dispersion potential of Ahlrich, et al, with variation of parameter D . Reduction of D increases depth of well and reduces collision diameter.

FIGURE II-6 - The cryostat for low temperature differential thermometer. Bellows assembly operates heat switch.

FIGURE II-7 - Low temperature end of cryostat shown in Figure II-6.

FIGURE II-8 - Closeup of heat switch assembly and calorimeter cans.

are cooled by copper wires clamped in gold-plated copper jaws; this is accomplished when the heat switch in the center of the picture is activated by pulling upon the central rod with the bellows mechanism. The samples are thermally isolated by releasing the jaws. The cryostat is now being electrically wired and the gas handling systems for the ^3He refrigerators and samples are being built.

Low temperature trennschaukel

D. Cain and W. L. Taylor

An accurate analytical technique is being developed for the in situ analysis of gas mixtures in low temperature trennschaukel experiments. The method employs self-heated thermistors as sensing elements; two are to be immersed in the unknown gas mixture, while two others are in a known reference gas. The pairs of thermistors form opposite arms of a Wheatstone bridge. When sufficient current is passed through the bridge, the temperature of the thermistors rises above that of the ambient gas due to Joule heating. The temperature, and therefore the resistance, of the thermistors is determined in the main by the ability of the surroundings to carry off heat. Thus, the resistance values in the arms of the bridge change with the thermal conductivity of the gas mixture, which in turn changes with gas composition. For a given temperature, bridge current, and reference gas, the amount of imbalance in the bridge is a measure of the composition of unknown gas.

Before installing the thermistors into the trennschaukel for in situ measurements, it was decided that the technique should first be demonstrated on the bench. Several sets of thermistors and associated electronics and hardware have been assembled for construction of a thermal conductivity gas analyzing bridge. An insulated box was fabricated in the shop to serve as an environmental chamber for the bridge. The bridge elements and gas mixtures (unknown and reference) were sealed into enclosures which are immersed in a water bath in the environmental chamber. A constant temperature circulator (Haake, Model FSE) controls the temperature of the bath, and, thereby, the environmental chamber. Millikelvin temperature control over a period of one hour has been achieved in the water bath, with fluctuations in the air around the bath somewhat larger. The power supply, digital voltmeter, standard resistor, and any other device that may be temperature sensitive are all kept in the temperature-controlled environment.

The bridge must be calibrated for each gas mixture of interest at constant (and known) temperature and bridge current. To this end, we have had prepared gas mixtures of accurately known composition over the range of compositions expected to be encountered. The reference gas will be introduced into both the cell which is to contain the reference thermistors and the one which is to contain the unknown thermistors. Under ideal conditions of perfectly matched thermistors, all resistances would be equal, and the bridge would be balanced; in reality, the bridge will show a small imbalance. Keeping the same reference gas in the reference cell, other known gas mixtures will be introduced into the unknown cell, and the amount of

imbalance recorded. In this way, we can generate a calibration curve which can later be used with the reference gas and a true unknown mixture. A thermistor bridge of this type has been shown to be as sensitive as a dual collector mass spectrometer for analyzing mixtures of ^{36}Ar - ^{40}Ar ; for Ar-Kr and Ne-Ar mixtures it is seven and ten times more sensitive, respectively [12].

Thermistors suitable for use at cryogenic temperatures have been obtained for installation into the trennschaukel. The trennschaukel has 12 tubes, one of which will be sacrificed for a reference cell, leaving 11 for the swing separation. After installing the thermistors, heater wires, and platinum resistance thermometers, the thermistors will be calibrated for the gas mixtures of interest under experimental conditions. This will allow concentration changes to be monitored in situ in a thermal diffusion experiment.

The systems of interest for the present work are He-Ne and ^3He - ^4He . Experiments will be conducted from approximately 250 K down to 25 K (or as low as the system will go). In addition, the bench system on which the technique is demonstrated will remain intact for use in analyzing gas mixtures from mutual diffusion experiments and other trennschaukel systems.

III. Separation chemistry

Thorium-229

W. R. Deal

Previously extracted uranium-233, in the form of U_3O_8 with low uranium-232 content, was processed during the reporting period to produce thorium-229 as two items,

79-2 (4.1 mg) and 79-3 (2.7 mg). Item 79-1 (4.1 mg) was reported in the previous semiannual report. The total thorium-229 production for the fiscal year was 10.9 mg, meeting the FY-1979 commitment.

Further discrepancies between the expected isotope ratios and the results received from mass spectrometry indicate that previous extractions of this feed material did not remove all the natural thorium present, a factor that must be considered in the prediction of future isotope ratios. This process will be suspended for FY-1980. Future demand for thorium-229 will determine whether or not the process is reactivated. The facility was placed on standby and all the feed material was returned to storage.

Protactinium-231 and Thorium-230

M. L. Hertz and P. E. Figgins

Mound Facility recovers thorium-230 and protactinium-231 from a uranium mill by-product known as "Cotter Concentrate" and ships the products to Isotope Sales at ORNL. Previous reports contain detailed descriptions of the origin and character of the Cotter Concentrate, the processing facilities, and development of the current recovery and purification processes.

This process has been suspended for FY-1980. Therefore, head-end processing of Cotter Concentrate was discontinued in June 1979 to allow time for complete processing of the separated protactinium concentrate by the end of FY-1979. The systems were cleaned up as much as possible without complete dismantling, and left ready for re-start on short notice, if desired.

A total of 101.4 mg of protactinium-231, as estimated by gamma analysis, was separated from the Cotter Concentrate, concentrated by evaporation and passed on to the final purification process. The concentrate solutions were purified by the standard method, and two protactinium products obtained. The first contained 116 mg of protactinium-231 (by alpha count) and weighed 143 mg. The second, which was kept separate because of suspected impurities, contained 16.2 mg of protactinium-231 and weighed 29.7 mg. These products, along with 56,920 mg of thorium-230, were shipped to ORNL and comprise the FY-1979 product.

Installation of a Westfalia centrifuge was completed in October 1979. An initial "cold" checkout will be made, after which the unit will be available for future use in clarifying the dissolved Cotter Concentrate, if the process should be re-started.

Uranium-234

P. L. Keister

Mound Facility has been separating and recovering high-isotopic purity uranium-234 from aged plutonium-238 since 1964. The chemical steps have been described elsewhere in detail [1].

The intermediate separation (anion exchange in nitrate media) of uranium from the second half of the uranium-rich A20 filtrate was completed during this period. The filtrate had been salted to 1.6M with $\text{Al}(\text{NO}_3)_3$ and adjusted to 0.3M HNO_3 using NH_4OH . Hydroxylamine nitrate was added as a reductant for plutonium, and the salted feed was loaded onto the column of Dowex 1x4 anion

exchange resin (nitrate form). The uranium was eluted with 7M HNO_3 , and the plutonium was eluted with 0.35M HNO_3 containing hydroxylamine nitrate. Alpha pulse height analyses of samples from the uranium fractions indicated a total of 10.4 g of uranium-234 with 16 mg of plutonium-238.

To prepare for the final separation step (anion exchange in chloride media), these uranium fractions were combined and converted to chloride form by a double precipitation with NaOH and subsequent dissolution in 9M HCl . Two runs were made to complete the final separation of A20. The chloride solution was loaded onto the column of Dowex 1x4 anion exchange resin (chloride form). The plutonium was eluted with 9M $\text{HCl}/0.05\text{M}$ NH_4I . A neptunium fraction was eluted with 4M HCl , and the uranium was eluted with 0.5M HCl . Alpha pulse height analyses of samples from the uranium fractions indicated a total of 9.1 g of uranium-234 with 5-6 ppm plutonium-238.

These A20 uranium fractions were combined, the uranium precipitated with NH_4OH , and the precipitate calcined to the oxide at 900°C . The total oxide weight of the final A20 product was 10.811 g. Final alpha pulse height analyses of samples indicated 12.7 ppm uranium-232 and 2.3 ppm plutonium-238 by weight. Based on alpha pulse height data and proportional counting of samples, the uranium-234 content was calculated at 8.884 g. Mass analysis of the sample indicated the final A20 product had an isotopic purity of 99.855% by weight.

Because product A20 did not meet the FY-1979 goal of 10.0 g of uranium-234 product,

another aged plutonium "cow" was selected for processing. This "cow" was designated batch A21 and contained 19 g of plutonium-238 with an estimated 3.1 g of uranium-234 based on an age of 18 years. It was received from storage in the form of encapsulated metal which had been fabricated for a heat source. The capsule was opened with a hacksaw, and the plutonium metal dissolved in hot, concentrated HNO_3 containing 0.05 to 0.1M MF. The plutonium was precipitated as the oxalate using dimethyloxalate. The oxalate precipitate was calcined and the plutonium returned to storage as the oxide.

