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MLM-1300

TID-4500

Category - UC-2

Progress Reports

200, 50

MOUND LABORATORY PROGRESS REPORT FOR OCTOBER, 1965

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Date: October 20, 1965

Issued: July 20, 1966

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.

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MOUND LABORATORY

MIAMISBURG, OHIO OPERATED FOR

UNITED STATES ATOMIC ENERGY COMMISSION

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

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SUMMARY

RADIOELEMENTS

Protactinium-231 Recovery Samples of ionium target material (containing 9% thorium-230) were irradiated with neutrons in the Materials Testing Reactor. The samples were cooled for one year after removal from the reactor before they were returned to Mound Laboratory. The product protactinium-231 is to be separated from the target material, after decanning, by dissolution of the thorium in acid followed by either solvent extraction or carrier precipitation.

Hydrolysis of Plutonyl Ions Work has been continued on three phases of hydrolytic studies: continued refinement of mathematical techniques for data processing, using the data obtained at 25°C for the hydrolysis of uranyl nitrate; study of the hydrolysis of uranyl nitrate at 0°C; and preparation of plutonyl nitrate hexahydrate.

Jezebel Leakage Neutron Spectrum A least-squares fit of a logarithmic plot of the Jezebel leakage neutron spectrum was made. The spectrum is considered to be the sum of a Maxwellian distribution of neutrons liberated in the fission process and a Maxwellian distribution of neutron energies undergoing at least one inelastic collision.

ISOTOPE SEPARATION AND PURIFICATION

Carbon Isotope Separation

Chemical Exchange Three different amines were examined in the chemical exchange system. Precipitation problems occurred in all three cases. When monoethanolamine in isopropanol was used a separation factor approaching 3.00 was obtained.

Neon Static tests are being run on the three-column neon tube bundle measuring the separation in the center column.

Argon Build-up of the argon-38 peak in the five-stage cascade is continuing gradually, approaching an estimated peak of 24% argon-38.

Krypton Using intermediate feed of 79% krypton-86, the draw-off has been enriched to 91%, the highest concentration to date.

Xenon

Thermal Diffusion The xenon tube bundle cascade has enriched xenon-124 to 2% and xenon-126 to 0.88%. Minimum equilibrium times were calculated for various xenon-124 product concentrations. A plan for xenon-124 profile build-up was also developed.

Chromatography The heats of adsorption of krypton and xenon on activated alumina H-151, 50/60 mesh, have been calculated to be -1970 and -3181 cal/mole, respectively. Nitrogen was used as the carrier gas. Some work was also done with activated alumina F-1, 50/60 mesh. This work was abandoned when

the adsorbent proved to be poor for krypton-xenon separations. This completes exploratory examination of adsorbents for krypton-xenon separation. On the basis of the exploratory work, Molecular Sieve 13X appears to have the most favorable characteristics.

Thermal Diffusion Research

Transport Coefficients Thermal diffusion column transport coefficients for Ne^{20} - Ne^{22} were found to be in good agreement with theory in experiments with one of the 12-ft (3 65-cm diameter) experimental hot wire columns. Measurements of the parasitic remixing coefficient were completed in the 6-ft (1 83-cm diameter) column.

Transport Properties Experiments have been performed on the helium-argon and helium-xenon systems to determine the thermal diffusion factor as a function of temperature and composition. These experiments have been performed in a recently installed Trennschaukel or "swing separator" system in which the experimental conditions may be closely controlled for long periods of time. The results show a disappointing experimental scatter. An error analysis was made of all the variables in the experiments and the conclusion was reached that the mass spectrometric analyses of the gas samples are not sufficiently precise. This is based upon the findings of the error analysis that no observed deviations of the control system could introduce such large discrepancies and, secondly, that no mechanism exists which would substantially enhance the thermal diffusion separation.

Helium Research

Vapor Pressure Thermometry Thermomolecular pressure data have been obtained for saturated helium-3 vapors with cold temperatures as low as 0.36°K. The data are compared with previous results and with the Weber-Schmidt equation. This completes the sequence with this set of connecting tube radii since data have now been collected for saturated and unsaturated vapors of both helium-3 and helium-4.

ANALYTICAL AND INSTRUMENTATION

Nuclear Magnetic Resonance Studies The nuclear magnetic resonance spectrometer was electronically modified to provide homonuclear spin decoupling in order to simplify complex spectra by eliminating proton-proton spin interactions. The decoupling of the three methyl protons from the two methylene ones of ethyl alcohol was demonstrated.

RADIOELEMENTS

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

PROTACTINIUM-231 RECOVERY

The recovery of protactinium-231 from neutron-irradiated ionium (thorium-230) is being studied. Processing in a hot cell will be required due to the presence of fission products and other gamma emitters. A separation and purification process is under development.

Ionium target material (9% thorium-230, 91% thorium-232) was prepared in December 1958 at Mound Laboratory in the form of thorium dioxide and shipped to the Materials Testing Reactor at Idaho Falls, Idaho, for irradiation. The samples were cooled at Idaho Falls for one year after removal from the reactor and were returned to Mound Laboratory.

