MLM-1274
TID-4500 (47th Ed.)
Category - UC-2
Progress Reports

MOUND LABORATORY PROGRESS REPORT FOR JULY, 1965

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

Date: July 21, 1965
Issued: February 11, 1966

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

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-1268	MLM-1231
MLM-1266	MLM-1227
MLM-1254	MLM-1221
MLM-1250	MLM-1217
MLM-1245	MLM-1216
MLM-1238	MLM-1209

MONSANTO RESEARCH CORPORATION

A SUBSIDIARY OF MONSANTO COMPANY

MOUND LABORATORY

MIAMISBURG, OHIO OPERATED FOR

UNITED STATES ATOMIC ENERGY COMMISSION

U.S. GOVERNMENT CONTRACT NO. AT-33-1-GEN-53

.

v

v

v

.

v

v

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

TABLE OF CONTENTS

	Page
Summary	5
Isotope Separation and Purification	
Carbon Isotope Separation	7
Argon	12
Krypton	12
Xenon	13
Thermal Diffusion Research	15
Helium Research	25
Analytical and Instrumentation	
Neutron Activation Analysis	28

.

7

4

4

.

4

SUMMARY

ISOTOPE SEPARATION AND PURIFICATION

Carbon Isotope Separation

Thermal Diffusion The swing system in the lower (carbon-13 product) stages of the methane thermal diffusion cascade was removed and interstage circulation pumps were installed. The pumps for the lowermost stages were miniature canned pumps of a new design.

Cascade calculations show that the optimum feed point to the existing cascade for feed of 54% enrichment is four stages from the waste end. Operation at this feed composition will require an additional holdup of four liters of $C^{13}H_4$.

Carbon Monoxide Distillation The low temperature fractional distillation column for enriching carbon monoxide in the carbon-13 isotope was delivered and installed. The fractionating column itself is 42-feet long. The total length, including the boiler and condenser, is 47 feet. The entire column is constructed of stainless steel.

Chemical Conversion In pilot experiments with material of 4.5% carbon-13 enrichment, high purity elemental carbon was produced in high yield from carbon dioxide. An 0.83 gram batch of elemental carbon of 93% carbon-13 enrichment was prepared from the available supply of highly enriched methane.

Chemical Exchange Experimental work to determine the effect of varying the amine solution flow rate on the carbon-13 separation factor was continued. An experimental run was made using a mixed amine solution. The results were not conclusive.

Stable Gaseous Isotopes

Argon After lowering the argon-38 peak into the third stage, over one liter of 17.8% argon-38 was withdrawn. The cascade was realigned to a five-stage configuration.

Krypton The third pass for enriching krypton-86 was started. Over 70% krypton-86 is being accumulated.

Xenon A second run on the six-stage cascaded system with the modified "Trennschaukel" gas circulating system enriched xenon-131 to 18%.

Cascade calculations were made for separation of xenon-124 from natural xenon (natural abundance = 0.096%) in the 24-column tube bundle system. The best performance was calculated for a feed point one stage up in the six-stage cascade.

Chromatography The heats of adsorption of krypton and xenon on Linde's Molecular Sieve 5A, 50/60 mesh were calculated to be -3091 cal/mole and -5127 cal/mole, respectively, based on separations made using helium carrier gas. On the basis of an incomplete series of separations using nitrogen as carrier gas, the heats of adsorption of krypton and xenon are estimated at -1350 cal/mole and -1680 cal/mole, respectively. Nitrogen appears to play an active role in chromatographic separations at low temperatures.

Thermal Diffusion Research

Transport Coefficients A complete set of experimental thermal diffusion column transport coefficients was obtained for neon-20 and neon-22 in one of the 12-foot experimental columns. The experimental values deviate considerably from theoretical values. The source of the deviation is thought to be in the experimental determination of the positive transport coefficient H' .

Transport Properties The theoretical expressions for the transport properties of gases are used as relations between measurable quantities. Values of the diffusion coefficient and thermal diffusion factor for helium-3 and helium-4 mixtures have been calculated and the thermal conductivity of helium-3 has been calculated from its viscosity. The results agreed with directly measured values, even in the latter case where there is notable discrepancy between purely theoretical calculations and experimental results. Since the use of relations between transport properties is independent of any force law, the data indicate that the various transport properties are mutually consistent and the force law used in the theoretical calculations is inadequate.

Collision Integrals A computer program was written to calculate collision integrals for an arbitrary intermolecular potential function. Collision integrals for the modified Buckingham ($\alpha = 14$) potential were calculated. The calculated values are in agreement with published values for this potential.

Helium Research

Helium-3 Refrigerator A flip coil for measuring small magnetic fields was built to measure the residual field of the superconducting solenoids. These results will be useful in the design of the adiabatic demagnetization cryostat for very low temperatures. Initial measurements show that a residual field of a few hundred gauss exists, and that the field has a complicated behavior when the magnet current is reversed. The residual field is higher and in the opposite direction near the ends of the solenoid as compared to the center.

ANALYTICAL AND INSTRUMENTATION

Neutron Activation Analysis The metal constituents in metal-organo compounds were determined by neutron activation analysis. With organic matrixes containing iron, aluminum or silicon technique has a relative error error between one and two percent.

ISOTOPE SEPARATION AND PURIFICATION

Under the sponsorship of the Division of Research, Mound Laboratory is responsible for furnishing material to be used in the physical sciences to further the progress of science and technology in the public interest. After recovery, purification and concentration, research quantities of isotopes are furnished to installations for research programs in the physical sciences. Purified helium-3 and the isotopes of other noble gases and carbon-13 are available for distribution in research quantities. Methods of separation and purification are being studied.

CARBON ISOTOPE SEPARATION

Thermal Diffusion The 12-column, eight-stage methane thermal diffusion system for carbon-13 enrichment was modified by the insertion of interstage circulation pumps between the lower (product) stages. Previously, a modified swing system was used for interstage gas circulation. The swing system has the important advantages of low interstage holdup, simplicity, and high reliability. The rate of interstage circulation with the swing system, however, is low, and would be inadequate with a transport rate of $C^{13}H_4$ higher than the observed rate of approximately 50 ml/day for the current 4-2-1-1-1-1-1-1 cascade using natural abundance feed.