The uranium-rich A21 filtrate was evaporated to concentrate the volume and to destroy the oxalate. Alpha pulse height analyses of samples indicated 3.9 g of uranium-234 and 0.7 g of plutonium-238. The intermediate separation, the final separation, and the final product preparation of batch A21 were completed as described above for A20. The total oxide weight of the final uranium product was 4.241 g. The weight of the uranium-234 was calculated at 3.473 g with 9.9 ppm uranium-232 and 3.8 ppm plutonium-238 by weight. The isotopic purity of product A21 was 99.634% by weight.

Table III-1 summarizes products shipped in FY-1979.

Table III-1 - URANIUM-234
PRODUCTS SHIPPED (FY-1979)

Product	^{234}U (g)	^{238}Pu (ppm)	Isotopic Purity (wt %)
A20	8.884	2.3	99.855
A21	1.116	3.8	99.634
	10.000		

IV. Separation research

Liquid thermal diffusion

W. M. Rutherford

Experimental and theoretical work continued on the performance of liquid phase thermal diffusion columns for isotope separation. Construction and preliminary testing of a new research column were described in the last report [1]. The design of the new column incorporates a number of features derived from the results of extensive experimental work with a variety of simply constructed practical scale devices. The first measurements on chlorine isotope separation in the chlorobenzene system were in good agreement with theory at a hot-to-cold wall spacing of 254 μm . This report describes the results of additional work at other spacings and with other compounds. New experimental methods were devised to accelerate the rate of data acquisition, and computer programs were developed to process the resulting experimental data.

The separation of a binary mixture in a thermal diffusion column is described by the following equation for the net transport of component 1 in the vertical, z , direction

$$\tau_1 = Hw_1 (1-w_1) - K dw_1/dz \quad (1)$$

where τ_1 is the transport in mass per unit time and w_1 is the mass fraction of the component. The quantities H and K are the initial transport coefficient and the remixing coefficient, respectively. The column coefficients are complicated functions of the dimensions and operating conditions of the column and of the properties of the fluid. Simple, approximate

expressions can be derived for the case of a Boussinesq fluid with constant average properties at the mean temperature of the column. Thus,

$$H = \frac{a^3 \rho^2 \alpha_T \beta g B (T_H - T_C)^2}{6! \eta \bar{T}} \quad (2)$$

$$K = \frac{a^7 g^2 \beta^2 \rho^3 B (T_H - T_C)^2}{9! \eta^2} \quad (3)$$

where a = hot-to-cold wall spacing

B = circumference

g = gravitational acceleration

T_H = hot wall temperature

T_C = cold wall temperature

$\bar{T}$ = average temperature

α_T = thermal diffusion factor

η = viscosity

ρ = density

$$\beta = - \frac{1}{\rho} \left(\frac{d\rho}{dT} \right)$$

Diffusive remixing along the z direction is neglected; therefore, the total remixing coefficient is equal to the convective remixing coefficient.

At total reflux $\tau_1 = 0$, and

$$\ln q_E = \ln \frac{w_{1B}(1-w_{1T})}{w_{1T}(1-w_{1B})} = HL/K \quad (4)$$

where q_E is the separation factor and L is the length along the column. The subscripts T and B refer to the top and bottom sample points, respectively.

Measurement of the experimental separation at total reflux yields only the ratio H/K . In order to determine the magnitudes of the individual coefficients, it is necessary to do an experiment for which $\tau_1 \neq 0$. Such an

experiment can be one in which a steady state, net flow is imposed on the column, or it can be one in which the transient behavior of the column is observed following start-up from an initially uniform concentration profile. For the latter case:

$$\frac{\partial w_1}{\partial t} = - \frac{1}{\mu} \left(\frac{\partial \tau_1}{\partial z} \right) \quad (5)$$

where t is the time and μ is the mass holdup per unit length.

In previous work, we have used the steady state technique almost exclusively because of the practical difficulties associated with removing small, representative samples from the experimental columns.

A new experimental system has been devised which solves the sampling problem. As shown in Figure IV-1, each end of the

FIGURE IV-1 - Liquid thermal diffusion apparatus for transient separation measurements.

column is fitted with a steam heated thermosiphon loop which circulates fluid continuously through the active section of the column. Each thermosiphon loop contains a High Pressure Equipment Co., 3-way, 1/16-in., high-pressure valve which serves as a sampling valve. The design of the valve is such that the liquid to be sampled is circulated past the valve seat. Extremely small, representative samples can be removed by evaporating liquid through the valve seat into an evacuated volume. A typical sample volume with this technique is on the order of 5 μ L, as compared to a typical volume of 170 μ L for the purge and sample technique used previously.

The new experimental procedure required the development of computer programs for reduction of the measurements of separation as a function of time. If we define dimensionless time by:

$$\theta = YHt/\mu L, \quad (6)$$

where

$$Y = \ln q_E, \quad (7)$$

then Equation 5 becomes, at total reflux

$$\frac{\partial w_1}{\partial \theta} = (1-2w_1) \frac{\partial w_1}{\partial y} + \frac{\partial^2 w_1}{\partial y^2}, \quad (8)$$

where

$$y = Hz/K \quad (9)$$

The computer program for calculating transient performance of multicomponent separation systems solves the multicomponent analog of Equation 8. It was revised to generate a family of curves of the form:

$$\ln q = f(\theta, Y) \quad (10)$$

with Y as the parameter. The quantity q in Equation 10 is the transient value of the separation factor defined for the steady state by Equation 1.

Experimental separation data were acquired in the form,

$$\ln q = f(t) \quad (11)$$

A computer program was written to generate a best fit to the data by interpolating among the set of curves represented by Equation 10. The fit was accomplished by simplex minimization of the mean square deviation in $\ln q$. Parameters of the simplex minimization were Y , H , and a time increment, δt , used to compensate for uncertainty in the starting time of the experiment.

The transient technique was used to determine the transport coefficients of the new research column at hot-to-cold wall spacings from 178 to 304 μm . Chlorobenzene, 1-chloropropane, ethyl bromide and carbon disulfide were used as working fluids. The measurements were based on the ^{35}Cl - ^{37}Cl substituted species for the chlorinated compounds, the ^{79}Br - ^{81}Br species for ethyl bromide and the ^{12}C ^{32}S ^{32}S - ^{12}C ^{32}S ^{34}S pair for carbon disulfide. The experimental series was completed for chlorobenzene. Work is still in progress on the other compounds. Dimensions and operating conditions for the experimental column are given in Table IV-1.

Some typical raw transient data and the fit thereto are shown in Table IV-2 and Figure IV-2. Table IV-3 is a compilation of the column coefficients for all the experiments. Depending on the hot-to-cold wall spacing and the compound, the time required for each experiment ranged from a little more than 1 hr (ethyl bromide at 304 μm) to 17 days (chlorobenzene at 178 μm).

Table IV-1 - DIMENSIONS AND OPERATING CONDITIONS FOR LIQUID THERMAL DIFFUSION COLUMN EXPERIMENTS

Hot wall i.d.	13.87 mm
Hot wall o.d.	18.677 mm
	18.778 mm
	18.880 mm
	18.931 mm
Cold wall i.d.	19.286 mm
Water jacket i.d.	57.0 mm
Active length	456 mm
Steam temperature	164°C
Water temperature	14.4°C
Water flow rate	9.6 liters/min

In order to calculate the column coefficients from theory, it is necessary to know the temperatures of the hot and cold walls of the working space. These temperatures are only indirectly available from the steam temperature and the inlet temperature of the cooling water. A computer program had been written to do the calculation; however, the program requires an experimentally derived value of the heat transfer coefficient at the column-cooling water interface. A series of thermal measurements was performed, therefore, to evaluate the heat transfer coefficient.

