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TABLE OF CONTENTS

	Page
Summary	5
Radioelements	
Half-Life Determination by Decaying Pairs	7
Hydrolysis of Plutonyl Ions	8
Isotope Separation and Purification	
Carbon Isotope Separation	10
Neon	11
Xenon	12
Thermal Diffusion Research	14
Helium Research	23

1

2

3

4

5

SUMMARY

RADIOELEMENTS

Half-Life Determination by Decaying Pairs The determination of the half-life of polonium-210 by alpha-counting has again been discontinued because of instrument malfunction. After 140 days and 36 observations, the half-life of polonium-210 was found to be 138.48 ± 0.16 days by the method of decaying pairs, 139.20 ± 0.34 days by the variational method, and 139.19 ± 0.42 days by the general method. The advantage of the decaying pair method in accuracy and precision is clearly evident after only one half-life period. A new series of measurements is being started in an effort to determine the limits of precision and the optimum conditions for half-life determination by the three methods of computation.

Hydrolysis of Plutonyl Ions Solid plutonium(VI) nitrate, which has been prepared successfully in small amounts, was prepared on a larger scale to improve the yield and to obtain single crystals of the product for single-crystal x-ray investigations. Samples of the product obtained from 10 g of plutonium-239 metal were used to obtain powder pictures whose patterns appear to be isostructural with powder patterns of uranyl nitrate hexahydrate.

ISOTOPE SEPARATION AND PURIFICATION

Carbon Isotope Separation

Chemical Exchange Two reactions were performed with monoethanolamine in isopropanol. A maximum separation factor of 3.49 was obtained. A similar reaction run using a mixed solvent of equal parts of isopropanol and methanol produced a maximum separation factor of 2.48.

Neon Static tests run on the three-column neon tube bundle showed a maximum separation factor of 160 at a pressure of 1000 torr for one 12-ft column.

Xenon

Thermal Diffusion The xenon six-stage tube bundle cascade has enriched xenon-124 to 2.8% and xenon-126 to 1.1%. The equilibrium time was calculated for an eight-stage system.

Thermal Diffusion Research

Transport Coefficients Flow experiments for $\text{Ne}^{20}\text{-Ne}^{22}$ separation in the 6-ft (183-cm) experimental column are being repeated to eliminate the possible influence of end effects. Static separation data taken in preparation for the flow experiments agree with data taken previously.

Flow separation data for $\text{He}^3\text{-He}^4$ in one of the 12-ft (366-cm) experimental columns were analyzed and transport coefficients were obtained. The initial transport coefficient H' agreed with theory; however, re-mixing coefficients showed large deviations.

Transport Properties Thermal diffusion ratios for various $\text{He}^3\text{-He}^4$ mixtures were calculated using four different approximations. The potential parameter α in the Modified Buckingham Potential was also

varied to test the sensitivity of $[k_T]_m$ to the repulsive portion of the potential. The results indicate that Trennschaukel experiments should easily be accurate enough to yield information about the intermolecular potential. Furthermore, it will probably be necessary to use higher approximations for $[k_T]_m$ when accurate experimental data are available for comparison.

There is some indication that the intermolecular forces, or more specifically, the interatomic forces, for helium-4 are different from those for helium-3 or that there are rather large errors in the theoretical calculations of the transport properties of helium-3. In an effort to obtain more information concerning the interatomic forces, the spectroscopic data for the He_2 molecule were examined. Using the standard formulae for the relations between the molecular constants for isotopic molecules, the spectra of He_2^3 and He_2^4 give no indication of a difference in the interatomic forces.

Helium Research

Vapor Pressure Thermometry Thermomolecular pressure corrections are necessary for precise vapor pressure thermometry. In the investigation of these corrections both experimentally and theoretically it has become clear that the correction depends on the material of the tube surface. In previous reports an equation similar to the Weber-Schmidt expression for thermomolecular pressure has been developed. In this development, one of the parameters that appears is the fraction f of molecules which give up all their tangential momentum in collisions with the tube wall. It will be shown that a variation of this parameter can account for the difference between measurements on stainless steel tubes and the thermomolecular pressure given by the Weber-Schmidt equation.