The principal nuclear reactions are:

The first reaction is the desired neutron capture to form protactinium-231, and the others are undesirable side reactions. Thus the isotopes expected to be present are the parent isotopes thorium-230 and thorium-232, the product protactinium-231, and also uranium-232, uranium-233 and fission products. The production of the isotope uranium-232 is unfortunate for several reasons. High concentrations of protactinium cannot be achieved because of the secondary neutron capture reaction. Also, short-lived daughters of uranium-232 are strong gamma emitters which add to the gamma shielding problems. In addition, the 1.91-yr thorium-228 (first daughter of uranium-232) will be recovered with the other thorium isotopes and will introduce a gamma shielding problem in the handling of the thorium fraction.

The irradiated thorium totalling 223 g is contained in ten aluminum capsules each containing 20-23 g and one capsule containing about 5 g. From the available irradiation data, it is estimated that the total quantity of material contains approximately 0.5 g of protactinium-231, 3 g of uranium-233, 0.08 g of uranium-232 and 1 g of fission products.

The material will probably be decanned with caustic and the thorium will be dissolved in either sulfuric acid or a mixture of nitric and hydrofluoric acids. Separation of the protactinium in the first step is

desirable, and either a solvent extraction step (e.g., using diisobutyl carbinol) or a carrier precipitation step (using manganese dioxide to carry the protactinium) appears feasible. Recovery of the thorium fraction involves separations from both uranium and the fission products. Experimental work with trace protactinium-231, thorium-232 and uranium-238 will be required before the process is finalized

HYDROLYSIS OF PLUTONYL IONS

Previous work¹ showed that three hydrolytic species are formed in the initial hydrolysis of uranyl nitrate at 25°C. Two of the species were $[(\text{UO}_2)_2(\text{OH})_2]^{+2}$ and UO_2OH^+ . The third species, which was postulated to be $[(\text{UO}_2)_3(\text{OH})_3]^{+4}$, has not been verified. In order to clarify this point, a computer program is being written which is a modification of the program used at the Oak Ridge National Laboratory for processing data obtained from hydrolytic studies.

The study of the hydrolysis of uranyl nitrate at 0°C was started. The initial data obtained were very poor because of difficulties experienced with equipment stability. However, it was determined that large amounts of static electricity were building up on the surface of the Styrofoam used as insulation for the water bath for experiments at 0°C. The pH meter was picking up this potential and, as a result, erroneous readings were obtained. The use of Styrofoam was discontinued, and measurements are again being made at 0°C.

The initial attempt to prepare plutonyl nitrate hexahydrate (using plutonium-239) free from any appreciable impurities was successful, insofar as a solid product was obtained which, when dissolved in 1N HNO_3 , showed only plutonium(VI) to be present. Further analysis will be performed on the product to see if it is stoichiometric.

Two grams of plutonium-239 metal were dissolved in 1N HCl. After dissolution of the metal, the acid solution was evaporated. The residue was then dissolved in approximately 150 ml of 1N HNO_3 . A 25% excess of silver(II) oxide, based on the equivalents of plutonium(IV) in solution, was added to the solution in four equal portions. This quantitatively oxidized the plutonium(IV) to plutonium(VI), as determined by spectrophotometric observation. The excess silver was then precipitated with 1N HCl, and the AgCl precipitate was allowed to digest overnight. The solution was then decanted and passed through an anion exchange column (nitrate form) five times. However, a chloride analysis after the fifth pass showed chloride to be present at a concentration of 1 mg/ml. The anion exchange was then stopped, and the solution was placed inside a vacuum desiccator containing KOH and P_2O_5 . A light brown solid remained in the beaker. This solid, which is $\text{PuO}_2(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, is now being analyzed.

JEZEBEL LEAKAGE NEUTRON SPECTRUM

In order to evaluate properly the series of experiments involving the fission cross-section measurements of plutonium-238 in the Jezebel critical assembly at Los Alamos, a detailed knowledge of the neutron spectrum of the assembly is required. Neutron spectral measurements were made on nuclear track plates,² but these data were never fitted to a reasonable theoretical curve.

¹MLM 1299, p. 7.

²L. Stewart *Nuclear Sci. and Eng.* 8, 595 (1960)

It is expected that the neutron spectrum would be a combination of a Maxwellian distribution of neutron energies from the fission process and a Maxwellian distribution from single inelastic scattering processes. Thus, an approximation of the energy distribution curve could reasonably be expected to be of the form:³

$$\phi(E) = A(Ee^{-\alpha E}) + \sqrt{E}e^{-\beta E} \quad (6)$$

where E is the neutron energy in Mev. Stewart's data range from 0.4 to 8.9 Mev. These data were plotted as $\phi(E)/\sqrt{E}$ versus E on a logarithmic scale and showed an approximate straight line fit above 1.4 Mev. A least squares fit was made of a straight line to these logarithmic data, establishing β . Calculated values of the form $\phi(E) = \sqrt{E}e^{-\beta E}$ were subtracted from Stewart's data points between 0.4 and 1.0 Mev, and the results were plotted as $\phi(E)/E$ versus E on a logarithmic scale. Again a least squares fit of a straight line was made, thus establishing A and α . The resultant best fit was then established as

$$\phi(E) = K[5.01 Ee^{-4.08E} + \sqrt{E}e^{-0.689E}] \quad (7)$$

where K is a normalization factor. The agreement of this curve with Stewart's data is shown in Figure 1. Stewart's error bars were included.