The gross heat flow in the column was determined as a function of water flow rate with the column evacuated in order to get the combined contributions from heat flow through the end seals and heat flow by radiation. The column was then filled with helium, a gas of known thermal conductivity, to determine the contribution of the working space to the heat flow. A value of the heat transfer coefficient, h_w , was selected to get the best match

Table IV-2 - TYPICAL EXPERIMENTAL DATA FROM TRANSIENT SEPARATION EXPERIMENTS

Experiment 1 Chlorobenzene $a = 305 \mu\text{m}$

Parameters for best fit:

$$H = 7.001 \times 10^{-5} \text{ g/sec}$$

$$Y = 0.2882$$

$$\delta t = 0.08055 \text{ hr}$$

Experiment 2 Chlorobenzene $a = 203 \mu\text{m}$

Parameters for best fit:

$$H = 1.457 \times 10^{-5} \text{ g/sec}$$

$$Y = 1.230$$

$$\delta t = 0.6524 \text{ hr}$$

$t(\text{hr})$	$\ln q$	$\ln q$ (calc)	Deviation	$t(\text{hr})$	$\ln q$	$\ln q$ (calc)	Deviation
0.50	0.0865	0.0878	0.0013	1.00	0.0628	0.0775	0.0147
1.00	0.1381	0.1364	-0.0017	2.00	0.1345	0.1200	-0.0145
2.00	0.2001	0.2008	0.0007	5.00	0.2385	0.2318	-0.0067
3.00	0.2363	0.2377	0.0014	8.00	0.3289	0.3284	-0.0005
5.00	0.2704	0.2710	0.0006	9.50	0.3675	0.3726	0.0051
7.00	0.2819	0.2819	0.0000	24.00	0.7000	0.7013	0.0013
RMS Deviation = 0.0011				32.50	0.8326	0.8323	-0.0003
				96.00	1.1860	1.1825	-0.0035

RMS Deviation = 0.0080

FIGURE IV-2 - Transient separation experiments with chlorobenzene in the liquid thermal diffusion research column. The solid curves are calculated for the best fit.

Table IV-3 - RESULTS FROM LIQUID THERMAL DIFFUSION COLUMN EXPERIMENTS

Compound	a (μm)	Net Heat Flow (W)		T_H ($^{\circ}\text{C}$)	T_C ($^{\circ}\text{C}$)	$10^5 H$ (g/sec)	Y	δt (hr)	Deviation
		Exptl	Calc						
Chlorobenzene	305	1118	1162	156.8	44.5	7.00	0.288	0.081	0.001
	254	1239	1327	155.5	48.7	3.46	0.562	0.100	0.006
	203	1481	1545	153.7	54.3	1.46	1.230	0.652	0.008
	178	1607	1682	152.6	57.8	0.48	1.639	0.044	0.039
1-Chloropropane	305	1039	982	158.2	39.8	11.57	0.198	-0.039	0.014
	254	1057	1132	157.0	43.7	5.98	0.434	0.260	0.004
Ethyl bromide	305	907	952	158.5	39.0	24.97	0.087	0.072	0.001
Carbon disulfide	305	1245	1361	155.2	49.4	19.94	0.179	0.056	0.011

between calculated and observed net heat flows. The results, which are reported in Table IV-4, are relatively imprecise. Fortunately, the sought-after wall temperatures are relatively insensitive to h_w .

Column coefficients for each experimental condition were calculated from theory by the usual integration procedure based on tables of physical properties compiled previously [2]. Isotopic thermal diffusion factors used in the calculations are given in Table IV-5. The value for chlorobenzene was back-calculated from the experimental H at 254 μm . The other values were taken from Reference 2.

The theoretical coefficients are given in Table IV-6 along with the corresponding experimentally derived values. Figures IV-3, -4, and -5 are plots of results for the chlorobenzene series as a function of a , the hot-to-cold wall spacing.

On the basis of these experiments, the performance of the new column appears to be highly satisfactory down to a spacing

Table IV-4 - HEAT TRANSFER COEFFICIENTS AT THE COOLANT-COLUMN INTERFACE

Water flow (liters/min)	h_w ($\text{W}/\text{cm}^2/^{\circ}\text{C}$)
3.96	0.053
9.54	0.065
24.1	0.065
30.0	0.125

Table IV-5 - ISOTOPIC THERMAL DIFFUSION FACTORS

Compound	m_1	m_2	α_T	α_O^a
Chlorobenzene	112	114	0.0282	3.18
1-Chloropropane	78	80	0.021	1.66
Ethyl bromide	108	110	0.02	2.18
Carbon disulfide	76	78	0.062	4.77

^aNote that $\alpha_O = \alpha_T \frac{m_2 + m_1}{m_2 - m_1}$,

where m_1 and m_2 are the molecular weights of the two species.

Table IV-6 - COMPARISON OF LIQUID THERMAL
DIFFUSION EXPERIMENTAL RESULTS WITH THEORY

Compound	a (μm)	$10^5 H$ (g/sec)		K (g cm/sec)		$\ln q_E$	
		Exptl	Theory	Exptl	Theory	Exptl	Theory
Chlorobenzene	305	7.00	6.53	0.01107	0.00994	0.288	0.299
	254	3.46	3.46 ^a	0.00280	0.00255	0.562	0.616
	203	1.457	1.564	5.4×10^{-4}	4.81×10^{-4}	1.230	1.483
	178	0.479	0.963	1.33×10^{-4}	1.77×10^{-4}	1.639	2.478
1-Chloropropane	305	11.57	11.88	0.0266	0.0341	0.198	0.159
	254	5.98	6.39	0.00628	0.00890	0.434	0.327
Ethyl bromide	305	19.2	28.1	0.100	0.120	0.087	0.107
Carbon disulfide	305	39.9	36.7	0.0508	0.0425	0.357	0.393

^a α_T was chosen to force agreement with the experimental value of H for this point.

of 200 μm . The equilibrium separation at 178 μm was found to be higher than the corresponding value at 203 μm . This is the first time that such a result has been achieved. In almost all previous work the maximum separation was reached at spacings equal to or larger than 200 μm , and the rapid onset of nonideal parasitic effects at lower spacings led to separations significantly smaller than those predicted theoretically. There seems, however, to be some impediment to the thermogravitational circulation in the 178 μm configuration. Both H and K are low relative to theory. Normally, parasitic effects would lead to a remixing effect larger than that predicted. The remixing coefficient is proportional to the square of the mass circulation rate in the column; hence, the conclusion is that circulation is restricted.

FIGURE IV-3 - Equilibrium separation factor for chlorobenzene in the new research column. The abscissa is linear in $1/a^4$.

FIGURE IV-4 - Initial transport coefficient for chlorobenzene liquid thermal diffusion experiments. The solid line is calculated from theory for $\alpha_t = 0.0282$.

FIGURE IV-5 - Remixing coefficient for chlorobenzene liquid thermal diffusion experiments. The solid line is calculated from theory.

Calcium isotope separation

W. M. Rutherford and K. W. Laughlin

Liquid phase thermal diffusion is being investigated as a means of separating calcium isotopes. Thermal diffusion has been successfully applied to the separation of practical quantities of isotopes of elements having simple liquid compounds. Calcium, however, does not form a compound which is liquid in the practical range of temperatures; therefore, it is necessary to work with solutions of calcium salts in suitable solvents. The solutions cannot be processed in a straightforward way because the thermal diffusion separation of solute and solvent is much larger than the expected isotope effect.

The initial phases of this work have been directed toward 1) the construction and testing of an apparatus designed to offset the solute-solvent separation effect by controlled injection and 2) the removal of pure solvent at the ends of the separation column. It was shown theoretically that this could be accomplished without affecting the isotopic separation if the solvent injection rate were chosen such that

$$\sigma = Hw_1 \quad (1)$$

where σ is the injection rate, H is the initial transport coefficient for the solvent solute pair, and w_1 is the solvent mass fraction.

We have previously reported the evaluation of solute-solvent separation parameters as functions of concentration for the

$\text{Ca}(\text{NO}_3)_2$ -water system, and have described the first experiment aimed at establishing a uniform solute concentration in the separation system [3]. A large, initially undetected leak diminished the significance of the experiment, although a slight separation of the isotopes was found in one set of samples.

Several additional experiments have now been completed, and a new, shorter column has been constructed for evaluation of the isotope effect without solvent injection. In addition, materials compatibility tests were run on aqueous solutions of calcium salts which might be used in place of $\text{Ca}(\text{NO}_3)_2$.

The experiments involving solvent injection were conducted with the apparatus described in the previous report. The column was a standard 304 stainless steel unit, 72 cm long, 2.5 cm annular diameter, with a hot-to-cold wall spacing of 254 μm . The system was filled for the second experiment with a solution containing 20 wt % $\text{Ca}(\text{NO}_3)_2$ in water. At this concentration, we have found that the initial transport coefficient for the solute-solvent separation is:

$$H = 7.25 \times 10^{-4} \text{ g/sec} \quad (2)$$

Thus, according to Equation 1 we require a solvent injection rate of 2.088 g/hr. The closest pump setting, 2.42 ml/hr, was chosen for the experiment.

Figure IV-6 is a plot of the $\text{Ca}(\text{NO}_3)_2$ concentrations at the top and bottom of the system as functions of time during the

FIGURE IV-6 - Solute concentrations during Experiment 2. The arrows indicate when samples were taken for isotopic ratio measurements. The smooth curves are calculated from theory.

experiment. The system was maintained in a relatively stable condition for 15 days, and five sets of samples were taken for isotope ratio determinations, starting on the sixth day.