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.

HALF-LIFE DETERMINATION BY DECAYING PAIRS

The determination of the half-life of polonium-210 by alpha-counting¹ has again been discontinued because of instrument malfunction. It was found necessary to replace a critical vacuum tube in the proportional counter, and this replacement resulted in a substantial change in the resolution time of the instrument.

However, counting appears to have progressed normally enough during the first 140 days to permit a comparison between the decaying pair method¹ on the one hand (Table 1) and the variational and general methods² on the other (Table 2). In addition, the resolution time of the counter was determined for each sample by the known half-life method,³ based on the calorimetric value of 138.3763 ± 0.0017 days for the half-life of polonium-210⁴ (Table 3).

A comparison of Tables 1 and 2 illustrates the advantage of the decaying pair method of half-life determination over the variational and general methods. Both the probable error and the absolute error are significantly improved when the uncertainty in the resolution time is eliminated by treating the samples in pairs.

Similarly, when the half-life can be treated as exact, the determination of the resolution time is greatly facilitated and its probable error is reduced (Table 3). However, polonium-210 is unique in having a half-life which is known with such accuracy and precision; the half-lives of most radioisotopes suitable for use in the known half-life method usually have uncertainties several orders of magnitude higher.

Table 1
HALF-LIFE OF POLONIUM-210 BY DECAYING PAIRS^a

Pair	Ratio	Half-Life (days)	Probable Error (days)	Absolute Error ^b (days)
1-2	0.72	138.94	± 0.14	+0.57
1-3	0.62	138.43	+0.15	+0.05
1-4	0.39	138.38	± 0.14	0.00
2-3	0.86	137.00	± 0.48	-1.38
2-4	0.54	137.88	± 0.27	-0.50
3-4	0.63	138.22	± 0.49	-0.15
Weighted Average		138.48	+0.16	+0.11

^a36 observations over 140 days

^bAssuming the true half-life is 138.3763 ± 0.0017 days⁴

¹MLM-1254, p. 7

²H. W. Kirby and J. Z. Braun, MLM-1263 (January 28, 1966).

³H. W. Kirby and J. Z. Braun, MLM-1202 (November 27, 1964).

⁴MLM-1209, p. 12.

Table 2

HALF-LIFE OF POLONIUM-210 BY THE VARIATIONAL AND GENERAL METHODS^a

Sample	Variational Method Half-Life (days)	General Method Half-Life (days)
1	139.42 ± 0.57	139.44 ± 0.59
2	138.81 ± 0.72	138.81 ± 0.74
3	138.32 ± 1.10	138.30 ± 1.12
4	143.59 ± 2.35	143.98 ± 2.65
Weighted Average	139.20 ± 0.34	139.19 ± 0.42

^a36 observations over 140 days

Table 3

**RESOLUTION TIME OF A PROPORTIONAL COUNTER BY THE
VARIATIONAL, GENERAL, AND KNOWN HALF-LIFE METHODS**

Sample	Variational Method Resolution Time (min x 10 ⁷)	General Method Resolution Time (min x 10 ⁷)	Known Half-Life Method ^a Resolution Time (min x 10 ⁷)
1	1.06 ± 0.13	1.08 ± 0.14	1.33 ± 0.01
2	1.18 ± 0.12	1.22 ± 0.12	1.29 ± 0.01
3	1.29 ± 0.16	1.34 ± 0.16	1.33 ± 0.01
4	0.80 ± 0.21	0.82 ± 0.24	1.33 ± 0.02
Weighted Average	1.12 ± 0.07	1.16 ± 0.08	1.31 ± 0.03

^aAssuming the true half-life is exactly 138.3763 days⁴

A new series of measurements will be started in the near future in an effort to determine the limits of precision and the optimum conditions for half-life determination by the three methods of computation.

HYDROLYSIS OF PLUTONYL IONS

Solid plutonium(VI) nitrate has been prepared successfully. However, only 1.3 g of product (approximately 39% yield) was obtained. The product was a brown powder which readily dissolved in nitric acid. The preparation was repeated on a larger scale to improve the yield and to try to obtain single crystals of the product for single-crystal x-ray investigations.