In the near future the existing cascade will be temporarily used for the separation of $C^{13}H_4$ from methane containing 54% carbon-13. Later, the system will be expanded by the addition of an 18-column tube bundle. The resulting higher transport rates increase the required interstage circulation rate. Refrigerator compressors were installed, therefore, to provide circulation between stages 3 and 4 and between stages 4 and 5. (Interstage circulating compressors were already in place in the upper states.) Canned circulating pumps of a new design (Figure 1) were inserted between stages 5 and 6, 6 and 7, and 7 and 8. These miniature pumps have a much lower volume than the refrigerator compressors (200 cc as opposed to 1500 cc) and are used in the high enrichment end of the system to minimize the system holdup of the desired isotope.

The new computer program (described under "CASCADE THEORY" in the section titled "THERMAL DIFFUSION RESEARCH") was used to determine the feed point location for a feed gas of 54 percent $C^{13}H_4$ in the existing methane cascade. The results of these calculations are shown in Figure 3. Obviously a feed point location 4 stages from the waste end meets the requirements of maximum production and a waste composition less than natural abundance (see Figure 2).

Before the methane cascade can be switched from a 1.1% to 54% $C^{13}H_4$ feed, an estimate of the additional $C^{13}H_4$ which must be added to the system to obtain the new equilibrium concentration profile is obtained by a graphical integration of $\int_V x dv$ where x is the concentration of $C^{13}H_4$ and v is the volume of the cascade. Table I gives the data for this numerical integration. The stage concentrations are averages of the top and bottom compositions as taken from the cascade calculations.

Figure 4 gives the equilibrium concentration profiles for the two feed compositions of 0.011 and 0.54 mole fraction $C^{13}H_4$. The difference between the two areas is about 4 liters of $C^{13}H_4$.

Figure 1. Canned Miniature Gas Circulating Pump.

Figure 2. Feed Points on Thermal Diffusion Column Cascade.

Figure 3 Effect of Feed Point Location on Production Rate of $C^{13}H_4$ (Waste = 1.0% $C^{13}H_4$, Product = 97.2% $C^{13}H_4$, and Feed = 54% $C^{13}H_4$).

Table I

**CALCULATION OF METHANE CASCADE HOLDUP FOR FEED
GAS CONCENTRATIONS OF 1.1 AND 54%**

Stage and Interstage	V (STP ml)	ΣV	Concentration Profile (mole fraction $C^{13}H_4$)	
			$X_{0.11}$	$X_{0.54}$
1	5600	5,600	0.0145	0.0249
	1500	7,100	0.0198	0.0398
2	2800	9,900	0.0301	0.0869
	1500	11,400	0.0403	0.134
3	2400	13,800	0.0464	0.244
	1500	15,300	0.052	0.353
4	2400	17,700	0.0887	0.466
	1500	19,200	0.125	0.578
5	2400	21,600	0.270	0.688
	200	21,800	0.416	0.798
6	1310	23,110	0.639	0.855
	200	23,310	0.862	0.911
7	1310	24,626	0.917	0.942
	200	24,826	0.971	0.972

Figure 4. $C^{13}H_4$ Concentration versus Cascade Volume. (The area beneath each curve represents the volume of $C^{13}H_4$ in the cascade.)

● Feed point = 0.333, $x_f = 0.011$, volume = 7,298 ml.

▲ Feed point = 4.0, $x_f = 0.54$, volume = 3,387 ml.

To be added = 3,911 ml.

Chemical Conversion Elemental carbon of 4.5% carbon-13 enrichment, prepared last month from carbon dioxide was purified. Before the purification step the carbon contained approximately 7% iron. (Iron is used as a catalyst in the preparation of the carbon.) The carbon sample was subjected to two one-hour treatments with dry HCl at 1100°C and less than atmospheric pressure. After the first treatment, ferrous chloride which had deposited on the walls of the purification vessel was carefully removed. After the second treatment samples of the purified carbon were submitted for the determination of iron by neutron activation analysis and for the determination of other impurities by emission spectrographic analysis. A sample of carbon dioxide was prepared and submitted for determination of carbon-13 enrichment.

The analytical results are given in Tables 2 and 3. The carbon was pure, and the overall yield was 96% of the carbon in the original carbon dioxide. Since the mass spectrographic sample, prepared by combustion of the carbon product, contained only a slight amount of water vapor (0.15%) the purified carbon contained little or no hydrogen.

Table 2

**Preparation and Purification of Elemental Carbon,
from Carbon Dioxide**

Carbon content of carbon dioxide	0.341 g
C ¹³ enrichment of carbon dioxide	4.50 %
Impure carbon recovered from deposition step (6.8% iron)	0.353 g
C ¹³ enrichment of impure carbon	4.46 %
Carbon recovered after purification (less than 0.005% iron by activation analysis)	0.327 g
C ¹³ enrichment of purified carbon	4.45 %

Table 3

**Impurities in Purified Partially Enriched Carbon
(Emission Spectrographic Analysis)**

Boron	5 ppm
Silicon	200 ppm
Magnesium	trace
Nickel	30 ppm
Iron	trace (<10 ppm)
Molybdenum	trace (<10 ppm)
Calcium	100 ppm
Copper	30 ppm

A 1550 ml batch of methane of 95.5% mass 17 enrichment was processed in three runs and yielded 0.83 grams of purified elemental carbon. Overall yield was 95% of the carbon originally present in the methane. Two samples of the purified carbon had carbon-13 enrichments of 94.0 and 92.7%. Other analytical results are not available as yet.

Chemical Exchange Several more experimental reactions were performed in the study of the effect of amine solution flow rates on the carbon-13 separation factor in the carbon dioxide-carbamate exchange system. The results of the additional reaction runs are shown in Figure 5. The circled points and curve are repeated from data reported previously. In general, the data are in agreement with that determined by Gupta and Taylor.²

Figure 5. Amine Flow Rate as a Function of Height Equivalent of Theoretical Stage (HETS).