³W. L. Stubbins, Private Communication

Figure 1. Jezebel Flux Spectrum.

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

Chemical Exchange Experiments involving three different amines were performed in the carbon dioxide-carbamate chemical exchange system. The first of these amines, piperidine, was run previously but with limited success because of difficulties in the carbamate decomposition. In the earlier experiment, the piperidine solution was made up using a mixed solvent composed of methanol and isopropanol. When used alone, the methanol limits the decomposition of the carbamate by its low boiling point. On the other hand, the isopropanol limits the solubility of the carbamate and, therefore, the concentration of the amine solution. The results of a reaction run using the mixed solvent indicated improved separation with no evidence of carbamate precipitation in the system.

A second amine was examined for possible use in the chemical exchange system. A trial run was begun using a 2M solution of 1,3-propanediamine in methanol. Precipitation problems forced an end to the run within one day. It is possible that lower concentrations of this amine would solve this problem, but it appears unlikely to be worthy of further examination in this type of solvent system.

In a third series of experiments monoethanolamine was used, this time with isopropanol as a solvent. A 2M solution was prepared and examined in the chemical exchange system. After two days of operation a fine precipitate appeared in the reactor. The precipitation problem was sufficient to preclude obtaining any significant results regarding separation, since flow rates become inconsistent under such conditions. Therefore, a second attempt was made to investigate the system, this time using a 1.3M solution in the same solvent. Even though the carbamate is saturated at this concentration, it was possible to obtain some results.

In Figure 2 the separation factor is plotted against time. While the plot is erratic (possibly due to localized precipitation at certain times), the separation factor is significantly improved over that determined from any previous results using this amine. The increase in separation factor is partially due to more complete dissociation of the carbamate by the higher boiling solvent. Analysis of the carbon dioxide retained in the amine solution will indicate how much improvement in decomposition was achieved.

NEON

Static tests were started on the recently completed 36-ft tube bundle cascade using natural neon and a heater temperature of 750°C. The pressure in the column was set at 1600 mm Hg, the starting point for accumulating data for the plot of separation vs. pressure for the columns. The 36-ft neon system is shown in Figure 3. The length of the column between the sample ports is 362 cm, which is the distance along

Figure 2. Separation Factor for Chemical Exchange

the hot space of the heater. In operation, bellows pumps circulate gas between adjoining stages of columns, thus making the top of one column and the bottom of the adjoining column equal in concentration. After an equilibrium time of 24 hr two samples were taken from the column for use in calculating the separation between the two sample ports, the separation factor is given by:

$$q = \frac{(C_{20}/C_{22}) \text{ Top port}}{(C_{20}/C_{22}) \text{ Bottom port}}$$

where: C_{20} = concentration of neon-20
 C_{22} = concentration of neon-22

The separation factor, q , was converted to $\ln q/\text{length (cm}^{-1}\text{)}$ and compared with curves calculated for temperatures of 750°C and 700°C

Results for three different pressures show the experimentally determined separation to be high by 19-36% of the theoretical value, indicating error in the sampling procedure. A slight deviation in the data was expected since the temperature cannot be directly read from a pyrometer and may not be exactly 750°C; the present methods used to calculate the temperature may be slightly in error. Nevertheless, an error of 19-36% is excessive and the experiment will be rerun. The entire sampling procedure was reviewed, the factors that may be affecting this procedure adversely are not enough equilibrium time between samplings at each pressure and too low a concentration of the lesser isotope in the sample for accurate analysis. These factors are being corrected

Figure 3. *Experimental Set-Up for Measuring Separation in the 36-Foot Neon System.*

krypton-86 which is being used as feed for further enrichment. Material currently being drawn off is enriched to 91% krypton-86, the highest concentration attained to date.

ARGON

The argon-38 profile in the five-stage argon cascade has been increasing gradually with a top draw-off of 1.6 ml/hr. A peak concentration of over 30% is expected in the fourth stage between 72 and 96 ft from the bottom of the cascade. The peak location is very sensitive to the top draw-off rate. The peak data obtained to date are shown in Table I.

Table I

ARGON-38 IN THE FIVE-STAGE CASCADE

Date	Peak Position in Feet from Heavy End	Argon-38 Concentration (%)
August 23, 1965	99	21.0
September 20, 1965	90	23.2
October 4, 1965	95	24.2

KRYPTON

A two-column, two-stage thermal diffusion cascade is being used for enriching krypton-84 and -86. Re-processing of raffinate yielded 2.7 liters of 79%

XENON

Thermal Diffusion In order to increase the enrichment of xenon-136, the six-stage swing cascade unit was converted from a 3-1-1-1-1-1 arrangement into an eight-stage unit of single columns. The modified Trennschaukel gas circulating system for interstage transport in this cascade consists of a swing compressor system at each end of the cascade. This is expected to be sufficient for the extended stages.

The xenon six-stage tube bundle cascade enriched xenon-124 to 2.04%. The xenon-126 content was 0.88%. The system was disrupted when the stepping switch for the fifth stage solenoid valves did not reset.