In this procedure, 10 g of plutonium-239 metal was dissolved in 6N HCl. After dissolution of the metal, the HCl solution was evaporated. However, in contrast to the method used in the previous preparation, the

solution was not evaporated to dryness. Before the solution had completely evaporated, 1N HNO₃ was added to bring the volume to approximately 75 cc. This evaporation and addition step was performed three times, until no chloride was present in the resulting solution. A 15% excess of silver(II) oxide, based on the equivalents of plutonium(IV) in solution, was added to the solution in four equal portions. This reagent quantitatively oxidized the plutonium(IV) to plutonium(VI), as determined by spectrophotometric techniques. The excess silver was then precipitated with 6N HCl; the precipitate was allowed to digest overnight, and the solution was then filtered.

The anion exchange step, which had been previously used to remove chloride, was eliminated. The solution, after filtering, was placed in an evacuated desiccator which contained KOH and P₂O₅ and was slowly evaporated. The complete evaporation took four days. After the third day, large single crystals of plutonyl nitrate were seen on the bottom of the beaker. After the solution had completely evaporated, the product was washed with chloroform.

It has been reported⁵ that plutonyl nitrate hexahydrate is insoluble in chloroform. However, when the chloroform solution used to wash the solid product was allowed to evaporate, single crystals were again found.

The solid product obtained has been divided into three samples. These are: (1) the large crystals grown from the original solution, (2) the crystallites left on the sides of the beaker, formed as the volume of solution decreased, and (3) the crystals grown from the chloroform solution. These samples are being subjected to chemical and x-ray analysis.

As of this date, no chemical analysis results have been obtained. However, x-ray powder pictures have been taken of samples 1 and 2. The powder picture of sample 2 compared very favorably with a powder picture taken of uranyl nitrate hexahydrate. The two patterns appear isostructural. If this observation proves to be correct, the complete structural determination of plutonyl nitrate hexahydrate will be greatly simplified.

⁵M. Y. Krevinskaya, V. D. Nikol'skii, B. G. Pozharskii and Y. Y. Zastenker, *Radiokhimiya*, 1, No. 5, 562-6 (1959).

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 Several experiments involving changes in concentration and solvents in monoethanolamine solutions were performed in the chemical exchange system for the study of carbon-13 separation. Two reactions were performed using a monoethanolamine solution in isopropanol. The first run was made using a 0.9M solution and no major precipitation problems occurred in the reactor. The maximum separation factor obtained in this run was 3.48, but the plot of the separation factor as a function of time indicated that the results were erratic.

In the second reaction run, a solution of 0.93M monoethanolamine in isopropanol was used. Again, precipitation was not observed in the reactor. The maximum separation factor achieved was 3.49, but the data were erratic. The two curves are shown in Figure 1 for comparison.

Figure 1. Separation Factor as a Function of Time for Monoethanolamine in Isopropanol.

One further experiment was performed. A 1M solution of monoethanolamine was prepared using a mixed solvent of isopropanol and methanol in equal portions. The purpose of this experiment was to determine the effect of changing the solvent character on separation without greatly changing the decomposition temperature. The results showed a maximum separation factor of 2.89. Figure 2 illustrates the inconsistency of the results.

Figure 2 Separation Factor as a Function of Time for Monoethanolamine in Isopropanol-Methanol Mixture

An analysis of an amine from a previous reaction run in which a maximum separation factor of 3.00 was obtained showed that the decomposition of the carbamate is still far from complete. It must be remembered, however, that the amine sample was taken from the system at the completion of the reaction, and the analysis can be compared only with the separation factor of 2.48 obtained at that same time. The problems with inconsistent results may be caused by inconsistent decomposition in the boiler. To determine the effect of changing the solvent character on the separation factor, a sample of the amine will be analyzed each time a sample of carbon dioxide is withdrawn.

NEON

A preliminary test with the new 36-ft, three-column neon tube bundle cascade was completed. The test consisted of a static experiment to obtain data for a plot of the logarithm of the static separation factor q_s as a function of pressure. The data for seven operating pressures are shown in Figure 3 (L is the length of the column). The pressure at which maximum static separation will occur was found to be 1000 torr.