Results of the isotopic ratio determinations on the five samples are given for the ^{40}Ca - ^{48}Ca pair in Table IV-7. Three of the samples show no separation of the isotopes; however, samples taken on day 11 and day 15 had separations well in excess of the estimated standard deviation in the separation factor. The separation factor is defined by

$$q = \frac{(w_{48}/w_{40})_B}{(w_{48}/w_{40})_T} \quad (3)$$

where w is the mass fraction, and the subscripts T and B refer to the top and bottom of the system, respectively. The

estimated standard deviation in q is ± 0.01 . The separation on day 11 amounted to a shift of approximately 5% in the isotopic abundance of ^{48}Ca ; however, the system was clearly unstable and on day 13 the separation factor had dropped to unity within the precision of the measurement.

The third and fourth experiments were run at much higher concentrations approaching the solubility limit of $\text{Ca}(\text{NO}_3)_2$ at room temperature. There is some evidence for a larger isotopic effect at higher concentrations. Panson, for instance, found no separation of lithium isotopes in 0.5M LiNO_3 , but at 5M LiNO_3 observed separation factors of up to 1.22 [4].

Experiment 3 was run at 38 wt % $\text{Ca}(\text{NO}_3)_2$. Solute-solvent separation data obtained

Table IV-7 - ^{48}Ca TO ^{40}Ca RATIOS IN LIQUID THERMAL DIFFUSION EXPERIMENTS

Experiment	Solution Concentration (wt %)	Solvent Injection Rate (g/hr)	Time (days)	$10^3 R_T$	$10^3 R_B$	g
2	20	2.42	6	1.96	1.96	1.000
			8	1.96	1.96	1.000
			11	1.95	2.05	1.048
			13	1.93	1.92	0.995
			15	1.94	1.98	1.022
3	38	6.03	7	1.95	1.91	0.979
4	41	6.03	11	1.95	1.97	1.011
			17	1.96	1.95	0.995

previously do not cover this concentration range. Since H decreases with concentration we can say only that

$$H < 5.7 \times 10^{-4}$$

where 5.7×10^{-4} is the value at 25 wt %, and the associated solvent injection rate, σ , required according to Equation 1, is

$$\sigma < 1.27 \text{ g/hr.}$$

The solvent injection rate for the experiment was selected at a much higher value, 6.03 g/hr, to determine whether the predicted inversion would occur in the solute-solvent concentration profile ($\text{Ca}(\text{NO}_3)_2$ more concentrated at the top).

Solute concentrations during the experiment, which are plotted in Figure IV-7, do not show the expected concentration inversion. Samples were taken for isotopic ratio determination on day 7. The results, reported in Table IV-7, show a negative separation slightly greater than twice the standard deviations.

Experiment 4, the results of which are plotted in Figure IV-8, was essentially

FIGURE IV-7 - Solute concentrations during Experiment 3. The arrow indicates when samples were taken for isotopic ratio measurements.

the same but with a slightly higher initial concentration. Again, the expected concentration inversion was not observed. Samples taken on days 11 and 17 of the experiment did not show significant isotopic separation (see Table IV-7).

At this point, it appeared desirable to confirm the existence of an isotope effect for calcium without the complication of solvent injection. Exploratory calculations indicated that this could be done with a column approximately half as long as the first column. At this length the solute-solvent separation is much smaller,

FIGURE IV-8 - Solute concentrations during Experiment 4. The arrows indicate when samples were taken for isotopic ratio measurement.

and it should be possible to stay below the solubility limit at the bottom of the column, yet retain enough solute at the top for isotopic ratio determination. The isotopic separation, of course, would also be significantly smaller in the shorter column.

A second column was constructed with a design identical to the first, but with a length of 36.5 cm instead of 72.1 cm. The column was filled with a solution that was adjusted to yield, at equilibrium, 0.5% $\text{Ca}(\text{NO}_3)_2$ at the top and 38% $\text{Ca}(\text{NO}_3)_2$ at the bottom. Two sets of samples were removed for isotopic ratio determination after sufficient time had elapsed to reach a steady state condition. The results, which are given in Table IV-8 and Figure IV-9 show a significant separation of the isotopes. The isotopic concentration of ^{48}Ca in the top sample is depleted by 5 to 6% relative to natural abundance. As expected from material balance considerations, the bottom sample is close to natural abundance. The natural logarithm of the separation factor is essentially linear with mass, as one would predict from theory.

This work demonstrates that there is a significant thermal diffusion separation of calcium salts in solution. The failure to find consistent separations in the solvent injection experiments is probably the result of convective instability in the experimental column. All four experiments were run under conditions which would tend to create an unstable density gradient with density increasing in the vertical direction. It is known that such gradients can destroy the separation in the column by rapid convective mixing of the column contents.

The obvious next step is to repeat the experiments under conditions such that a stable density gradient is maintained at all times. This will require: 1) solvent injection rates lower than those specified by Equation 1; 2) delayed initiation of solvent injection to allow time for formation of a stable gradient; and 3) rapid circulation of fluids through the ends of the column to avoid concentration and density differences between inflow and outflow streams.

Table IV-8 - CALCIUM ISOTOPIC ANALYSES
FOR SHORT COLUMN EXPERIMENT WITHOUT
SOLVENT INJECTION

Sample	Wt %				
	⁴⁰ Ca	⁴² Ca	⁴³ Ca	⁴⁴ Ca	⁴⁸ Ca
1-Top	96.92	0.639	0.137	2.13	0.180
1-Bottom	96.84	0.647	0.140	2.18	0.190
2-Top	96.91	0.639	0.138	2.14	0.181
2-Bottom	96.84	0.647	0.140	2.18	0.190
Feed Material (Natural Abundance)	96.86	0.643	0.140	2.17	0.188

FIGURE IV-9 - Separation relative to ⁴⁰Ca in a 36.5 μ m thermal diffusion column.

VERIFICATION OF ANALYTICAL PROCEDURE

Procedures used in preparing and analyzing isotopic ratio samples were verified by analysis of a synthetic calcium isotope mixture.

A calcium nitrate solution of natural isotopic abundance was spiked with a small amount of highly enriched ^{44}Ca purchased from Oak Ridge. The sample was thereafter processed in the same way as the other samples. Results of the analysis are compared in Table IV-9 with results calculated from the combination of 1) literature values for the isotopic abundances, 2) the Oak Ridge ^{44}Ca assay, and 3) the measured dilution ratio. The agreement is considered satisfactory in relation to the probable error in experimental measurement of the dilution ratio.

Table IV-9 - ISOTOPIC ANALYSIS OF A SPIKED CALCIUM SAMPLE

	Exptl (at. %)	Calc (at. %)
Ca-40	95.819	96.04
Ca-42	0.626	0.62
Ca-43	0.130	0.13
Ca-44	3.258	3.07
Ca-48	0.166	0.17

ALTERNATIVE CHEMICAL SYSTEMS

Systems other than $\text{Ca}(\text{NO}_3)_2\text{-H}_2\text{O}$ may have better characteristics for use in a calcium isotope separation system. Parameters which are important are solubility, stability, and compatibility with materials suitable for constructing thermal diffusion columns. Two experiments were performed in the most recent work on the compatibility of calcium salts and selected metals. One involved CaCl_2 and

titanium and the other involved $\text{Ca}(\text{SCN})_2$ and 304 stainless steel, our standard column material.

Titanium was chosen because of its known resistance to chloride solutions. Titanium and aqueous CaCl_2 solution compatibility near column service temperature was unclear; thus, a small mock-up column made of titanium was constructed. The column was filled with a 25 wt % CaCl_2 solution and pressurized to 125 psig. The column was then subjected to a temperature of 180°C for six weeks.

The test column had no cooling jacket so the column was at a higher temperature than would be encountered in normal service. After the test the column was cut apart and examined under magnification. No apparent corrosion took place; therefore, a titanium column seems to offer a solution to the stress corrosion cracking problem that occurs with aqueous halide salt solutions and 304 stainless steel.

Work involving lithium by Panson [4] and by Korsching and Wirtz [5] suggests that higher concentrations of a salt in aqueous solution produce larger isotopic separations than do lower concentrations. The aqueous phase solubility of $\text{Ca}(\text{SCN})_2$ is quite high; therefore, an aqueous solution of $\text{Ca}(\text{SCN})_2$ was evaluated in corrosion tests. A small bar of 304 stainless steel was weighed and placed in a boiling, 60 wt % solution of $\text{Ca}(\text{SCN})_2$ for one week. After completion of the test the bar was re-weighed. It showed no significant weight loss or surface effects; however, the $\text{Ca}(\text{SCN})_2$ apparently decomposed and thus seems too unstable for the calcium work.