Another reaction run was performed to determine the effect of a second amine component to the monoethanolamine solution. A two-molar monoethanolamine solution was prepared, which was 0.1 molar in diethanolamine. The solvent was methanol. The solution mixture was then run under conditions comparable to one of the reaction runs using the monoethanolamine only. Preliminary results indicated the carbon-13 separation factor was not improved.

²Gupta, A. R. and Taylor, T. I., US At. Energy Comm. Rept., TID 16834, Pt. II (Sept. 1, 1962).

ARGON

After the argon-38 had been enriched to 26.0% in the 96-foot, 11-column cascade, this peak was lowered into the third stage of the cascade. Then 1,100 stp ml of gas were removed from the system with an average argon-38 concentration of 17.8%.

In order to obtain a higher enrichment of argon-38, the system length was increased from 96 to 120 feet by realignment of the columns from 8-1-1-1 to a 7-1-1-1-1 configuration. The rearranged cascade is shown in Figure 6. The initial argon-36 product rate will be started at 2.5 ml per hour. The new cascade is expected to enrich argon-38 to between 30 and 40% and to allow simultaneous draw-off of that concentration without the necessity of altering the peak location in the cascade.

Figure 6. New arrangement of eleven 24-foot columns to form 120-foot cascade. Gas circulates between stage 1 and stage 2 through a compressor, and between all other stages through bellows pumps.

KRYPTON

In a two-column, two stage thermal diffusion cascade, the second pass was completed for enriching krypton-84 and -86. This pass enriched the krypton to 51.7% krypton-86. The third pass was equilibrated, and average flow was started at 12 ml per hour. The draw-off contained over 70% krypton-86. The third pass feed was reduced to 44% krypton-86 by withdrawing two liters of intermediate product of 73.8% krypton-86 after 176 hours draw-off time. The raffinate is being reprocessed to recover two additional liters of product before the fourth pass is started to separate 90% krypton-86. Figure 7 shows the theoretical product concentration expected for various initial reservoir concentrations of krypton-86. Actual concentrations have agreed within 10% of theoretical.

Figure 7. Final Concentration of Kr^{86} as a Function of Initial Concentration.

XENON

Thermal Diffusion The eight-column, six-stage thermal diffusion unit with a modified Trennschaukel gas circulating system for interstage transport was recharged to enrich xenon-131. After four days, the xenon-131 was enriched to 18.6%.

Calculations for the three tentative plans for separation of xenon-124 from natural xenon (natural abundance = 0.096%) in the new 24-column, six-stage tube bundle were completed. The calculations were based on treating xenon as a binary system of mass 124 and mass 129.

Plan 1. This plan uses rapid circulation of a finite amount of gas across the bottom of the cascade. This non-equilibrium calculation is approximated by the computer calculations at four equal incremental decreases in the reservoir compositions. The results are shown in Figure 8. The operation of the tube bundle is as indicated by the saw-tooth curve. For example, production is fixed at 2.08 grams per day until the reservoir composition drops to 0.0912% xenon-124. The production rate is then dropped to 1.94 grams per day and held there until the reservoir composition becomes 0.0864% xenon-124. This procedure is repeated as many times as desired.

Plan 2. In this plan the feed is pumped very slowly across the bottom of the cascade so that the feed point composition in the column is equal to the waste composition of 0.756% xenon-124 (20% removal of 124 from the feed).

Plan 3. Here the first stage of 6 columns is used as a stripper for the xenon-124.

The plans are compared for an arbitrarily chosen production rate of 2.0 grams per day in Table 4

Table 4

Comparison of Plans for Operation of Xenon-124 Tube Bundle
(compositions in mole percent)

	Xenon-124 in Feed	Xenon-124 in Waste	Xenon-124 in Product	Product Rate g/day	Waste Rate g/day	Feed Rate g/day	Feed Point
Plan 1	0.096	0.0959	1.034	2.0	-	-	-
	0.091	0.0912	0.982	2.0	-	-	-
	0.0864	0.0864	0.931	2.0	-	-	-
	0.0816	0.0781	0.589	2.0	-	-	-
	Ave. 0.830						
Plan 2	0.096	0.0701	0.756	2.0	51.0	53.0	Waste End
Plan 3	0.096	0.0631	0.935	2.0	51.0	53.0	Stage 1, Top

Figure 8. Xe^{124} Composition as a Function of Production Rate.

The first two cuts from Plan 1 produce a higher composition product but in order to remove 20% of the xenon-124 available in the reservoir, five cuts must be made. The average composition of the product is 0.830%. Plan 3 produces the highest product composition and on a continuous basis. It appears that Plan 3 is the best operating procedure.

Chromatography The series of separations using the synthetic Zeolite (Linde's molecular Sieve 5A, 50/60 mesh) with a helium carrier gas were completed. The retention times of krypton and xenon were measured at 210°K, 233°K, and 243°K. The calculated heats of adsorption are -3091 and -5127 calories per mole for krypton and xenon, respectively.

A series of separations were begun using nitrogen as the carrier gas on the same adsorbent. On the basis of experiments run at 166°K and 210°K, values of the "heats of adsorption" of krypton and xenon on this adsorbent are estimated at -1350 and -1680 calories per mole, respectively.

Thus, at these low temperatures nitrogen takes a more active role than is customary for a carrier gas. Nitrogen, evidently, is adsorbed as it moves along the adsorbent, displacing the krypton and xenon. This gives the effect of krypton and xenon having reduced heats of adsorption. Further, this manifestation indicates that separations at lower temperatures would yield reduced peak tailing using a nitrogen carrier gas. This reduced peak tailing at lower temperatures has been observed experimentally.