Minimum equilibrium times (T_e) for the tube bundle at various product concentrations of xenon-124 have been calculated from the equation

$$T_e = \frac{\text{Xenon-124 Holdup}}{n_i H x_f (1 - x_f)}$$

where: n_t = number of columns in first stage
 H = transport coefficients for one column
 x_f = mole fraction of xenon-124 in the feed

The xenon-124 hold-up was calculated by multiplying the concentrations in each stage and interstage times the respective STP volumes. The xenon-124 concentrations were obtained from programmed computer data. Table 2 shows the hold-up calculation for 1.03% xenon-124. A plot of T_e versus xenon-124 product concentrations is given in Figure 4. These are minimum times, and the actual equilibrium time is expected to be higher.

Table 2

XENON TUBE BUNDLE HOLD-UP FOR 1.03% XENON-124

	STP Volume (liters)	Xenon-124 Concentration (mole fraction)	Xenon-124 (liters)
	-	0.00096	-
Stage #1	1.5	0.00103	0.001545
1-2 interstage	2.65	0.00110	0.002915
Stage #2	1.25	0.00114	0.001425
2-3 interstage	2.65	0.00118	0.003127
Stage #3	1.25	0.00136	0.001700
3-4 interstage	2.52	0.00153	0.003856
Stage #4	1.0	0.00191	0.001910
4-5 interstage	2.54	0.00229	0.005817
Stage #5	0.75	0.00345	0.002587
5-6 interstage	2.48	0.0046	0.011410
Stage #6	0.25	0.0075	0.001875
6 top	0.54	0.0103	0.005560
Total	19.38		0.043727

Amount of xenon-124 in initial feed = (0.00096) (19.38) = 0.018604 liters

Total xenon 124 in system	0.043727
Xenon-124 in initial feed	-0.018604
Xenon-124 hold-up	0.025123 liters = 0.1394 g

Calculations were also made for the timing of feed tank changes to be followed for static profile build-up and product draw-off operations. These are given in Table 3. At present, the profile is being built up in the tube bundle to approximately 2.5% xenon-124. The feed has been changed after it has been depleted to approximately 0.06%. This reduces the amount of xenon raffinate.

Figure 4. Calculated Xenon-124 Minimum Equilibrium Time.

Table 3

CALCULATED BUILD-UP AND DRAW-OFF PARAMETERS FOR THE XENON-124 TUBE BUNDLE

Static (Profile Build-Up)				Operating (Product Draw-off)		
Product Concentration (X_p) (%)	Xe-124 Required to Build Up Profile (g)	Number of Feed Changes ^a (in 100 liters)	Time between Feed Changes ^b (days)	Xe-124		
				Draw-Off Rate (P) (g/day)	Draw-Off Rate (X_p) • (P) (g/day)	Draw-Off Time between Feed Changes ^c (days)
1.03	0.24268	2.3	3.5	2.0	0.0206	5.4
1.34	0.28908	2.6	4.0	1.5	0.0201	5.5
2.57	0.42426	3.8	4.5	0.75	0.0192	5.7
3.78	0.54646	4.9	4.9	0.5	0.0189	5.8
7.35	0.94941	8.5	5.4	0.25	0.0184	6.0
17.3	2.1320	19.2	6.3	0.1	0.0173	6.4

^aXenon-124 (in grams) in system divided by 20% of xenon-124 (in grams) in 100 liters of feed.

^bMinimum equilibrium time divided by the number of feed changes.

^c20% of xenon-124 (in grams) in 100 liters of feed divided by xenon-124 draw-off rate.

Draw-off at approximately 2.5% xenon-124 is expected to be made at ~128 ml/day (0.75 g/day) in accordance with the results of the computer program. The feed will be changed every 5 days during draw-off so that the profile of xenon-124 is not lowered

In order to obtain higher concentrations of xenon-124 from the tube bundle the fifth stage, containing three columns, will be realigned into stages of one column each, yielding a 6-5-5-4-1-1-1-1 configuration. A computer program is being run to get concentration and product draw-off data for a configuration of this type.

A comparison of hot-wire temperature data and computer data reported previously⁴ was re-evaluated. The computer data used previously were based on a lower cold wall temperature than the one used during the experiment. The lower temperature occurred prior to the installation of the water recirculating system for the columns. New computer data were obtained using 306°K for the cold wall temperature instead of 288°K. In Figure 5, it can be seen that at about 200°C the experimental and computer results are equal.

Figure 5. Hot-Wire Temperatures for the 24-Foot Xenon Thermal Diffusion Columns.

Chromatography Xenon obtained as a reactor off-gas contains the radioisotope krypton-85 as an impurity. This impurity is removed chromatographically. Continuing research in this area is directed to further reducing the krypton-85 level while at the same time increasing the xenon yield.

A series of separations on activated alumina H 151, 50/60 mesh, at 170°, 195° and 220°K was completed. Nitrogen was used as the carrier gas. Heats of adsorption derived from these experiments were -1970

⁴MLM-1299, p. 28.

cal/mole and -3181 cal/mole for krypton and xenon, respectively. Short retention times were observed and the chromatographic peaks showed little tailing.

Other experiments were made on activated alumina F-1, 50/60 mesh, at 170°K. Poor separations were observed, therefore no further work is planned with this adsorbent. Molecular Sieve 4A, 50/60 mesh, was also ruled out for this use.