Figure 3. Separation as a Function of Pressure for Column 2 of the 36-ft Tube Bundle.

Using the 2500 ml of neon-21 enriched to 10% accumulated from the 96-ft cascade as initial feed material, the tube bundle was put in operation. At an operating heater temperature of 750°K, a pressure of 817 torr was reached. After the system equilibrated for three days, the concentrations shown in Figure 4 were obtained. At a pressure of 817 torr, the column is operating at 37% of its separating capacity; accordingly, a higher neon-21 concentration than 22.4% is expected when the maximum separation pressure of 1000 torr is reached. At the present draw-off rate of 10% neon-21 from the 96-ft cascade, three weeks are needed to accumulate enough gas to fill the bundle to 1000 torr. The bundle will then be operated at this pressure. Highly enriched neon-20 and neon-22 will be removed from the ends of the bundle at small rates and the column will be replenished with more gas containing 10% neon-21, keeping the system pressure at 1000 torr. Continual operation of the bundle in this manner will yield highly enriched neon-21 at the middle of the system.

XENON

Thermal Diffusion Using fission product xenon as feed in an eight-column, eight-stage, hot-wire thermal diffusion cascade with a modified Trennschaukel gas circulating system for interstage transport, xenon-136 was enriched to 70%. A sufficient amount of gas of this concentration was accumulated for use as intermediate feed for a second pass. This second pass is expected to enrich the xenon-136 above 90%.

Natural xenon is being used as feed in a 24-column, six-stage thermal diffusion concentric tube cascade to enrich the light mass fraction. Table 4 shows the isotopic comparison of the product with the feed.

With a Veeco leak in the product line the draw-off rate was set at 5 ml/hr, the calculated value for 2.5% xenon-124 product draw-off. Sample analyses showed the results as presented in Table 5.

Figure 4. Concentrations in the Cascade after 3 Days of Static Operation at a Pressure of 817 torr.

Table 4

COMPARISON OF ENRICHED LIGHT XENON FRACTION
WITH NATURAL XENON

Xenon Isotope	Natural Xenon (mole %)	Enriched Xenon-124 (mole %)
124	0.096	2.83
126	0.090	1.11
128	1.92	8.21
129	26.44	62.07
130	4.08	4.91
131	21.18	12.56
132	26.89	7.60
134	10.44	0.61
136	8.87	0.11

The product draw-off rate was reduced to 4 ml/hr as a precaution.

Figure 5 shows the feed changes, draw-offs and increase in xenon-124 concentration for the last continuous run.

Table 5

CHANGES IN COMPOSITION DURING DRAW-OFF

Isotope	Concentration (mole %)	
	At Start of Draw-off	28 Hours after Draw-off Was Started
Xenon-124	2.75	2.58
Xenon-126	1.08	1.04

Figure 5. Xenon Tube Bundle Cascade Product Concentration During Draw-off.

Calculations were made for the tube bundle cascade with stage 5 split into single-column stages. The cascade configuration would then be 6-5-5-4-1-1-1-1. With this eight-stage configuration the equilibrium time to obtain 10% xenon-124 would be approximately 40 days. With the six-stage system equilibrium time for 10% xenon-124 would be about 60 days. The draw-off rate for the eight-stage system was calculated to be approximately 28 ml/day to obtain 10% xenon-124.

THERMAL DIFFUSION RESEARCH

Transport Coefficients The recent discovery of a diffusion barrier in the top of column E1⁶ (see Table I of MLM-1299) has prompted a reassessment of experimental flow data for Ne²⁰-Ne²² separation taken

⁶MLM-1299, p. 30.

previously for column E5.⁷ It appears quite likely that a similar, but smaller, barrier is present in this column; therefore, a new series of flow experiments is being run.