THERMAL DIFFUSION RESEARCH

Cascade Theory In the usual steady state binary isotope cascade problem there are seven composition and flow variables. These include:

1. Product flow rate, P
2. Product composition, x_p
3. Waste flow rate, W
4. Waste composition, x_w
5. Feed flow rate, F
6. Feed composition, x_F
7. Composition in the cascade at the feed point, x_{FC}

Any three of these variables can be chosen independently. The two previously existing computer programs, one of which was completed last month, use different combinations of these variables as input. For instance Program 039, the first binary cascade program takes x_F , x_p , and x_{FC} as input. The program described last month, Program 170, takes x_F , P , and W as input.

This month a third program, Program 180 was completed and checked. Program 180 takes as input the quantities x_F , x_p , and x_w . These programs are complementary. Problems that would require tedious interpolation of results with one program can often be solved quickly with one of the others. For instance in determining the best feed point location for enriched feed to the methane thermal diffusion cascade, 142 calculations were required with Program 170 whereas only 7 calculations were required with Program 180 to develop the same information.

Transport Coefficients Flow experiments with neon-20-neon-22 were completed in column E1 at a wire temperature of 800°C, and sufficient data were obtained (Figure 9) to calculate experimental values of the thermal diffusion column transport coefficients H' , K'_C and K_D . Column E1 is 12 ft. long, has a cold wall radius of 1.27 cm and a hot wire radius of 0.0794 cm. The experimental transport coefficients are given in Table 5 along with values calculated from theory using Lennard Jones shape factors.

Table 5

**Comparison of Experimental and Theoretical
Transport Coefficients for Column E1**

	$\frac{g}{H' \text{ (cm-atm}^2\text{)}}$	$\frac{g \text{ cm}}{K'_C \text{ (sec-atm}^4\text{)}}$	$\frac{g}{K_D \text{ (cm-sec)}}$	$\frac{K'_C}{H'}$	$\frac{K_D}{H'}$
Experimental	1.19×10^{-4}	1.56×10^{-2}	2.14×10^{-3}	131.6	18.1
Theoretical	1.53×10^{-4}	2.08×10^{-2}	2.95×10^{-3}	135.9	19.3

The transport coefficient ratios, K'_C/H' and K_D/H' determined in earlier static experiments, are in good agreement with theory with deviations of +3 and +6% respectively. The individual coefficients, which are evaluated by multiplying the observed values of K'_C/H' and K_D/H' by the measured value of H' , deviate considerably from theory.

Figure 9. Separation of Ne^{20} and Ne^{22} as a Function of Flow Rate in Column E1 at 807 torr ($K_C = 10K_D$).

The most probable explanation for this deviation is in the experimental procedure for the determination of H' ; however, it was also thought that column conditions (i.e. wire temperature and alignment) may have changed in the interval between the static separation measurements and the flow measurements. To check this, a second set of static experiments was run and the results were compared to results of the previous ones. Both sets of results are shown in Figure 10. It is obvious that the column conditions did not change, and the explanation for the deviation in H' must lie elsewhere. Other experimental procedures are being checked.

Transport Properties The transport properties of helium at low temperatures are of particular interest. The theoretical calculation of the transport properties of a gas can be thought of as consisting of two steps. The first step is the solution of the Boltzmann equation and the writing of the expressions for the transport properties in terms of collision integrals. The second step is the evaluation of these integrals using an assumed force law between the molecules. The validity of a calculation of this type is tested by comparing the final results to experimentally measured values of the transport properties. However,

Figure 10. Separation of Neon 20-22 as a Function of Pressure in Column E1.

when discrepancies are noted between the calculated and observed values, it is not clear from this overall comparison whether the trouble is due to the form of the expressions for the transport properties, the assumed potential model, or the experimental data.

A procedure for separating these various aspects of the theoretical calculations has been developed^{3,4,5}. The procedure is based on the technique of writing the theoretical expressions for the transport properties as relations between measurable quantities by using the recursion formula for the collision integrals³ and substituting the transport properties for the collision integrals wherever possible in the theoretical expressions. The procedure can best be explained by a specific example.

The theoretical expression for the thermal conductivity of a binary mixture, λ_{mix} , can be written as⁶,

$$\lambda_{mix} = -4 \left[\frac{x_1^2}{L_{11}} + \frac{x_2^2}{L_{22}} - \frac{2x_1x_2L_{12}}{L_{11}L_{22}} \right] \left[1 - \frac{L_{12}^2}{L_{11}L_{22}} \right] \quad (1)$$

where

$$L_{11} = -\frac{4x_1^2}{\lambda_1} - \frac{16}{25} \frac{x_1x_2}{(M_1+M_2)^2} \frac{T}{pD_{12}} \left[\frac{15}{2} M_1^2 + \frac{25}{4} M_2^2 - 3M_2^2 B_{12}^* + 4M_1M_2 A_{12}^* \right]$$

$$L_{12} = \frac{16}{25} \frac{x_1x_2M_1M_2}{(M_1+M_2)^2} \frac{T}{pD_{12}} \left[\frac{55}{4} - 3B^* - 4A^* \right]$$

and L_{22} is obtained from L_{11} by interchanging the subscripts. In the above equations, M_1 , M_2 , λ_1 and λ_2 are the molecular weights and thermal conductivities of the pure components, x_1 and x_2 are their mole fractions, T is the temperature, p is the pressure, D_{12} the diffusion coefficient and A_{12}^* and B_{12}^* are ratios of collision integrals⁶ which depend on the temperature and force law, and which are usually near unity. To obtain an expression for λ_{mix} of this form, the quantities $\sigma^2\Omega^{(1,1)*}$ and $\sigma^2\Omega^{(2,2)*}$ have been replaced using the expressions⁶.

$$\sigma^2\Omega^{(1,1)*} = \frac{0.002628 (T^3(M_1+M_2)/2M_1M_2)^{1/2}}{pD_{12}}$$

and

$$\sigma^2\Omega^{(2,2)*} = \frac{8.21717 \times 10^{-3} (T/M)^{1/2}}{\lambda}$$

where $\Omega^{(1,1)*}$ and $\Omega^{(2,2)*}$ are the collision integrals for diffusion and viscosity, respectively, and σ is a distance parameter in the intermolecular force law. The constants in the two above equations are chosen such that the units are consistent. Equation (1) can be rearranged into the form⁵

³E. M. Holleran and H. M. Hulbert, *J. Phys. Chem.*, **56**, 1034 (1952).