The exploratory evaluation of adsorbents for the xenon-krypton separation is now essentially completed. A summary of results for the various adsorbents that have been studied is given in Table 4.

Table 4

MEASURED HEATS OF ADSORPTION FOR ADSORBENTS USED
IN CHROMATOGRAPHIC SEPARATIONS

Adsorbent	Carrier Gas	Qa(Kr) (cal/mole)	Qa(Xe) (cal/mole)	$\frac{Qa(Xe)}{Qa(Kr)}$
Activated Charcoal 50/60 mesh	N ₂	2793	5025	1.80
Silica Gel 70/80 mesh	N ₂	2045	3812	1.86
Molecular Sieve 5A 50/60 mesh	He	3091	-5127	1.66
Molecular Sieve 5A 50/60 mesh	N ₂	1208	1901	1.57
Molecular Sieve 13X 50-60 mesh	N ₂	1249	-1953	1.56
Activated Alumina H 151 50-60 mesh	N ₂	1970	-3181	1.61

The ratios of the heats of adsorption, $Qa(Xe)/Qa(Kr)$, are similar for all adsorbents, therefore, a choice of adsorbent on this basis alone is not sufficient. The tailing and desorption properties shown by the adsorbents did vary, however, as can be seen in Figures 6 and 7 for two such adsorbents. Even though the krypton appeared to be passed after 17 min on the charcoal column a small radioactive peak was seen at column bakeout. With a Molecular Sieve 13X column at an even lower temperature, this peak was not observed. Further, the total separation time was much lower for the Molecular Sieve 13X column than for the charcoal column. The poor desorption characteristic observed with charcoal was also displayed by Molecular Sieve 5A and silica gel. Activated alumina H 151 has a slight overlap between the two peaks. On this basis, Molecular Sieve 13X seems to be indicated as a favorable adsorbent for this separation. Further tests will be made to verify that Molecular Sieve 13X meets all requirements and is indeed superior to the activated charcoal now in use.

THERMAL DIFFUSION RESEARCH

Transport Coefficients Two sets of measurements are required to determine the coefficients H' (transport), K'_c (convective remixing) and K'_d (ordinary diffusive remixing) in the differential equation for isotope transport in a thermal diffusion column:

$$\tau = H' p^2 c(1-c) - (K'_c p^4 + K'_d) \frac{dc}{dz} \quad (8)$$

where τ is the net transport of one of the isotopes, p is the pressure, c is the fraction of one of the isotopes, and z is the length along the column. The required experiments are (1) measurement of static separation as a function of pressure and (2) measurement of separation as a function of flow rate

Figure 6. Chromatogram of Krypton-Xenon Separation with an Activated Charcoal Column at 210°K

Figure 7. Chromatogram of Krypton-Xenon Separation with a Molecular Sieve 13X Column at 167°K.

The transport coefficient H' for $\text{Ne}^{20}\text{-Ne}^{22}$ in column E1 was measured using flow data obtained at two different operating pressures. (Dimensions and temperatures for column E1 are given in Table 5.) The apparatus used is shown in Figure 8. Gas was circulated through the top of the column at 2.0 liters/min and a measured flow rate was maintained at the bottom of the column. The flow rate was determined by measuring the rate of pressure increase in a calibrated vessel. Pressure was maintained constant in the column by an absolute pressure regulator. The column was operated for 48 hr at constant pressure and flow rate; then top and bottom samples were taken. To eliminate end effects the top sample was taken at a port 30.5 cm below the top of the column

Table 5

CHARACTERISTICS OF COLUMNS USED
FOR THERMAL DIFFUSION
TRANSPORT MEASUREMENTS

Column	Length (cm)	Cold Wall Radius (cm)	Hot Wall Radius (cm)
E 1	366	1.27	0.08
E 5	183	0.94	0.08

Column	Cold Wall Temp. (°C)	Hot Wall Temp. (°C)
E 1	15	800
E 5	15	820

This procedure was performed for a series of flow rates, and the data were plotted in Figure 9 as the natural logarithm of the separation vs. flow rate. From these data H' was calculated, and the results obtained are given in Table 6. Values of K'_c and K'_d are also given in the table. These values were obtained from the ratios K'_c/H' and K'_d/H' which were determined in earlier static experiments.⁵

The theoretical values of the coefficients given in Table 6 were calculated from Lennard-Jones shape factors. A value of 0.0227 was assumed for the $\text{Ne}^{20}\text{-Ne}^{22}$ thermal diffusion factor at 288°K. This value was interpolated from the Trennschaukel results of Watson, et al.⁶

Figure 8. Schematic Diagram of Thermal Diffusion Apparatus for Determining H' .

⁵MLM-1274 p. 18.

⁶W. W. Watson, A. J. Howard, N. E. Miller and R. M. Shiffrin, *Z. Naturforsch.*, **18a**, 242 (1963).

Table 6

**THERMAL DIFFUSION COLUMN TRANSPORT COEFFICIENTS
FOR SEPARATION OF NEON-20 - NEON-22 AT 800°C**

Parameter	p = 810 torr	p = 460 torr	Predicted
	Measured	Measured	
H' (g sec ⁻¹ atm ⁻²)	1.63×10^{-4}	1.61×10^{-4}	1.53×10^{-4}
K'_c (g cm sec ⁻¹ atm ⁻⁴)	2.37×10^{-2}	2.34×10^{-2}	2.08×10^{-2}
K_d (g cm sec ⁻¹)	3.01×10^{-3}	2.98×10^{-3}	2.95×10^{-3}

Figure 9. Separation of Neon-20 and Neon-22 in Column E1 at 800°C.