Before the flow experiments were started, the measurements of the static separation as a function of pressure were repeated to assure that the recent installation of a new wire had not materially altered the behavior of the column. The results of the static measurements are shown in Figure 6, along with the results of two previous runs in September 1964 and July 1965, each with a different wire. The two theoretical curves are calculated for a wire temperature of 820°C from the Jones and Furry⁸ theory with Lennard-Jones shape factors. The thermal diffusion factor of 0.0227 was interpolated from Watson's data⁹ and the 0.0240 figure is taken from recent measurements with column E1.¹⁰

Figure 6. Static Separation Factor as a Function of Pressure for $\text{Ne}^{20}\text{-Ne}^{22}$ in Column E5.

⁷MLM-1238, p. 29.

⁸R. C. Jones and W. H. Furry, *Revs. Modern Phys.*, 18, 151 (1946).

⁹W. W. Watson, et al., *Z. Naturforsch.*, 18a, 242 (1963).

¹⁰MLM-1300, p. 19.

For the flow experiments the column is being operated in a way similar to that reported for column E1 last month (i.e., the full length of the column is not used). The experiments are being done on a 152-cm section of the 183-cm column.

The transport coefficient H' for $\text{He}^3\text{-He}^4$ separation in column E4 was measured using flow data at a pressure of 1100 torr. Dimensions and temperatures for column E4 are given in Table 6. The apparatus used is shown in Figure 7. Gas was circulated through the bottom of the column at 10 liters/min and a measured flow rate was maintained from the column 4 ft above this point. The flow rate was determined by measuring the rate of pressure increase in a calibrated vessel. A constant pressure of 1100 ± 2 torr was maintained in the column using an absolute pressure regulator. The column was operated for 48 hr at constant pressure and flow rate. Samples were then taken at sample ports A and C at the bottom of the column. Port C was used instead of port D to eliminate end effects caused by the 10 liter/min feed circulation loop at the bottom of the column. The helium-3 concentration varied along the length of the 12-ft column, causing variation in the values of the column transport coefficients. A 3-ft column was used to assure, for practical purposes, a constant helium-3 concentration along the length of column. The average concentration of helium-3 in the 3-ft section was 3%. It was thus possible to obtain an accurate value of H' for 3% $\text{He}^3\text{-He}^4$ separation. Samples were taken for various flow rates, and the data are plotted in Figure 8 as the natural log of the separation factor as a function of flow. From these data H' was calculated and the results are given in Table 7. 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 earlier in static experiments.¹¹

Table 6

**DIMENSIONS AND OPERATING CONDITIONS
OF EXPERIMENTAL THERMAL DIFFUSION COLUMNS**

Column	Length (cm)	Cold Wall Radius (cm)	Hot Wall Radius (cm)	Cold Wall Temp. (°C)	Hot Wall Temp. (°C)	Gas
E 4	366	2.05	0.0794	15	800	$\text{He}^3\text{-He}^4$
E 5	183	0.943	0.0804	15	820	$\text{Ne}^{20}\text{-Ne}^{22}$

Table 7

**THERMAL DIFFUSION COLUMN TRANSPORT COEFFICIENTS FOR SEPARATION
OF 3% $\text{He}^3\text{-He}^4$ AT 800°C AND 1100 TORR PRESSURE**

Parameter	Measured	Predicted
$H' (\text{g sec}^{-1} \text{ atm}^{-2})$	1.77×10^{-4}	1.78×10^{-4}
$K_c' (\text{g-cm sec}^{-1} \text{ atm}^{-4})$	6.19×10^{-3}	7.69×10^{-3}
$K_d (\text{g-cm sec}^{-1})$	5.88×10^{-3}	4.52×10^{-3}

¹¹MLM-1227, p. 23.

Figure 7. Schematic Diagram of the Apparatus Used to Measure H' for a 3% $\text{He}^3\text{-He}^4$ Separation.

Figure 8. Separation as a Function of Flow Rate for the $\text{He}^3\text{-He}^4$ Separation in the 3-ft Section of Column E4.

The theoretical values of the coefficients given in Table 7 were calculated from Lennard-Jones shape factors. A value of 0.0618 was assumed for the thermal diffusion factor at 288°K and a helium-3 concentration of 3%.

The experimental value of H' agrees well with the theoretical one; however, both experimental remixing coefficients deviate from theory. The directions and magnitudes of the deviations suggest that the diffusion coefficient used in the theoretical calculation may be incorrect, or that the temperature dependence of the diffusion coefficient for He³-He⁴ may not be adequately represented by the Lennard-Jones model in the high-temperature region.