⁴S. Weissman and E. A. Mason, *J. Chem. Phys.*, **37**, 1289 (1962).

⁵S. Weissman, "Advances in Thermophysical Properties at Extreme Temperatures and Pressures," *The Am. Soc. Mech. Eng., N. Y.*, (1965) p. 12.

⁶J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, N. Y., (1954), Chapter 8.

$$(pD_{12})^2 a + (pD_{12})b + (pD_{12})B_{12}^*c + B_{12}^*d + e = 0 \quad (2)$$

where the parameters are:

$$\begin{aligned} a &= 25(M_1 + M_2)^2 x_1 x_2 (\lambda_1 + \lambda_2 - \lambda_{mix}) / T \\ b &= \lambda_1 \lambda_2 \left[30(M_1 x_2 + M_2 x_1)^2 + 25(M_1 x_1 + M_2 x_2)^2 + 16M_1 M_2 A_{12}^* (x_1 - x_2)^2 \right] \\ &\quad - \lambda_{mix} \left[30(M_1 x_2^2 \lambda_1 + M_2 x_1^2 \lambda_2) + 25(M_1^2 x_1^2 \lambda_2 + M_2^2 x_2^2 \lambda_1) \right. \\ &\quad \left. + 16M_1 M_2 A_{12}^* (x_1^2 \lambda_2 + x_2^2 \lambda_1) \right] \\ c &= 12 \left[\lambda_{mix} (M_1^2 x_1^2 \lambda_2 + M_2^2 x_2^2 \lambda_1) - (M_1 x_1 + M_2 x_2)^2 \lambda_1 \lambda_2 \right] \\ d &= 0.96 x_1 x_2 T \left[15(M_1 M_2)^2 + 8M_1 M_2 A_{12}^* \right] \lambda_{mix} \lambda_1 \lambda_2 \\ e &= -0.4 x_1 x_2 T \left[75(M_1 - M_2)^2 + 88M_1 M_2 A_{12}^* \right] \lambda_{mix} \lambda_1 \lambda_2 \end{aligned}$$

Furthermore, the quantity B_{12} can be written in terms of the temperature derivative of the diffusion coefficient⁷:

$$B_{12}^* = \frac{1}{12} \left[1 - 2 \left(\frac{\partial \ln D_{12}}{\partial \ln T} \right)_p \right] \left[2 \left(\frac{\partial \ln D_{12}}{\partial \ln T} \right)_p - 9 \right] + \frac{1}{3} \left(\frac{\partial^2 \ln D_{12}}{\partial (\ln T)^2} \right)_p \quad (3)$$

using the recursion formula for the collision integrals¹ which is obtained by taking the derivative with respect to the reduced temperature under the integral sign in the expression,

$$\Omega^{(l,n)*} = 2 \left[(n+1)! (T^*)^{n+2} \right]^{-1} \int_0^\infty e^{-K/T^*} K^{n+2} S^{(l)} dK$$

where $T^* = Tk/\epsilon$, K is the reduced energy, k is the Boltzmann constant, ϵ is the energy parameter in the force law and $S^{(l)}$ is a collision cross section.

Equations 2 and 3 can be used to predict the diffusion coefficient over a wide range of temperatures in the following fashion. Equation 2 constitutes a relation between the three quantities D_{12}^* , A_{12}^* and B_{12}^* . It should be possible to obtain values of all three from three values of λ_{mix} at different compositions and the same temperature; however, curves of B_{12}^* vs D_{12} at different compositions for a given A_{12}^* have about the same slope, lie close together, but seldom intersect. A simultaneous solution is impractical, nevertheless, it is possible to choose values, based on experiment or realistic force laws, for two of the quantities and determine the third. Since A_{12}^* varies little with temperature and force law, theoretical values can be used^{4,5,7}. Equation 1 then becomes a relation between D_{12} and B_{12}^* . Two procedures can then be used; a theoretical value of B_{12}^* can yield D_{12} , or an experimental value of D_{12} can determine B_{12}^* , and thus from Equation 3, $(\partial \ln D_{12} / \partial \ln T)_p$. This latter procedure has been used to determine D_{12} over a wide range of temperatures using room temperature values of λ_{mix} and D_{12} . The agreement with directly measured values is good⁵. The former has also been used successfully to obtain values of D_{12} at the same temperature as the λ_{mix} data⁵.

The same general procedure as given above can be used to determine D_{12} from the viscosity of a binary mixture, η_{mix} . This determination has been done⁴ for helium-3 and helium-4 mixtures at 2.64 and 4.15°K

⁷S. Weissman, S. C. Saxena and E. A. Mason, **Phys. Fluids**, **3**, 510 (1960).

using the data of Becker, et al⁸. The agreement between the viscosity-derived values of D_{12} and the experimental values is excellent.

Recently, measurements of the thermal conductivity of mixtures of helium-3 and helium-4 were reported⁹. The procedure outlined above has been applied to this data. The values of D_{12} [obtained from λ_{mix} and theoretical values¹⁰ of B_{12}^*] are in good agreement with the directly measured values and those obtained from viscosity measurements⁴. The following tabulation lists the various values of D_{12} ; also the percentage deviations from the experimental data are given. The temperatures are those of the experimental λ_{mix} . The experimental values¹¹ of D_{12} and values from η_{mix} are interpolated.

$D_{12} \text{ cm}^2/\text{sec} \times 10^4$							
T °K	Experi- mental	From η_{mix}	% Dev.	Theoreti- cal ⁸	% Dev.	From λ_{mix}	% Dev.
2.080	4.80	5.01	+ 4.4	4.77	- 0.6	5.07	+ 5.6
3.009	8.84	9.16	+ 3.6	9.02	+ 2.0	9.28	+ 5.0

The estimated uncertainty¹¹ of the measured D_{12} is about 6%.