Molecular beam scattering

R. W. York and W. L. Taylor

HELIUM-ARGON TOTAL SCATTERING CROSS SECTIONS

The helium-argon series of total scattering cross section experiments has been concluded successfully with a total of 58 experiments. This series covers the relative velocity range from $0.8 - 2.0 \times 10^5$ cm/sec. Included were eight experiments performed with the source and target species inverted to permit an indication of any unknown systematic errors which might affect the accuracy of the data. Reduction of the experimental data and application of resolution and velocity distribution corrections will be undertaken at a later date.

NEON-ARGON TOTAL SCATTERING CROSS SECTIONS

The neon-argon experimental cross sections reported previously [6] were corrected for the apparatus resolution and converted to the relative center-of-mass system for comparison with theoretical values. A new computer program was written to evaluate the resolution corrections using an improved numerical integration method for the calculations. The various cross sections of interest are given in Table IV-10 with the last three columns representing the results of the present data analysis. The resolution corrections, ΔQ , are no more than a few percent for a neon beam on an argon target, reflecting the high resolution of the apparatus. The "effective cross section" is given by

$$Q_{\text{eff}} = Q_{\text{exp}} + \Delta Q. \quad (1)$$

In order to account for the fact that there is no singular relative velocity for the collision partners, the appropriate Berkling function [7], F , must be applied to the effective cross section. F is a correction factor which is a function of the quotient $X = v_b/v_t$, where v_b is the beam velocity and v_t is the most probable target speed. In the present experiments the beam is assumed to be monochromatic and the target is assumed to possess a Maxwellian velocity distribution. Hence

$$Q(v_b) = Q_{\text{eff}}/F_{a_0}(6,X) \quad (2)$$

where $F_{a_0}(6,X)$ is the appropriate tabulated function in the reference. In order to compare it to theoretically calculated cross sections, it is necessary to transform the $Q(v_b)$ to the relative center-to-mass velocity employed in the theory. In the first approximation

$$Q(v_r) = Q(v_b) (v_b/v_r)^{\frac{2}{s-1}} \quad (3)$$

where v_r is the relative velocity, $S = 6$ is the inverse power dependence of the long range attractive portion of the potential, e.g., $V(r) = -C(\sigma/r)^S$. $Q(v_r)$, where $v_r = (v_b^2 + v_t^2)^{1/2}$, is given in the last column of the table. The data are plotted along with theoretical cross sections for five intermolecular potentials in Figure IV-10. The solid circles represent the present data with beam source conditions adjusted so that dimerization, or "clustering," of neon atoms does not occur in the nozzle-skimmer region of the beam. The open circles represent experiments where source pressure was increased to a point at which dimerization theoretically should occur. This appears to be the case as the cross sections are longer in all cases. The open triangle represents an argon beam and neon target gas. This

Table IV-10 - EXPERIMENTAL TOTAL CROSS SECTIONS FOR THE NEON/ARGON^{a)} SYSTEM

Experiment No.	v_b (10^4 cm sec ⁻¹)	T_b/T_t (°K)	v_t (10^4 cm sec ⁻¹)	Q_{exp} (Å ²)	ΔQ (Å ²)	$Q(v_b)$ (Å ²)	$Q(v_r)^{d)}$ (Å ²)
51A	3.951	75/100	2.308	277	2	257	243
51B	3.951	75/100	2.308	280	2	260	246
50A	4.562	100/100	2.308	257	3	245	233
50B	4.562	100/100	2.308	256	3	244	232
49A	4.997	120/100	2.308	250	3	240	232
49B	4.997	120/100	2.308	248	3	239	229
48A	5.586	150/100	2.308	231	3	225	218
48B	5.586	150/100	2.308	227	3	221	214
47A	5.586	150/220	3.424	260 ^{b)}	4	242	227
47B	5.586	150/220	3.424	249	4	231	217
47C	5.586	150/220	3.424	238	3	221	207
46A	5.586	150/325	4.162	266 ^{b)}	4	237	218
46B	5.586	150/325	4.162	266 ^{b)}	4	237	218
46C	5.586	150/325	4.162	257	4	230	210
46D	5.586	150/325	4.162	242	4	216	198
38A	5.587	300/300	5.655	290 ^{c)}	22	251	218
38B	5.587	300/300	5.655	285 ^{c)}	21	247	214
45A	6.034	175/375	4.470	259 ^{b)}	5	233	213
45B	6.034	175/375	4.470	259 ^{b)}	5	233	213
45C	6.034	175/375	4.470	236	4	211	194
45D	6.034	175/375	4.470	253	5	227	208
44A	6.588	208.6/375	4.470	244 ^{b)}	5	224	208
44B	6.588	208.6/375	4.470	248 ^{b)}	5	227	211
44C	6.588	208.6/375	4.470	238	5	218	202
44D	6.588	208.6/375	4.470	238	5	218	202
43A	6.842	225/350	4.319	246 ^{b)}	6	229	214
43B	6.842	225/350	4.319	250 ^{b)}	5	232	218
43C	6.842	225/350	4.319	235	5	218	205
43D	6.842	225/350	4.319	226	5	210	197
42C	7.368	260.9/350	4.319	227	6	215	202
41A	7.901	300/350	4.319	235	7	225	214
41B	7.901	300/350	4.319	235	7	225	214
40A	8.534	350/350	4.319	227	7	220	211
40B	8.534	350/350	4.319	227	7	220	211
39A	9.015	375/375	4.470	215	7	209	201
39B	9.015	375/375	4.470	216	8	211	202

a) Neon beam; argon target gas (unless otherwise noted).

b) Cluster formation in neon beam.

c) Argon beam; neon target gas.

d) $v_r = (v_b^2 + v_t^2)^{1/2}$

FIGURE IV-10 - Neon-argon total cross sections. The experimental points are: ●, Neon beam, argon target, no neon dimerization in beam; ○, neon beam, argon target, theoretical possibility of significant neon dimerization in beam; Δ, argon beam, neon target; □, Shinn (Ref. 8). The theoretical curves are: —, Lennard-Jones (12-6) potential with parameters by Hogervorst (Ref. 10); ---, Exp-6 potential with parameters by Hogervorst (Ref. 10); -.-, Exp-6 potential with parameters by Mason and Rice (Ref. 11); —·—, ESMSV potential by Ng, et al (Ref. 12); and ···, Dymond-Alder potential with parameters by Lin and Robinson (Ref. 13).

"inverted experiment" is about 7% high and could be an indication of the magnitude of possible systematic errors in the experiments. The open squares are earlier measurements [8] made at the University of Virginia. In the mid-range of velocities the independent measurements (solid circles and open squares) agree to within 5%. The University of Virginia data do not rise as one would expect, although, as Shinn pointed out, the lowest points are the least reliable.

Theoretical calculations were made using the WKB calculated phase shifts to evaluate the cross sections. First the validity of the calculation was checked according to the criteria of Munn et al [9]. It was found that our lowest relative energy was approximately 3-1/2 times the minimum allowed so that the WKB approximation should be reasonably accurate for the phase shifts. It can be noted in the figure that all the potentials considered rise more rapidly at low energies relative to the experimental data, so further consideration should be given to the numerical procedures used to evaluate the phase shifts. On the other hand, of the potentials investigated, which are shown in Figure IV-11, only the ESMSV potential includes a $-C_2(\sigma/r)^8$ term in the long range attraction and this is known to have a significant effect at low energies. On the basis of the two sets of data one certainly could not choose a potential that is entirely satisfactory and at this point only a few general observations can be made. The absolute magnitude of the data at higher velocities as well as the location of the inflection, or "glory," appears to be predicted more accurately by either the Exp-6 or the L.J. potential. On the other hand, as noted above, none of

the potentials exhibits low energy behavior in agreement with the data. Because the total cross section is sensitive to the value of σ in the potential, one could infer from the inset in Figure IV-11 that the large values are preferable. Further analyses of the effects of the potential are necessary and are in progress.

DETECTION SYSTEM

The rotatable, triply-pumped detector housing, which was previously described [6], has been received from the fabricator and has undergone initial leak testing satisfactorily. Thus far, no leaks have been found although some irregularities in fabrication necessitated the return of the housing to the vendor for rework. The rework has now been completed and the housing is ready for final delivery to Mound. The complete system will be installed in the beam chamber during the next reporting period.

VELOCITY SELECTION

The rotor for the velocity selector has been rebalanced and realigned. It now runs smoothly without vibration to 30,000 rpm. This represents a major improvement over previous performance. A new, all stainless steel diffusion pump with increased pumping speed was added to the bell jar vacuum system to permit higher vacuum conditions, thus promoting a higher signal-to-noise ratio.