Transport Properties Thermal diffusion ratios for binary isotopic and unlike gas mixtures are presently being measured in a 20-tube Trennschaukel. Experimental uncertainties in this work are expected to be reduced to less than 5%. If this can be accomplished, then the experimental thermal diffusion measurements can be used as a sensitive test of the intermolecular potential function.

The general expression for the thermal diffusion ratio is quite complicated. It is both concentration- and temperature-dependent, the latter arising from the temperature dependence of the collision integrals. The m th approximation of the thermal diffusion ratio for a binary mixture, which is most conveniently written in the determinant notation of Chapman and Cowling,¹² is

$$[k_T]_m = \frac{5}{2} \frac{x_1 D_{01}^{(m)} \left(\frac{M_1 + M_2}{2M_1} \right)^{1/2} + x_2 D_{0-1}^{(m)} \left(\frac{M_1 + M_2}{2M_2} \right)^{1/2}}{D_{00}^{(m)}} \quad (1)$$

where x_1 and x_2 are the mole fractions of the two components of masses M_1 and M_2 . The $D^{(m)}$ are determinants whose elements are functions of the collision integrals and molecular weights. Expressions for these elements up to and including $m = 3$ have been derived by Mason and are presented elsewhere.^{13, 14} In this work Mason has also shown that Equation 1 can be simplified if one has a binary system of heavy isotopes. In this case one has

$$[k_T]_{m \text{ (heavy)}} = [k_T^*]_m \left(\frac{M_1 - M_2}{M_1 + M_2} \right) x_1 x_2 \quad (2)$$

where $[k_T^*]_m$ is a reduced thermal diffusion ratio dependent only upon the reduced temperature T^* .

In order to test the accuracy of the various approximations, $[k_T]_m$ and $[k_T]_{m \text{ (heavy)}}$ were calculated for $m = 1, 2$ for He³-He⁴ mixtures of different compositions. In addition, it was desired to test the sensitivity of this calculation to the intermolecular potential so the entire set of calculations was carried out for two values of the parameter, α , which appears in the Modified Buckingham Potential. The results are shown in Figures 9-14.

¹²S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases*, London, Cambridge University Press, 1952.

¹³E. A. Mason, *J. Chem. Phys.*, 22, 169-186 (1954).

¹⁴E. A. Mason, *J. Chem. Phys.*, 27, 75-84 (1957).

Figure 9. Thermal Diffusion Ratios for 0.00001 He^3 -0.99999 He^4 .

Figure 10. Thermal Diffusion Ratios for 0.05 He^3 -0.95 He^4 .

Figure 11. Thermal Diffusion Ratios for 0.1 He^3 -0.9 He^4 .

Figure 12. Thermal Diffusion Ratios for 0.163 He^3 -0.837 He^4 .

Figure 13. Thermal Diffusion Ratios for 0.5 He³-0.5 He⁴.

Figure 14. Thermal Diffusion Ratios for 0.99999 He³-0.00001 He⁴.

It is immediately apparent that the calculation is very sensitive to the potential parameters (i.e., less than 10% change in a gives rise to greater than 10% variation in $[k_T]_m$ in all cases). In addition, if $[k_T]_2$ is assumed to represent the correct value, both the complete first approximation and the heavy isotope second approximation differ from this as much as 5% in some cases. The agreement between $[k_T]_1$ (heavy) and $[k_T]_2$ is most likely coincidental.

One may conclude, therefore, that the "correctness" of the repulsive part of the intermolecular potential may be determined to very roughly the same degree as the experimental uncertainty in the Trennschaukel measurements. In addition, as the experimental results become more reliable one must examine more closely whether a given approximation is adequate for comparison with experiment. In view of the large discrepancy among the various approximations, the rate of convergence is not at all obvious and calculation of the third approximation will be necessary.