The results are also shown in Figure 11. The triangles are the directly measured values, the filled circles are values calculated from λ_{mix} , the open circles are values calculated from η_{mix} , and the crossed circles are values obtained from η_{mix} using classical values for A_{12}^* . The agreement between the open circles and the crossed circles illustrates the insensitivity of the final results to A_{12}^* . Also, the figure shows theoretical quantal calculations by Buckingham and Scriven¹² using an exponential-six type potential and by Cohen, Offerhaus and DeBoer¹³ using a 12-6 potential; the more recent calculations¹⁰ are intermediate between these two. Classical values are also shown. The lowest filled circle is based⁹ on unreliable experimental λ_{mix} .

The results in the tabulation above and Figure 11 show not only that, for this particular system, the form of the relations between measurable quantities, as given by the Chapman-Enskog theory, is indeed valid even when quantum effects are important, but also that the experimental data for D_{12} , λ_{mix} and η_{mix} are all consistent. This latter conclusion is essentially independent of any assumed intermolecular force law since the quantities A_{12}^* and B_{12}^* are quite insensitive to the force law and do not contribute significantly to the final values.

Attempts were made to calculate the derivative $(\partial \ln D_{12} / \partial \ln T)_p$ from the observed λ_{mix} using Equation 3. However, accurate values of B_{12}^* could not be attained from λ_{mix} and D_{12} . To understand why this is so, consider Equation 2, which can be rearranged into the form

$$B_{12}^* = \frac{\alpha - \beta \lambda_{mix}}{\gamma - \delta \lambda_{mix}} \quad (4)$$

where α , β , γ , and δ can be written in terms of x_1 , x_2 , M_1 , M_2 , λ_1 , λ_2 , D_{12} and T using the expressions which follow Equation 2. From Equation 4, it follows that

- ⁸E. W. Becker, R. Misenta, and F. Schmeissner, **Z. Physik**, **137**, 126 (1954).
⁹K. Fokkens, V. Vermeer, K. W. Taconis and R. deBruyn Ouboter, **Physica**, **30**, 2153 (1964).
¹⁰L. Monchick, E. A. Mason, R. J. Munn and F. J. Smith, U. S. At. Energy Comm. Rept., IMP-AEC-34, (March 1, 1965).
¹¹P. J. Bendt, **Phys. Rev.**, **110**, 85 (1958).
¹²R. A. Buckingham and R. A. Scriven, **Proc. Phys. Soc. (London)** **B65**, 376 (1952).
¹³E. G. D. Cohen, M. J. Offerhaus, and J. de Boer, **Physica**, **20**, 501 (1954).

Figure 11. Diffusion Coefficient of He³ and He⁴ as a Function of Temperature. The open circles are based on η_{mix} with quantal A_{34}^* ; the crossed circles are based on η_{mix} and classical A_{32}^* ; the filled circles are based on λ_{mix} and quantal A_{34}^* and B_{34}^* ; the triangles are directly measured values. The solid curves are theoretical calculations starting from the highest one. Cohen, Offerhaus, and DeBoer; Monchick, Mason, Munn and Smith, and Buckingham and Scriven. The dashed curves represent classical calculations.

$$\frac{dB_{12}^*}{B_{12}^*} = - \left[\frac{\beta\lambda_{mix}}{\alpha - \beta\lambda_{mix}} + \frac{-\delta\lambda_{mix}}{\gamma - \delta\lambda_{mix}} \right] \frac{d\lambda_{mix}}{\lambda_{mix}}$$

For the particular case of helium-3 and helium-4 mixtures at very low temperature the differences in the denominators on the right hand side of the above equation are small. Therefore, the coefficient of $d\lambda_{mix}/\lambda_{mix}$ is very large; consequently, an error of 3% in λ_{mix} is equivalent to an error of 100% in B_{12}^* and more accurate thermal conductivity data than are available are needed to determine B_{12}^* from λ_{mix} . A similar analysis shows that, likewise, an error of 3% in D_{12} can cause 100% error in B_{12}^* . However, when the procedure is reversed, as in the case of the values given in the preceding table, an error of one percent in B_{12}^* would cause an error of only 0.03% in D_{12} .

This situation appears to arise only for systems composed of substances of low molecular weight at very low temperatures and did not occur in the previous calculations³.

The thermal diffusion factor, α_T , can be written in terms of the other transport properties in a manner analogous to that of λ_{mix} ; this expression is

$$\alpha_T = 2 \left[2 - \frac{d \ln D_{12}}{d \ln T} \right] \left(\frac{x_1 S_1 - x_2 S_2}{x_1 Q_1 + x_2 Q_2 + x_1 x_2 Q_{12}} \right) \quad (5)$$

where

$$S_1 = \frac{5}{3} \frac{M_1^2}{M_1 + M_2} \frac{pD_{12}}{\eta_1 RT} - \frac{4M_1 M_2 A_{12}^*}{(M_1 + M_2)^2} + \frac{15M_2(M_1 - M_2)}{2(M_1 + M_2)^2}$$

$$Q_1 = \frac{10}{3} \frac{M_1}{(M_1+M_2)^2} \frac{pD_{12}}{\eta_1 RT} \left[M_1^2 + 3M_2^2 + \frac{8}{5} M_1 M_2 A_{12}^* \right]$$

$$Q_{12} = 1.5 \left(\frac{M_1 - M_2}{M_1 + M_2} \right)^2 + \frac{32 M_1 M_2 A^*}{(M_1 + M_2)^2} + \frac{20}{9} M_1 M_2 \left(\frac{pD_{12}}{\eta_1 RT} \right) \left(\frac{pD_{12}}{\eta_2 RT} \right)$$

and S_2 and Q_2 can be generated from S_1 and Q_1 by interchanging the subscripts.