Mutual diffusion

D. Cain, K. D. Westrick and W. L. Taylor

The study of the diffusion coefficients of krypton-noble gas systems has been completed

FIGURE IV-11 - Intermolecular potentials for the neon-argon system. The larger graph depicts the well and long-range attractive regions of potentials; the inset shows the repulsive regions of potentials. The curves are the same as in Figure IV-10.

over the presently attainable temperature range--approximately 340 to 1300 K [14]. Attention has since shifted to the helium-neon, argon, xenon, and argon-xenon systems. Table IV-11 shows the temperature ranges over which diffusion coefficients of binary mixtures of the noble gases have been measured at Mound. As can be seen, the mixtures of current interest are the only remaining asymmetric systems whose temperature dependence has not been well characterized. Helium-argon has been studied over a very brief temperature range while helium-neon has been investigated only below room temperature [15]; the other two systems mentioned have not been investigated at Mound at all.

Table IV-12 shows the experimental diffusion coefficients, D_{12} , measured to date for helium-argon, xenon, and argon-xenon.

The data have been adjusted to atmospheric pressure and are for systems tending toward an equimolar equilibrium concentration. Other experimental diffusion coefficient values have been obtained from the literature and adjusted (where necessary) to equimolar composition [20]. Initial comparisons are favorable, although a detailed study has not yet been done for helium-xenon or argon-xenon. The situation with helium-argon, however, is very different.

The lone high temperature diffusion coefficient for helium-argon listed in Table IV-12 is a result of a request of R. A. Aziz of the University of Waterloo [21]. In a recent paper on the interatomic potential of the helium-argon system, Aziz [22] found that the high temperature diffusion coefficients of Hogervorst [23] could not be calculated from potentials determined

Table IV-11 - TEMPERATURE RANGES (K) OF MOUND DIFFUSION DATA

	Xe	Kr	Ar	Ne	He
He	--- ^a	358-1194 ^b	305-335 ^{c, a}	77-364 ^c	77-888 ^c
Ne	304-922 ^d	350-1222 ^b	296-1363 ^e	77-1400 ^f	
Ar	--- ^a	339-1195 ^b	--- ^g		
Kr	358-1199 ^b	196-1036 ^h			
Xe	--- ^g				

^aExperiments in progress over a range of temperatures from 350 to 1300 K.

^bRef. 14

^cRef. 15

^dRef. 16

^eRef. 17

^fRef. 18

^gNo past or present work done on these systems at Mound.

^hRef. 19

Table IV-12 - DIFFUSION COEFFICIENTS AT ONE ATMOSPHERE
PRESSURE, EQUIMOLAR EQUILIBRIUM CONCENTRATION

Ar-Xe		He-Xe		He-Ar	
Temperature (K)	D_{12} (cm ² /sec)	Temperature (K)	D_{12} (cm ² /sec)	Temperature (K)	D_{12} (cm ² /sec)
343.9	0.1501	351.1	0.7428	1307.4	10.049
499.6	0.2947	657.9	2.1099		
512.8	0.2975	793.5	2.7656		
656.3	0.4766	941.5	3.8553		
822.3	0.7241	1217.2	5.8779		
948.0	0.9163				
1106.5	1.1686				

solely from differential cross sections. Since high temperature diffusion data are often used to determine the repulsive wall of the interatomic potential, and since we had previously found evidence that the data of Hogervorst are too low at high temperature for some systems [14], Prof. Aziz asked that we peg the helium-argon diffusion coefficient curve at high temperature.

Figure IV-12 is a full logarithmic plot of D_{12} as a function of temperature and helps point out part of the problem. The open circles represent the high temperature data (300-1400 K) of Hogervorst [23]. The open triangles are the only other data found in the literature above 500 K [24], while the closed triangles are considered to be the most accurate data available [20], but extend only up to 400 K [25]. The "x" on the plot is the solitary point determined in present study and is a value arrived at through a detailed study of several experiments. While it is not readily apparent on the logarithmic scale, the present data point is well over 10% higher than the curve

FIGURE IV-12 - Diffusion coefficient, D_{12} , as a function of temperature for He-Ar. The experimental points are: x, present work; O, Hogervorst (Ref. 23); Δ , Suetin et al (Ref. 24); $\blacktriangle$, van Heijningen et al (Ref. 25). The solid line represents a correlating function given by Equation 1 (Ref. 20).

defined by Hogervorst's data. However, there are no other data in this temperature range to lend weight to either experimenter's work.

The line drawn through the data points in Figure IV-12 is a plot of the function

$$D_{12} = \exp [-4.1886 + 1.552 \ln T - \ln (\ln \frac{4.10 \times 10^7}{T})^2 - 1.71/T] \quad (1)$$

This equation is due to Marrero and Mason [20] and refers to equimolar compositions at atmospheric pressure. The theoretical basis of the correlation is the contribution of various parts of the intermolecular potential to the diffusion coefficient. However, for the temperatures of interest in this study, Equation 1 is an interpolation among experimental diffusion data below 500 K and molecular beam data above 1000 K. The quoted uncertainties are $\pm 5\%$ at temperatures around 1000 K.

Table IV-13 shows a comparison of Equation 1 with the present experimental data and

that of Hogervorst at 1300 K. It can be seen in tabular form, but is not so apparent on the logarithmic plot, that Hogervorst's data fall outside the listed error limits of Equation 1, while the present work is well within. Figure IV-12 shows that the lower temperature data of Hogervorst (<700 K) and the data of the others are adequately predicted by Equation 1.

Finally, we note that Arora et al [26] were not able to reproduce Hogervorst's diffusion data above 700 K to within the quoted 1.5% uncertainty for the system helium-argon. The authors used interatomic potentials derived from their own diffusion data taken over a temperature range of 275 to 323 K to extrapolate D_{12} values to 1400 K. We have not yet had the opportunity to calculate collision integrals and verify this, or to compare predictions with our own data. Thus, the conclusion is that, based on the present experimental work plus indirect indications (interpolations and extrapolations), the data of Hogervorst are too low at high temperatures (≥ 700 K).

Table IV-13 - COMPARISON OF EXPERIMENTAL DIFFUSION COEFFICIENTS WITH EQUATION 1

	Temperature (K)	(D_{12}) _{exp} (cm^2/sec)	(D_{12}) _{calc} (cm^2/sec)	% dev
Present work	1307.4	10.049	9.729	3.29
Hogervorst (Ref. 23)	1300	8.74	9.633	-9.27

Lithium chemical exchange with cryptands

B. E. Jepson and G. C. Shockey

It is a general rule in chemical exchange that the greater the bonding difference between two species of an element, the greater the isotope effects at equilibrium [27]. The isotope exchange of lithium ions in a two-phase system utilizing an aqueous phase and an organic phase of macrocyclic ligands is represented by the following reaction:

where L = ligand

and TFA = trifluoroacetate.

In the context of the above general rule, the hydration numbers, subscripts x and y in Reaction 1, are of interest. In the aquo complex, four water molecules form the inner hydration sphere with an indeterminate number of molecules less strongly bound in the outer hydration sphere [28,29]. Macrocyclic ligands offer a means to reduce the hydration number, y, in the organic phase complex.

The ligands examined in this report are (221) cryptand and (211) cryptand, the structures of which are shown in Figure IV-13. The lithium ion is bonded within the cavity of these structures by ion-dipole, ion-ion, and short range repulsive forces. Single-stage separation factors for (221) in the range of 1.035 have been found [30,31]. It is desirable from the aspect of maximizing the bonding differences that the hydration water in the lithium cryptate be at a minimum.

HYDRATION OF LITHIUM CRYPTATE

The preparation of the lithium cryptate solutions involved equilibrating a 2M aqueous solution of LiTFA with 0.15M and 0.14M chloroform solutions of (221) cryptand and (211) cryptand, respectively. The lithium concentration in the organic phase after equilibration was found to be 0.08M for both cryptands. A blank organic phase (no ligand present) was prepared by contacting 2M LiTFA with chloroform. The chloroform used in all cases contained 0.75% ethyl alcohol. LiTFA solubility in CHCl_3 was previously found to be 0.0003M and can be considered negligible in this work. Fifteen Karl Fischer titrations yielded water concentrations as follows:

FIGURE IV-13 - Cryptand structures.

blank, 0.07 ± 0.01 (SD) M;

(211), 0.07 ± 0.01 (SD) M;

and (221), $0.13_5 \pm 0.01$ (SD) M.