The experimental results for H' suggest that the value of the thermal diffusion factor should be slightly higher than 0.0227. The best fit to the experimental data would result for a thermal diffusion factor of 0.0240.

As shown in Figure 10 this value is close to the trend inferred from the measurements of Raman, et al.⁷ and of Mundy and Grew.⁸ It lies somewhat below the results of Fischer.⁹

⁷S. Raman, T. K. S. Narayanan, and S. Dave, Government of India Atomic Energy Commission Report AEET-204, Bombay, India (1965).

⁸J. N. Mundy and K. E. Grew, *Phys. Fluids*, 4, 1320 (1961).

⁹A. Fischer, Thesis, Zurich (1961).

Figure 10. Thermal Diffusion Factor for Ne²⁰-Ne²²

The diffusive remixing coefficient K_d is in excellent agreement with theory; however, the measured convective remixing coefficient K'_c is somewhat high. This is probably the result of a small amount of parasitic remixing.

Parasitic Remixing Parasitic remixing effects result from asymmetric thermal diffusion column geometry and temperature distribution. For an asymmetric column the transport equation becomes

$$\tau = H' p^2 c(1-c) - [(K'_c + K'_p)p^4 + K_d] \frac{dc}{dz} \quad (9)$$

where K'_p is the parasitic remixing coefficient

A series of experiments, the object of which was to relate K'_p to known deviations from symmetry, was completed. Static separation versus pressure measurements were made for Ne²⁰-Ne²² separation in column E5. (Dimensions and operating conditions for this column are given in Table 5.) In successive experiments the wire was displaced horizontally 0, 0.16, 0.32 and 0.48 cm from the axis of the column. (Eccentric chucks were used to create the displacements. The wire remained straight and vertical at all times.) Results of the 0, 0.16 and 0.32-cm displacements were reported previously.¹⁰ The experiments for a 0.48-cm wire displacement were completed and the results are reported here.

Separation data for the 0.48-cm wire displacement were difficult to obtain. With this highly asymmetric geometry the convective circulation in the column appeared to be very unstable at pressures well below those at which turbulence would be expected in a symmetric column. The instability was manifested by

¹⁰MLM-1299, p. 30.

sudden increases of approximately 20 torr in column pressure while hot and cold wall temperatures remained constant. These increases are thought to result from a transition from laminar to turbulent convective flow.

The stability problem was circumvented for purposes of this investigation by making the separation measurements at pressures considerably lower than those used for the 0, 0.16, and 0.32-cm displacements. In Figure 11 are plotted the results of static separation measurements in the pressure range from 100 to 500 torr. The coordinates of this plot correspond to the linear form of the static solution of Equation (9):

$$\frac{Lp^2}{\ln q} = \frac{K_d}{H'} + \left(\frac{K_c' + K_p'}{H'} \right) p^4 \quad (10)$$

where L is the column length and q is the separation factor

$$q = \left(\frac{l-c}{c} \right)_{top} \left(\frac{c}{l-c} \right)_{bottom} \quad (11)$$

where c = concentration of neon-22.

A least-squares analysis of the data (including a point at 696 torr not shown on Figure 11) gave the slope and intercept indicated. The coefficients thus derived are tabulated in Table 7 along with similar information for the smaller wire displacements. The ratio $(K_c' + K_p')/K_c'$ (obtained by assuming $K_p' = 0$ at $\epsilon = 0$) is plotted against displacement divided by column radius in Figure 12.

Figure 11. Static Separation Data for a Wire Displacement of 0.48 cm in Column E5.

Table 7

COEFFICIENT RATIOS FOR ASYMMETRIC THERMAL DIFFUSION COLUMN GEOMETRY

Wire Displacement (cm)	Experiment			Theory	
	K_d/H' (cm atm ⁻²)	$(K_c' + K_p')/H'$ (cm atm ⁻²)	$(K_p' + K_c')/K_c'$	K_d/H'	K_c'/H'
0.00	38.2	29.3	- -	37.9	32.9
0.16	30.5	68.4	2.33	- -	- -
0.32	36.1	126	4.30	- -	- -
0.48	30.5	123	4.19	- -	- -

Figure 12. Parasitic Remixing as a Function of Wire Displacement.

Also plotted in Figure 12 is a result obtained earlier in a single experiment with Column E1.¹¹

A theoretical treatment by Dickel¹² states that

$$\frac{K_c' + K_p'}{K_c'} = 1 + \frac{47}{6} \left(\frac{\epsilon}{\Delta X} \right)^2 \quad (12)$$

¹¹MLM-1238, p. 29

¹²G. Dickel, Z. Naturforsch., 16a, 755 (1963).

where ϵ is the displacement and ΔX is the average distance from the hot wall to the cold wall. This relationship is shown in Figure 12. The theory does not agree with the experimental results; however, the theory was derived for plane parallel geometry, and extension to the extreme cylindrical geometry of these experiments does not appear to be justified.