The calculation of α_T using these equations is, unfortunately, extremely sensitive to small errors in the temperature dependence of D_{12} , since the term $(\partial \ln D_{12} / \partial \ln T)_p$ usually has a value not far from 2. The following tabulation gives the values of α_T to be compared to the experimental data^{12,13}.

α_T for Helium-3 and Helium-4

T °K	Experimental	Theoretical	From D_{12}
100	0.071	0.084	0.082
50	0.072	0.086	0.085
10		0.085	0.084
5		0.094	0.096
2		0.105	0.130

The results are also displayed in Figure 12. The open circles are Watson's¹⁴ data, the squares are van der Valk's¹⁵ data, and the filled circles are based on Equation 5.

The agreement between the experimental values and those derived from the other transport properties seems to be acceptable, in view of the large uncertainties involved in these calculations. The theoretical values are expected to agree with the experimental better than they do. This indicates that the Lennard-Jones 12-6 force law used in the theoretical calculation¹⁰, while it is good enough to calculate D_{12} , is not accurate enough to calculate α_T . The good agreement with the DeBoer et. al. calculation below 4°K is probably fortuitous.

To further study the adequacy of the potential model used in the theoretical calculations, the properties of purified helium-3 were examined. At the time that the theoretical calculations¹⁰ were made, the most notable discrepancy between observed and theoretical values¹⁰ appeared to be for the viscosity of helium-3 between 1° and 4°K. After these calculations were made, more thermal conductivity data have become available⁹.

The thermal conductivity of a pure monatomic gas is related to its viscosity by:

$$\lambda = \frac{15}{4} \frac{R}{M} \eta f$$

where f is a correction factor for higher approximations in the Chapman-Enskog theory and only differs from unity by about one percent. Figure 13 gives the thermal conductivity of helium-3 in milliwatts per cm-°K as a function of temperature; the solid line represents the theoretical values¹⁰; the circles are experimental⁹; and the squares are based on viscosity measurements⁸. It is evident that the viscosity and thermal conductivity are consistent and the theoretical values are too high. The implication again is that the potential

¹⁴W. W. Watson, A. J. Howard, N. E. Miller, and R. M. Shiffren, *Z. Naturforsch.*, **189**, wrw (1963).

¹⁵F. van der Valk, Thesis, Amsterdam University (1963).

¹⁶W. E. Keller, *Phys. Rev.*, **105**, 41 (1957).

Figure 12. Thermal Diffusion Factor of He^3 and He^4 as a Function of Temperature. The open circles are the experimental values of Watson, Howard, Miller and Shiffren; the squares are those of van der Valk; the filled circles are based on the diffusion coefficient and the viscosity. The theoretical calculations are: ——— based on classical theory; - - - - - Cohen et al; - · - · - Buckingham and Scriven; and - - - - - Monchick .

Figure 13. Thermal Conductivity of Pure Helium-3 as a Function of Temperature. The open circles are the experimental data of Fokkens, Vermeer, Taconis and De Bruyn Ouboter, the open squares are based on viscosity data and the filled squares are based on self-diffusion data. The curve is the theoretical calculations of Monchick, et al.

model is inadequate in contrast to the conclusion reached earlier¹⁰ that the viscosity data are in error. It should be pointed out that exactly the same kind of comparison between the viscosity and thermal conductivity of helium-4 has been done previously¹⁶. The experimental data for both properties are mutually consistent and the theoretical calculations¹⁶ reproduce these fairly well.

Thus, it seems as if there is still a great deal of theoretical work to be done in order to understand the intermolecular forces between the helium isotopes, and to be able to obtain adequate theoretical values of the properties of helium-3.

Collision Integrals In the Chapman-Enskog theory of gases the transport properties of a dilute gas are expressed as functions of a set of collision integrals. These integrals, which are functions of the intermolecular potential between the molecules of the gas, have been calculated for several special potential functions (e.g. the Lennard-Jones (12-6) and modified Buckingham potentials). These calculations have been used extensively in evaluating the transport properties of gases. It has been found that these potentials are inadequate for describing the transport properties over a wide range of physical conditions. Calculations of collision integrals for more flexible potential functions are needed for this purpose. Also, collision integrals are needed for the large number of potential functions which have been proposed in the literature. Such calculations would serve as a test of the validity of these potential functions.

A computer program was written to satisfy both of the above needs. The techniques used in the program were made as independent of the potential function as possible to use the program for any realistic intermolecular potential. To test the program collision integrals for the modified Buckingham potential ($\alpha = 14$) were calculated. Collision integrals for this potential were reported by Mason¹⁷. For this test the following collision integrals were calculated: $\Omega^{1,1}$, $\Omega^{2,2}$, $\Omega^{3,3}$, and $\Omega^{4,4}$.

The difference between Mason's values and the values calculated at Mound are shown in Table 6. A positive number indicates that Mason's value is larger.

Table 6

Percent Difference Between Mason's Values
and Calculated Mound Values

$T^*/^{\circ}K$	$\Omega^{1,1}$	$\Omega^{2,2}$	$\Omega^{3,3}$	$\Omega^{4,4}$
0.1	0.3	-0.3	0.04	-1.1
0.2	0.1	-0.2	0.0	-0.7
0.4	0.2	0.0	0.1	-0.3
1.0	0.0	0.0	0.0	-0.3
2.0	-0.01	-0.2	-0.2	-0.5
4.0	-0.1	-0.3	-0.4	-0.4
10.0	-0.04	-0.1	-0.06	-0.07
40.0	0.3	0.4	0.9	0.9
100.0	2.5	3.0	4.5	5.0
200.0	6.6	7.7	10.0	10.7

¹⁷Mason, E. A., J. Chem. Phys., 22, 169 (1954).

The estimated accuracy of Mason's values is 0.2%, except at low temperatures, where it may be as large as one percent.¹⁷ In general, for T^* equal to or less than 40°K, the values are in agreement to within the stated accuracy of Mason's value.