If it is assumed that the water in excess of that in the blank is present as hydration water of the lithium cryptate, values can be assigned to the subscript y in Reaction 1. For (211) exchange, $y = 0.0 \pm 0.2$; and for (221) exchange, $y = 0.8 \pm 0.2$. An inspection of space filling CPK (Corey-Pauling-Koltun) molecular models of the lithium cryptates illustrates why the cryptands are capable of excluding most or all hydration water. The cavity sizes, 1.1 Å radius for 221 and 0.8 Å radius for 211, are much too small to accommodate a water molecule [32]. The water oxygen ligand atom must closely approach the oxygen ligands of the cryptand if it is to attain close proximity to the complexed lithium cation. Also the lithium cryptate must exist as an ion pair with the TFA^- anion.

EXCHANGE RATE KINETICS WITH 211 CRYPTAND

Details of the procedure for evaluating the heterogeneous exchange rate kinetics have been previously described [30]. In general, it involves contacting two phases with different isotopic compositions and

following the change in isotopic compositions as a function of time. The results for 211 kinetics are shown in Table IV-14 along with a parallel study of 221 kinetics. The concentrations, phase volume ratios, and mixing techniques for the two studies were as close to identical as possible. Exchange with 221 was essentially complete within 0.5 min; however, some resistance to exchange was noted with 211 exchange. Since conditions for mass transfer in both systems were very similar, a reaction rate limitation is suggested. A plot of $-\log(1-F)$ as a function of time (F = fraction exchanged) in the range of 58% to 94% exchange completion yields a rate constant of $k = 0.2 \text{ min}^{-1}$ corresponding to a half-time of 3.5 min. The more rapid exchange during the first fraction of a minute probably was the result of some net interfacial mass transport due to slight variations from equilibrium values in the starting lithium concentrations.

CONCLUSIONS

One molecule of water of hydration is present in the organic phase 221 cryptand complex of lithium trifluoroacetate while the 211 complex excludes all water of

Table IV-14 - EXCHANGE RATE KINETICS OF LITHIUM-CRYPTAND
CHEMICAL EXCHANGE AT $T = 25^\circ\text{C}$

Time (min)	^7Li (at. %)			
	221 Cryptand		211 Cryptand	
	Organic Phase	Aqueous Phase	Organic Phase	Aqueous Phase
0	98.05	4.28	98.05	4.28
0.5		15.36		8.54
2.0		15.32		9.88
10		15.82		11.22
1440	14.83	15.49	11.23	11.67

hydration. Since the last water is the most strongly bound, it is not surprising that the exchange rate of Reaction 1 is slow for exchange with 211. The large stability constant of lithium cryptate supports the reaction rate limitation. The stability constant of $\text{Li}(211)^+$ in water is $\log K_s = 5.5$ while that of $\text{Li}(211)^+$ is $\log K_s = 2.5$, a K_s difference of three orders of magnitude [32].

V. Calculations in plutonium chemistry

Short algorithms for plutonium chemistry problems

G. L. Silver

Recently, a number of books on optimization have appeared [1,2], and while some of them describe the sequential simplex algorithm, none of them makes the observation that this algorithm can be shortened to the point that it becomes a powerful tool for computing equipment as simple as the programmable pocket calculator. It has recently been shown, however, that the algorithm can be abbreviated by retaining but one of the traditional operations (C_w), and augmenting this operation by a new operation designated as "diminished expansion" [3].

Parkinson and Hutchinson have made an extensive study of the arithmetic operations in the traditional simplex algorithm, and have concluded that the numerical factors traditionally used in this routine may not be the best possible selection [4]. Since the abbreviated routine suggested here has fewer factors than the traditional simplex routine, it would

appear that a similar study for the abbreviated routine would be both interesting and useful. In the absence of such a study, however, an expansion of about 25% beyond the reflection point may be appropriate.

Listed in Tables V-1 and V-2, respectively, are two- and three-variable minimization routines abbreviated as described above. These routines may be used to solve a variety of chemistry problems by the method of proportional equations [5]. The routines are suitable for the HP-67 or HP-97 calculators manufactured by the Hewlett Packard Company. The meaning of the symbols is described in Reference 3. For the routines listed in Tables V-1 and V-2, matrices are useful mnemonics for data entry. For the two-variable routine, enter the data as follows:

POINT	REGISTERS	FUNCTION VALUE REGISTER
X1,Y1	1,2; 5,6	7
X2,Y2	3,4; 5,6	8
X3,Y3	5,6	9

For the three-variable routine, enter the data as follows:

POINT	REGISTERS	FUNCTION VALUE REGISTER
X1,Y1,Z1	5,9,13; 8,12,16	1
X2,Y2,Z2	6,10,14; 8,12,16	2
X3,Y3,Z3	7,11,15; 8,12,16	3
X4,Y4,Z4	8, 12, 16	4

After each point is entered, execute the objective function at Label 0, and store its value at the appropriate register. Objective functions should be so written that trial values of X and Y are recalled from registers 5 and 6, respectively, in the two-variable minimization routine, and

Table V-1 - PROGRAM FOR MINIMIZING A TWO-VARIABLE FUNCTION*

001	*Label A Gosub 1 *Label B Gosub 1 Clear Flag 0 Rcl 7 Pause Rcl 5 Rcl 3	050	Sto 7 Rcl 4 Rcl 2 Sto 4 Stack Roll Down Sto 2 Rcl 3 Rcl 1 Sto 3 Stack Roll Down
010	Rcl 1 Gosub 3 Sto 5 Rcl 6 Rcl 4 Rcl 2 Gosub 3 Sto 6 Gosub 0 Rcl 8	060	Sto 1 Return *Label 3 Add 2 Divide Subtract Last X Exchange X & Y Decimal
020	$X \leq Y?$ Goto 4 Exchange X & Y Sto 9 Goto B *Label 1 Rcl 9 Rcl 8 $X \leq Y?$ Goto 2	070	4 Flag 0? Goto 5 Clear X 1 Decimal 2 5
030	Sto 9 Stack Roll Down Sto 8 Rcl 6 Rcl 4 Sto 6 Stack Roll Down Sto 4 Rcl 5 Rcl 3	080	*Label 5 Multiply Subtract Return *Label 4 Set Flag 0 Rcl 5 Rcl 3 Rcl 1 Gosub 3 Sto 5 Rcl 6
040	Sto 5 Stack Roll Down Sto 3 *Label 2 Rcl 8 Rcl 7 $X \leq Y?$ Return Sto 8 Stack Roll Down	090	Rcl 4 Rcl 2 Gosub 3 Sto 6 Gosub 0 Sto 9 Goto B *Label 0 Return

*Press button "A" to begin optimization process.

Table V-2 - PROGRAM FOR MINIMIZING A THREE-VARIABLE FUNCTION*

001	*Label A	040	Sto I	080	Decrement I
	Clear Flag 2		Gosub 1		Rcl (i)
	Clear Flag 3		Return		Add
	Gosub B		*Label 1		3
	Gosub B		Rcl (i)		Divide
	*Label C		Decrement I		Subtract
	Clear Flag 0		Rcl (i)		Last X
	Gosub B		$X \leq Y?$		Exchange X & Y
010	Rcl 1		Return		Decimal
	Pause		Exchange X & Y		4
	*Label E	050	Sto (i)	090	Flag 0?
	8		Increment I		Goto 4
	Gosub 3		Stack Roll Down		Clear X
	Gosub 3		Sto (i)		1
	Gosub 3		Gosub 2		Decimal
	Gosub 0		Gosub 2		2
	Flag 2?		Gosub 2		5
	Sto 4		Return		*Label 4
	Flag 3?		*Label 2		Multiply
020	Goto C		Rcl I		Subtract
	Rcl 2	060	4	100	Increment I
	$X \leq Y?$		Add		Increment I
	Goto D		Sto I		Increment I
	Exchange X & Y		Rcl (i)		Sto (i)
	Sto 4		Decrement I		Rcl I
	Goto C		Rcl (i)		4
	*Label D		Exchange X & Y		Add
	Set Flag 0		Sto (i)		Return
	Set Flag 2		Increment I		*Label 0
030	Set Flag 3		Stack Roll Down		Rcl 8
	Goto E		Sto (i)	110	Square
	*Label B	070	Return		P, S Exchange
	4		*Label 3		Rcl 2
	Sto I		Sto I		Square
	Gosub 1		Rcl (i)		Add
	3		Decrement I		Rcl 6
	Sto I		Rcl (i)		Square
	Gosub 1		Decrement I		Add
	2		Rcl (i)		P, S Exchange
			Add		Return

*Press button "A" to begin optimization process.

from registers 8, 12, and 16 in the three-variable minimization routine. (The three-variable routine shown in Table V-2 includes the test function $X^2 + Y^2 + Z^2$ at Label zero to illustrate this recall. "P, S Exchange" signifies interchange of the primary and secondary storage registers.) For the two-variable routine, registers A, B, C, D, E, I, O, and all secondary storage registers are unused, whereas for the three-variable routine, only registers 0, 17, 18, 19, A, B, C, D, E are unused. (Flag 0 is a command cleared flag, whereas flags 2 and 3 are test cleared flags. Changing the numerical factors in the operations of diminished expansion (E) and contraction (C_w) provides a tactic for dealing with the problem of false convergence.) In the two-variable routine, the best (minimum) value of $f(X,Y)$ is stored at register 7, and the corresponding values of X and Y are stored at registers 1 and 2, respectively. For the three-variable routine, the best (minimum) value of $f(X,Y,Z)$ is found at register 1, and the corresponding values of X, Y, and Z at registers 5, 9, and 13, respectively.