Transport Properties It has been pointed out previously that, of all the macroscopic properties of a gas, the thermal diffusion factor is the most sensitive to the intermolecular forces. Therefore, in order to measure isotopic thermal diffusion factors a 20-tube Trennschaukel and an environmental chamber were constructed. Before attempting to measure isotopic thermal diffusion factors, it is necessary to systematize and perfect the techniques involved in using the apparatus. To this end measurements of the thermal diffusion factor, a_T , of the helium-argon and helium-xenon systems have been made.

The former system was chosen because a_T is large, and therefore relatively easy to measure in the system. It is also well known¹³⁻¹⁷ and can be used as a standard with which to compare the present experimental results. The latter system was chosen because it is of interest, a_T is large^{13,18,19}, and considerable confusion exists at present as to its temperature and composition dependence. The results for a mixture of 50% helium and 50% xenon^{13,18} show no temperature dependence while the results from xenon tracer measurements¹⁹ definitely show a temperature dependence.

In order to see why this is unusual consider the theoretical expression for a_T :

$$a_T = (6C^*-5) \frac{x_1 s_1 - x_2 s_2}{x_1^2 Q_1 + x_2^2 Q_2 + x_1 x_2 Q_{12}} (1 + k) \quad (13)$$

where C^* is a ratio of collision integrals, x_1 and x_2 are the mole fractions of the components; s_1 , s_2 , Q_1 and Q_2 are functions of the molecular weights of the gases and certain collision integrals, and k is a small correction (1-10%, usually) based on the higher approximations in the Chapman-Enskog theory. Now almost all of the temperature dependence of a_T is due to the factor $(6C^*-5)$ which is independent of composition; hence, while it may be possible that all of the data presently in the literature are consistent (especially since the molecular weights of helium and xenon are very different), it certainly appears unlikely

The experimental values of a_T are obtained from the measurement of the steady-state compositions of portions of a gaseous mixture which has been exposed to a temperature gradient. The equation which applies to the Trennschaukel is

$$a_T = \frac{1}{20} \frac{\log q}{\log (T_h/T_c)} \quad (14)$$

¹³B. E. Atkins, R. E. Bastick and T. L. Ibbs, *Proc. Roy. Soc. (London)*, **A172**, 142 (1937).

¹⁴M. F. Laranjeira and J. Kistemaker, *Physica*, **26**, 431 (1960).

¹⁵S. C. Saxena and E. A. Mason, *Mol. Phys.*, **2**, 379 (1959).

¹⁶S. Weissman, S. C. Saxena and E. A. Mason, *Phys. Fluids*, **3**, 510 (1960).

¹⁷E. A. Mason, S. Weissman and R. P. Wendt, *Phys. Fluids*, **7**, 174 (1964).

¹⁸K. E. Grew, *Proc. Roy. Soc. (London)*, **A189**, 402 (1947).

¹⁹D. Heymann and J. Kistemaker, *Physica*, **25**, 556 (1959).

where T_h and T_c are the hot and cold temperatures and q is the separation factor defined as

$$q = (x_1/x_2)_h / (x_1/x_2)_c \quad (15)$$

The quantities $(x_1/x_2)_h$ and $(x_1/x_2)_c$ are the ratios of the mole fractions of the lighter component to the heavier component at the hot and cold temperatures, respectively. Thus, it is seen that in order to obtain accurate values of a_T two conditions are necessary: (1) the temperature difference in the apparatus must be held constant until the steady state is reached and must be accurately measured, and (2) the compositions of the gas must be determined very accurately.

A detailed error analysis of equation (14) has been made. The results show that the uncertainty in a_T can be expressed as

$$\frac{da_T}{a_T} = \frac{1}{2.303} \left[\frac{2}{\log q} \left(\frac{dx_1}{x_1} + \frac{dx_2}{x_2} \right) + \frac{1}{\log T_h/T_c} \left(\frac{dT_c}{T_c} + \frac{dT_h}{T_h} \right) \right] \quad (16)$$

where $100 (da_T/a_T)$ is the percentage error in a_T corresponding to uncertainties of dx_1 , dx_2 , dT_c and dT_h in the mole fractions and temperatures, respectively. Examples of typical values are: $dT_c = 0.6^\circ\text{K}$, $dT_h = 0.5^\circ\text{K}$, $T_c = 500^\circ\text{K}$ and $T_h = 520^\circ\text{K}$, which lead to an uncertainty in a_T of about 5% due to temperature effects alone; $dx_1 = dx_2 = 0.0005$, $x_1 = x_2 = 0.5$ which lead to an uncertainty in a_T of about 4% due to uncertainty in the compositions. Therefore, the total uncertainty in the values of a_T should be about 10%. A 50-50 mixture is the most favorable case (i.e., as one of the mole fractions approaches zero, the uncertainty in a_T becomes larger for the same value of dx).