At 100°K and 200°K there is a relatively large difference between the values. At these temperatures there is a significant contribution to the collision integrals from collisions occurring at reduced energies greater than 100°K. For these energies Mason used the following algebraic equation to calculate the cross sections.

$$Q^l(E) = a_1^l + a_2^l E^{-1/2} + a_3^l E^{-1} + a_4^l E^{-3/2}$$

The constants a_1^l , etc. were determined by using the cross sections at $E = 10, 20, 50$, and 100. For $l = 1$ the constants are:

$$a_1^1 = 0.19709$$

$$a_2^1 = 3.06660$$

$$a_3^1 = -8.40009$$

$$a_4^1 = 10.65300$$

The modified Buckingham potential has a physically unrealistic maximum, and apparently, Mason considered the potential to be unrealistic above an energy of 100. For $\alpha = 14$ this maximum in the potential occurs at a reduced energy of 27,000. For $T^* = 200$ or 100°K the contribution to the collision integrals for energies above 20,000 is negligible. For energies below 20,000 the cross sections were calculated directly. The result of this is that Mound's cross sections are substantially lower than Mason's for high energies as shown in Figure 14. Theoretically, the effect of this difference in cross sections would be that Mound's collision integrals would be lower than Mason's. As shown in Table 7 this is what occurred. Hence, the differences at 100 and 200°K, and to a slight degree at 40°K, arise because, effectively, different potentials were used.

Figure 14. Cross Sections Used by Mason Compared to Mound Calculations.

These calculations for the modified Buckingham potential have shown that Mound's program is functioning properly. The accuracy of Mound's calculations have not yet been determined. The results shown in Table 7 indicate that the error in the test calculations was less than one percent. The numerical methods used in the program are currently being studied to place an upper limit of 0.1% on the error in the calculations. It will be feasible to calculate collision integrals for the large number of potential functions which have been proposed in the literature using the computer.

HELIUM RESEARCH

Helium-3 Refrigerator A measurement of the possible residual field of the superconducting solenoids was made using a flip coil and ballistic galvanometer. These results will be useful in the design of the adiabatic demagnetization cryostat for very low temperatures. A complicated residual field pattern was found which must be considered to obtain a field-free region for the measurement of very low temperatures.

The measurement of the field was made with a 1000 turn flip coil which could be moved along the axis of the solenoid. The leads of the coil were connected to a ballistic galvanometer. The calculated sensitivity of the system was 0.62 gauss/mm deflection of the galvanometer. A resistance network was constructed to reduce the sensitivity to compare the flip coil to the Westinghouse calibration at high fields. A preliminary comparison showed that the calculated sensitivity was in agreement with the Westinghouse calibration.

The measurements revealed several interesting facts. First, when the magnet power supply was first turned on with the current at nominally zero, a field of ≈ 30 gauss appeared at the center of the coil. When the power supply was turned off the field remained the same. To destroy this field the solenoid was disconnected and the heater on the persistent mode switch was turned on. Thus, the explanation is that when the power supply is turned on, an initial current surge energizes the solenoid, and when the power is turned off the persistent switch goes superconducting before the current in the solenoid can decay. Therefore, a persistent current is set up.

Second, after the field in the solenoid was raised to ≈ 3000 gauss and then the power was returned to zero, a residual field remained which was higher at the ends of the solenoid than at the center.

Third, after the persistent switch heater was turned on, the field at the center of the coil changed sign while the field at the ends was reduced. When the current to the solenoid was reversed, the same field behavior was observed, but with opposite sign. These data are summarized in Table 7. It was found that the residual field could be reduced to zero by going through a stepdown procedure of reversing the field several times, each time going to a lower field. All of the effects appeared to be reproducible.

Figure 15 shows the residual field after the following sequence: The field was increased to three amperes, then decreased, and the power supply shut off. The solenoid remained at 4.2°K overnight. The next morning, the heater to the persistent current switch was turned on and the data in Figure 15 were taken. The situation is similar to steps (3), (6), and (9) in Table 7.

The effect discussed above is connected with persistent currents developed in the wire or between turns of the solenoid. The exact explanation is not yet clear. The presence of these currents must be kept in mind in experiments utilizing the magnets.

Table 7

Residual Field in Superconducting Magnet

	<u>Sequence Step</u>	<u>Probe Position</u>	<u>Galvanometer Deflection (cm.)</u>	<u>Field Direction (Arbitrary)</u>
(1)	Current to 3.0 amps			
(2)	Current off	Center End	1.8 4.8	up up
(3)	Persistent heater on	Center End	1.9 2.8	down up
(4)	Reverse current to 3.0 amps			
(5)	Current off	Center End	1.5 4.8	down down
(6)	Persistent heater on	Center End	1.6 3.1	up down
(7)	Current to 1.9 amps			
(8)	Current off	Center End	2.5 5.2	down down
(9)	Persistent heater on	Center End	1.6 3.1	up down
(10)	Reverse current to 3.0 amps			
(11)	Current off	Center End	1.2 off scale	up up
(12)	Persistent heater on	Center End	2.9 6.0	down up

Figure 15. Residual Field in Superconducting Magnet.

ANALYTICAL AND INSTRUMENTATION

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

NEUTRON ACTIVATION ANALYSIS

Neutron activation analysis was used to determine iron, aluminum and silicon in metal-organo complex materials. The following nuclear reactions were used:

$\text{Fe}^{56} (n,p) \text{Mn}^{56}$	0.84 Mev	100%
$\text{Al}^{27} (n,p) \text{Mg}^{27}$	0.84, 1.015 Mev	80%
$\text{Si}^{28} (n,p) \text{Al}^{28}$	1.78 Mev	100%

The samples were irradiated for one half-life or 15 minutes, whichever was shorter, at a 14 Mev neutron flux of 10^8 n/cm²/sec. and allowed to decay appropriately. The induced gamma radiation was counted with a 400 channel pulse height analyzer. The weight of metal present was calculated by comparison of count rates to those of standards subjected to the same conditions.

Since the compounds were of a single metallic constituent, no interferences were present. Thus, the technique in the cases studied was straight forward, and has an associated relative error, dependent on the statistical error due to the sample count rate, of ± 1 to 2%.