There is some indication that the intermolecular forces, or more specifically the interatomic forces, for helium-4 are different from those for helium-3 or that there are rather large errors in the theoretical calculations of the transport properties of helium-3.¹⁵ In an effort to obtain more information concerning the interatomic forces, the spectroscopic data for the He₂ molecule were examined.^{16,17} Using the standard formulae for the relations between the molecular constants for isotopic molecules, the spectra of He₂³ and He₂⁴ give no indication of a difference in the interatomic forces.

The formulae referred to above were derived by Dunham¹⁸ and are presented by Herzberg.¹⁹ These formulae, which relate the molecular constants of one molecule to those of an isotopically substituted molecule, are:

$$\omega_e^t = \rho \omega_e \quad (3)$$

$$\omega_e x_e^t = \rho^2 \omega_e x_e \quad (4)$$

$$\beta_e^t = \rho^2 \beta_e \quad (5)$$

$$\alpha_e^t = \rho^3 \alpha_e \quad (6)$$

where ω_e and $\omega_e x_e$ are the vibrational constants, β_e and α_e are the rotational constants, and ρ is the square root of the ratio of the reduced masses.

The above expressions were used to calculate the molecular constants of the $a^3\Sigma^+ \mu$ state of He₂³ from experimental molecular constants of He₂⁴ for the same state. This is the lowest-lying stable electronic state for He₂ and there are suitable data available.^{16,17}

¹⁵S. Weissman, *Bull. Am. Phys. Soc.*, **10**, 735 (1965).

¹⁶M. S. Ginter, *J. Chem. Phys.*, **42**, 561 (1965).

¹⁷G. H. Dieke and E. S. Robinson, *Phys. Rev.*, **80**, 1-5 (1950).

¹⁸J. S. Dunham, *Phys. Rev.*, **41**, 721 (1932).

¹⁹G. Herzberg, *Spectra of Diatomic Molecules*, 2nd ed., New York, D. Van Nostrand Company, Inc., 1950, p. 145.

Table 8 gives the observed and calculated values of the molecular constants for this state. The agreement between the two sets of values is a strong indication that the potential energy curves for the two molecules are the same

Table 8
MOLECULAR CONSTANTS FOR $a^3\Sigma^+ \mu \text{He}_2^3$

Constant	Observed (cm ⁻¹)	From He ₂ ⁴ (cm ⁻¹)	Difference (%)
ω_e	2085.65	2085.02	0.03
$\omega_e x_e$	51.61	51.83	0.4
β_e	10.222	10.232	0.1
α_e	0.3727	0.3465	7.6

The fact that the spectroscopic data on the $a^3\Sigma^+ \mu$ state of He₂ are consistent for both isotopes does not prove unequivocally that forces are also identical when two ground state atoms approach each other. This molecular state corresponds to one helium in the 1s² ¹S ground state and one atom in the 1s2s ³S excited state. However, the indication is now that the theoretical calculations of the transport properties of helium-3 need to be reexamined.

HELIUM RESEARCH

Vapor Pressure Thermometry Thermomolecular pressure corrections are necessary for precise vapor pressure thermometry. In the experimental and theoretical investigation of these corrections, it has become clear that the effect depends on the material of a tube surface. In a previous report²⁰ an equation similar to the Weber-Schmidt expression for thermomolecular pressure has been developed. In this development, one of the parameters that appears is the fraction, f , of molecules which give up all their tangential momentum in collisions with the tube wall. It will be shown that a variation of this parameter can account for the difference between measurements using stainless steel tubes and the thermomolecular pressure given by the Weber-Schmidt equation.

Recalling the form of the equations from Reference 20, the differential pressure change as a function of temperature and mean free path is given by²¹

$$\frac{dP}{dT} - \frac{1}{2} \frac{P}{T} \left\{ \frac{\pi}{24} \frac{\gamma}{K} \frac{1}{1 + \frac{\gamma\beta}{K}} \frac{a^2}{\lambda^2} \left[1 + 4K \left(\frac{1 + 2\frac{\gamma\beta}{K}}{1 + \frac{\gamma\beta}{K}} \right) \frac{\lambda}{a} \right] + \frac{\left[\frac{1}{4K} \left[1 + \frac{\frac{2\pi}{3} K \gamma \left(\frac{\gamma\beta}{K} \right)^2 \right]}{\left(1 + \frac{\gamma\beta}{K} \right)^2} \right] \frac{a}{\lambda}}{1 + \frac{1}{4K} \left(1 + \frac{\gamma\beta}{K} \right) \frac{a}{\lambda}} \right\}^{-1} \quad (7)$$