The two figures give comparisons between the data obtained at Mound Laboratory and data reported in the literature; $1/a_T$ is plotted rather than a_T since it is expected that $1/a_T$ should be linear when plotted against composition.¹⁷ Figure 13 gives the results for helium-argon. It can be seen that the present results are in qualitative agreement with the literature values but are too scattered. Figure 14, which gives the results for helium-xenon, also shows that the present results are in qualitative agreement with literature values but are also too scattered. It is important to note that the points scatter below (corresponding to values for a_T that are too high) as well as above the literature values. Some of the points correspond to as much as 30% greater than the literature values for a_T . It is impossible that such large separations are occurring in the Trennschaukel because almost any conceivable faulty experimental procedure would tend to make the separation, and hence the value of a_T , too small. The only two possible sources of an enhanced separation are pumping speed and impurities in the gas, which can be ruled out because these effects acting cumulatively do not cause errors of more than about 10%.

Therefore it must be concluded that either the temperature or composition measurements are erratic. The ΔT measurements may be eliminated as a possible source of large errors because the temperatures have been controlled in such a manner that the largest variation or spread that has been tolerated is 2° . This corresponds to an average deviation of about 1° , which corresponds to an error in a_T of no more than 7%. Thus the indication is that the scatter must be due to erratic analysis of the compositions.

The compositions are measured with a mass spectrometer. Spectrometers of two different mass ranges are available, one from 2 to 44 and one from 12 to 136. Therefore, it is difficult to obtain good helium-xenon data, which probably accounts for the scatter. In the case of the helium-argon data, one potential source of error is high backgrounds of helium and deuterium from other work. Experiments are being planned to investigate these effects.

Figure 13. The Helium-Argon System Showing the Theoretical Values Calculated in the Chapman-Cowling (CC) and the Kihara (K) First Approximations.

A small increase in the error in the composition (i.e., $dx_1 = dx_2 = 0.005$ rather than $dx_1 = dx_2 = 0.0005$) can lead to error in α_T of over 40%. Thus, in order to obtain the accurate values of α_T which can presently be obtained using the Trennschaukel, it is necessary to improve the procedure for obtaining the mass spectrometric results.

HELIUM RESEARCH

Vapor Pressure Thermometry Thermomolecular pressure measurements have been made for saturated helium-3 vapors with a cold bulb temperature ranging from 0.36°K to 0.71°K, which is equivalent to a range of $P_w(0.29 \text{ cm}) = 0.020 \text{ torr}$ to 1.550 torr.

The working temperature for this experiment was achieved through the use of a pumped liquid helium-3 bath to cool a paramagnetic salt slurry which, in turn, cooled the vapor pressure bulb upon demagnetization of the 30-kilogauss superconducting solenoid. Otherwise, the data were collected as in previous runs²⁰ with a reference tube of 0.29-cm radius versus tubes with radii of 0.14, 0.055 and 0.0271 cm. The results for all three tube radii were in agreement with previous work.

The results obtained for the 0.14-cm radius tube are shown in Figure 15 where they are compared to the Weber-Schmidt equation as well as previous Mound data for unsaturated helium-3 and -4 and saturated

Figure 14. The Helium-Xenon System.

²⁰MLM-1231, p. 29.

helium-4. It is seen that, within the experimental scatter, the present data are in complete agreement with the earlier work. As reported previously,²¹ the data for saturated helium-4 vapor show large deviations from the data for the unsaturated gas, and these data are represented by a dashed line in the figure for the sake of clarity. Since the present data indicate that no such effect exists for saturated helium-3, one can now conclude that the previously²¹ suggested explanation for the anomalous helium-4 results is indeed correct. That is, the anomalous results for saturated helium-4 vapors are due to a superfluid film flow effect and otherwise have nothing to do with the state of the gas, whether saturated or unsaturated.

Figure 15. Comparison of Mound Pressure Data and the Weber-Schmidt Equation

Thus, it is concluded that the data for unsaturated helium-4 vapor reflect the true thermomolecular pressure differences whereas the data for saturated helium-4 reflect the more complex effect of thermomolecular pressure differences added to film flow pressure drops. The data for both the saturated and unsaturated helium-3 are thought to represent only the thermomolecular pressure differences since no superfluid film is known to exist for this isotope and since the two types of data are coincident.

Unexplained, consistent deviations from the Weber-Schmidt equation appear in the present data just as in all previous Mound data. A recent publication²² of independent thermal transpiration results indicates similar deviations. A revision of the Weber-Schmidt equation would appear to be in order.

²¹MLM-1238 p 33.

²²T. Edmonds and J. P. Hobson J. Vac. Sci. Technology, 2, 182 (July/August, 1965).

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.

NUCLEAR MAGNETIC RESONANCE STUDIES

In order to simplify the interpretation of complex nuclear magnetic resonance (NMR) spectra the spectrometer was modified electronically to provide proton-proton spin decoupling. The complexity of the spectra arises from the splitting of the energy levels of one group of chemically equivalent protons by another group. This results in a multitude of absorption lines which overlap one another to give the complex spectrum. However, one can destroy this coupling of nuclear spins by equally populating the spin-states of the offending group of equivalent protons. This is accomplished by irradiating one set of protons with high radio-frequency power at its resonance frequency while recording the spectrum of the other set.

Figure 16 gives an example of this technique of "double resonance" applied to ethyl alcohol. Spectrum A was obtained without spin-spin decoupling. Spectrum B was obtained while the $-CH_3$ group and the $-CH_2$ group were simultaneously irradiated with high RF power and low RF power, respectively. The reverse procedure was used to obtain spectrum C.

Figure 16. Spin-Spin Decoupling in Ethyl Alcohol.