Charles Wohl of the Particle Data Group, Lawrence Berkeley Laboratory, has prepared a two-variable, abbreviated, sequential simplex routine which requires less than 80 steps [6]. While shorter than the routine given in Table V-1, it does not appear to execute as quickly as that routine. It was Wohl who suggested that the point of diminished expansion (E) and the contraction point (C_w) be calculated from the same subroutine, a most valuable suggestion for the preparation of short optimization routines. Using this procedure, the numerical factor for the expansion operation in Tables V-1 and V-2

has been taken as 1.25, and the numerical factor for the contraction operation as 0.4. As remarked above, other values for these factors may be selected, provided the value of the former exceeds unity, and the value of their product is one half. For example, 10/9 and 0.45 is a satisfactory choice, and these numbers may be a better selection for three-, and higher, dimensional simplex routines. Readers skilled in the art of programming can probably further shorten and simplify the contents of Tables V-1 and V-2, as the process of making improvements in computer programs seems to be an interminable one.

Program for plutonium valences in environmental water

G. L. Silver

It does not seem to be generally recognized that the equilibrium distribution of plutonium species in water of the natural environment can be estimated if some of the properties of the water are known. The properties of natural water which make possible such estimations are: pH, redox potential, and alpha coefficients (sometimes called "alpha factors") for the four oxidation states of the plutonium. In principle at least, all of these parameters are subject to experimental determination. Listed in Table V-3 is a program prepared for the Hewlett Packard Co. models HP-67 or HP-97 calculators; this program rapidly performs oxidation state distribution calculations for plutonium (or uranium, neptunium, and americium -- neglecting the uncommon, divalent state of this last element, however).

To use this program, it is necessary to know the numerical value of several

Table V-3 - PROGRAM FOR DETERMINING THE SPECIATION OF PLUTONIUM IN AQUEOUS SOLUTIONS, AND THE MOLAR SOLUBILITY OF THIS PLUTONIUM WHEN IN EQUILIBRIUM WITH TETRAVALENT PLUTONIUM HYDROUS OXIDE

001	*Label A	050	Divide	090	Multiply
	Clear Registers		Sto 3		Sto 6
	Clear X Register		Sto 7		Print X
	Decimal Notation		Rcl B		Clear X
	Run/Stop		Rcl 0		Return
	Sto 1		Multiply		*Label D
	Run/Stop		Rcl 2		Rcl 9
	Sto 2		Multiply		Rcl 0
	Run/Stop		Rcl 1		Multiply
010	Sto E		Divide		Exponentiation
	Run/Stop	060	Rcl 8	100	5
	Sto 9		Divide		6
	*Label B		Sto 4		Multiply
	Clear X Register		Sto + 7		Rcl B
	Run/Stop		Rcl C		Multiply
	Sto A		Sto + 7		Rcl 4
	Run/Stop		Rcl D		Divide
	Sto B		Rcl 8		Sto 7
	Run/Stop		Multiply		Rcl 3
020	Sto C		Sto 6		Multiply
	Run/Stop	070	Sto + 7	110	Sto 3
	Sto D		Rcl 7		Print X
	*Label C		Reciprocal		Rcl 7
	Clear X Register		Sto 7		Rcl 4
	Run/Stop		Rcl 3		Multiply
	Rcl E		Multiply		Sto 4
	Subtract		Sto 3		Print X
	Decimal		Print X		Rcl 7
	0		Rcl 7		Rcl 5
030	5		Rcl 4		Multiply
	9	080	Multiply	120	Sto 5
	1		Sto 4		Print X
	6		Print X		Rcl 7
	Divide		Rcl C		Rcl 6
	Ten to Power		Rcl 7		Multiply
	Sto 8		Multiply		Sto 6
	Run/Stop		Sto 5		Print X
	Square		Print X		Rcl 3
	Square		Rcl 7		Add
040	Sto 0		Rcl 6	130	Rcl 4
	Rcl 2				Add
	Square				Rcl 5
	Multiply				Add
	Rcl A				Return
	Multiply				
	Rcl 1				
	Divide				
	Rcl 8				
	Square				

parameters of importance in plutonium chemistry. It is necessary to know the numerical value of K1, the equilibrium constant for reaction 1:

as well as the numerical value of K2, the equilibrium constant for reaction 2:

To begin the program, press button "A". Then, during the periods of pause, enter the necessary numbers in the following order (numerical values in parentheses indicate typical numerical values which have been used in the past):

1. K1 (6.97E-04)
2. K2 (13.2)
3. Standard potential of Pu(VI)/Pu(V) couple, volts (0.9164)
4. Solubility product of tetravalent plutonium hydroxous oxide (1E-56)
----Location of "B"-----
5. Alpha coefficient for Pu(III) (AW)
6. Alpha coefficient for Pu(IV) (AX)
7. Alpha coefficient for Pu(V) (AY)
8. Alpha coefficient for Pu(VI) (AZ)
----Location of "C"-----
9. Measured redox potential of environmental water, volts
10. Measured acidity of natural water, molar

The program then calculates and displays the following oxidation state proportions: Pu(III) first (stored at register 3); Pu(IV) second (stored at register 4); and

Pu(VI) last (stored at register 6). The program may be restarted at locations "B" and "C" by pressing buttons "B" and "C", respectively. Press button "D" to calculate the absolute molar solubilities of the oxidation states in equilibrium with hydrous tetravalent plutonium oxide. The last number then displayed in the working (X) register is the total equilibrium solubility of the plutonium in the system with properties defined by the user. Solved examples which may be used to test the program for satisfactory operation are given below:

- A. E = +0.96 volt, $\text{H}^+ = 0.34\text{M}$, AW = 5.6, AX = 9.1, AY = 1, AZ = 1.1 [7]
- B. E = 0.99915 volt, $\text{H}^+ = 0.598437\text{M}$, no complexation of Pu ions (all alpha coefficients are therefore taken as unity) [8]
- C. E = 0.99951 volt, H = 0.604668M, AW = AY = AZ = 1, AX = 1.0496 [8]
- D. E = 0.9437 volt, H = 0.1M, K1 = 6.56E-04, K2 = 12.8, AW = 63.08, AX = 279.6, AY = 189.0, AZ = 65.45 [9]

The Run/Stop command causes the calculator to stop and await input from the user, who, after having entered the desired numerical data, again presses the Run/Stop button. "Ten to power" implies ten raised to the number given in the working register, and 0.05916 is the Nernst Equation factor for 25°C. "Decimal notation" instructs the calculator on the format for output (this step may be deleted); "Sto + 7" means that a number is added to the contents of register 7; "Exponential" followed by 56 means that the equilibrium constant for the reaction

Alpha coefficients for plutonium (or uranium, neptunium, and americium) ions may be subject to direct determination by a process such as measurement of the increased solubility of a sparingly soluble compound in natural water. Such techniques have not yet been given adequate consideration, however, to allow a judicious appraisal of their merit [10,11]. Regions of predominance of oxidation states as calculated with the program can, at least in the case of no complexation of the various ions, be checked by consulting a potential-pH diagram for plutonium [12]. Examples illustrating application of the program have been discussed in many references [13,14,15,16]. There are more complicated methods for computing plutonium valence state distributions, but the advantages of such methods are questionable [17].

Because the constants K_1 and K_2 involve ions with charges as high as +4, the numerical values of these constants may be quite sensitive to the ionic strength of the medium in which the environmental plutonium occurs, and the values of these constants may be quite different for saline solutions, such as occur in the sea, and for fresh water from unpolluted brooks and ponds [18]. There are no completely satisfactory computational methods for adjusting the values of equilibrium constants from a medium in which they have been measured to some other, dissimilar medium. This has been repeatedly emphasized in many places; a particularly colorful example is the discourse provided by La Mer, who pointedly remarks that the activity coefficient of the calcium ion is not the same in solutions of calcium chloride and sodium chloride, even when the ionic strengths of the two solutions are identical [19].

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