²⁰MLM-1287 p. 24

²¹Equations 7 and 9 above as given in MLM-1287 are incorrect, the correct forms are given here

where now in terms of K , γ , and β , the Weber-Schmidt constants are:²¹

$$K_1 = \beta + \frac{K}{\gamma} \quad (8)$$

$$g = \frac{1}{4K} \left[1 + \frac{\frac{2\pi}{3} K \gamma \left(\frac{\gamma\beta}{K} \right)^2}{\left(1 + \frac{\gamma\beta}{K} \right)^2} \right] \quad (9)$$

$$K_2 = K \left(\frac{1 + 2\gamma\beta/K}{1 + \gamma\beta/K} \right) \quad (10)$$

$$h = \frac{1}{4K} \left(1 + \frac{\gamma\beta}{K} \right) \quad (11)$$

It is helpful here to review the physical significance of K , γ and β . $K = (2-f)/f$ is a measure of the fraction of molecules reflected diffusely from the tube wall. The term $\gamma = 9a/4\beta_f^2$ is a measure of the deviation from the Maxwellian distribution of the molecules making their last collision with the wall. There is also a geometry factor α in γ . $\beta = \beta_f\beta_v$ is a measure of the deviation from the Maxwellian distribution of the molecules making their last collision in the gas.

Equation 7 has been solved to obtain the pressure difference between two fixed temperatures for many different values of K , γ and β . A preliminary comparison with the experimental results has been made. Figure 15 shows the measured thermomolecular pressure difference in two stainless steel tubes (data points). The curve shows the result for the same radii tubes calculated from the original Weber-Schmidt equation. There is clear disagreement. Figure 16 shows the same data with two superimposed curves. These curves were calculated from Equation 7 with the same values of γ and β but different values of K . Curve (1) which fits the Mound data is for $K = 1.0$, $\gamma = 2.4$ and $\beta = 1.6$. The particular values of γ and β reflect the fact that the velocity distribution function of the gas is not Maxwellian. The determination of theoretical values for γ and β is a problem of much greater difficulty than the one treated here. It is clear that they may be functions of K . Here γ and β are assumed to be independent of K .

Turning to the effect of varying K in Figure 16, it is seen that the data and the Weber-Schmidt curve are fit reasonably well with just a variation of K . A value of $K = 1$ means $f = 1$ and $K = 1.25$ means $f = 0.9$, where f is the fraction of molecules that give up all their tangential momentum in collisions with the wall. At this point it is of interest to note two facts: (1) the Weber-Schmidt data were taken on glass tubes, and (2) independent measurements of f for several gases on different surfaces have been made by Millikan.²² He finds $f = 1.0$ for air or carbon dioxide on polished metal surfaces and $f = 0.89$ for air on glass. The variation in f to fit the thermomolecular pressure data is of the same order and sense.

²²R. A. Millikan, *Phys. Rev.*, 21, 217 (1923).

Figure 15. Measured Thermomolecular Pressure Difference in Two Stainless Steel Tubes.

Figure 16. Curves Using the Same Data as in Figure 15 but Different Values of K .

In view of these results an apparatus with Pyrex tubes has been built for thermomolecular pressure measurements. The configuration is slightly different from the stainless tube apparatus. The large-diameter glass tube is 2 in. in diameter rather than 0.25 in. as for the stainless steel tube. Thus, what is measured over a large pressure range is ΔP rather than $\Delta\Delta P = \Delta P_1 - \Delta P_2$. Preliminary measurements with the glass tubes are shown in Figure 17. The data in this figure lie below the Weber-Schmidt curve. The solid curve is ΔP for the small tube. The dashed line represents the effect of the 2-in. tube. Preliminary calculations indicate that a value of $f \approx 0.85$ fits these data.

Figure 17. Preliminary Measurements with Glass Tubes.