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SUMMARY

RADIOELEMENTS

Polonium-208/Polonium-209 X-ray diffraction patterns of an eight-month old sample of an isotopic mixture of polonium-208/polonium-209 were identical to the alpha phase of polonium-210 metal. Apparently, the face-centered cubic PbPo which grows acts as a seed for the growth of the alpha phase.

ISOTOPE SEPARATION AND PURIFICATION

Carbon Isotope Separation

Thermal Diffusion Material of molecular mass 18 has steadily accumulated in the 12-column, 8-stage methane thermal diffusion system. Infrared analysis showed conclusively that this material was $C^{13}H_3D$. It appears that the $C^{13}H_3D$ forms in the thermal diffusion system by an exchange reaction between $C^{13}H_4$ and $C^{12}H_3D$.

Chemical Exchange Two reaction runs were carried out using a mixed amine solution. The results were inconclusive because the carbamate did not dissociate completely. Two experiments were conducted using N-(3-aminopropyl) cyclohexylamine in methanol. Some isotope separation was observed, but the carbamate crystallized during the runs.

Stable Gaseous Isotopes

Helium A 12-in. cylindrical charcoal trap reduced the tritium level of product helium-3 from $2.5 \times 10^{-9}\%$ to $6.4 \times 10^{-11}\%$.

Neon The new three-column neon tube bundle is being checked in preparation for start-up. It should enrich 10% intermediate neon-21 to above 70%.

Argon The five-stage argon cascade has built up an argon-38 peak of approximately 28%. Draw-off of over 25% is expected to begin when the peak shifts to a gas port.

Krypton The fourth pass for enriching krypton-86 was made. Over 89% krypton-86 was accumulated. Additional processing to reach 95% is planned.

Xenon Thermal Diffusion: The new 24-column six-stage thermal diffusion cascade system constructed in two tube bundles (water jackets) was started using natural xenon as feed. A calcium trap is being installed to remove hydrogen accumulation. To date xenon-124 has been enriched above 0.6% from the natural abundance of 0.096%.

Chromatography: The heats of adsorption of krypton and xenon on Linde Molecular Sieve 5A, 50/60 mesh have been calculated to be -1208 and -1901 cal/mole, respectively, based on separations using nitrogen as the carrier gas. Preliminary measurements on molecular Sieve 13X, 50/60 mesh, indicate the heat of adsorption to be about -1240 and -1969 cal/mole for krypton and xenon, respectively, using nitrogen for the carrier gas. Calculations of nitrogen adsorption on Molecular Sieve 5A at the temperatures used indicate that the measured quantities may more nearly be heats of solution of krypton and xenon in nitrogen rather than heats of adsorption on the Zeolite.

Thermal Diffusion Research

Transport Coefficients Discrepancies between theory and experiment for recent thermal diffusion column experiments with neon can be explained by a stagnant gas barrier in the column. Experiments are in progress to test this hypothesis.

Collision Integrals The accuracy of the collision integrals has been investigated. The purpose of this investigation was to design a computer program to calculate collision integrals accurate to one part in 1000. The accuracy to which the angles of deflection and the cross sections must be calculated in order to obtain this accuracy in the collision integrals was determined. The number of points in the integrations necessary to obtain the required accuracy in the angles of deflection was then determined. Also, the accuracy of the interpolation method used to obtain intermediate values of the cross sections was studied.

Molecular Beam Scattering A narrow band velocity selector has been proposed for use in obtaining a monoenergetic beam of particles in the molecular beam scattering system. Design and construction of the selector are being studied. Theoretical performance figures were compared to previously used selectors described in the literature.

Helium Research

Low Temperature Distillation The possibility of maintaining a relatively constant level of liquid helium in a pumped bath for use in the distillation separation of helium-3 and helium-4 has been investigated. It has been found that a valve inside the cryostat at the end of the transfer tube may be used to control the flow of liquid helium to the bath. To avoid large losses of helium from the bath, it is necessary for the stream of incoming gas or liquid to be directed away from the surface of the bath. It appears that an intermediate dewar between the standard storage dewar and the cryostat will be necessary to provide a continuous supply of helium to such a system.

Vapor Pressure Thermometry Further consideration of the equations for gas flow in a tube has shown that an equation identical in form to the different Weber-Schmidt equation can be derived. This equation is being developed to provide the proper thermomolecular pressure corrections to be used in helium-3 and helium-4 vapor pressure thermometry. Four physical constants appear in the equation: (1) the fraction of molecules being diffusely reflected from the tube wall, (2) a geometrical factor containing the ratio of the tube area to volume, (3) deviation from maxwellian velocity distribution of molecules making collisions with the tube wall, (4) deviation from maxwellian velocity of molecules making collisions in the gas. These four factors are being varied to determine the reason for differences in the measured thermomolecular pressure by different investigators.

In addition, a simplified differential Weber-Schmidt equation which applied only to the high pressure region was investigated. It was observed that the power index used by Weber-Schmidt to calculate the viscosity did not adequately represent viscosity data presently available. Two previously reported equations were

investigated by computer calculations and compared to the Weber-Schmidt equation and Mound experimental data. The first equation used experimental viscosities and did not consider the term containing the slip coefficient. The second equation used a rigid sphere model containing the slip coefficient. A comparison of calculation with the Weber-Schmidt equation and Mound experimental data demonstrated better agreement with the latter.

ANALYTICAL AND INSTRUMENTATION

Emission Spectroscopic Analysis

Beryllium in Air A direct reader procedure was developed for the determination of beryllium in air. It was possible to determine 1 μg beryllium with an average deviation of $\pm 0.1 \mu\text{g}$.

Impurities in Gold A direct reader procedure was developed which could detect impurities in gold at levels below 6×10^{-5} mg.

ORGANIC RESEARCH

Adhesive Shrinkage Studies The total shrinkage of Eastman 910 adhesive (methyl 2-cyano-acrylate) was determined using thermal, free-radical and anionic polymerization conditions. When polymerization was conducted thermally or by free radical initiators, concurrent anionic polymerization was inhibited by the addition of boron trifluoride 2-acetic acid complex. The total shrinkage of the cured samples, determined from the initial and final densities of the material, was found to be independent of the method of polymerization. Total shrinkage in all cases was about 15.1%.

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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.

POLONIUM-208/POLONIUM-209

X-ray diffraction patterns of the isotopic mixture of polonium 208/209 metal (prepared in December 1964) were identical to the alpha phase (simple cubic) of polonium-210 metal; however, extremely weak lines of beta (rhombohedral) polonium are present. Thermal effects from self-heating of polonium-208 and polonium-209 are only 4% of polonium-210; consequently, the rate of formation of lead is reduced from 0.5% per day to 0.02% per day. Apparently, the face-centered cubic lead polonide (PbPo) which forms acts as a seed for growth of the simple cubic phase. The reappearance of the beta form after cooling may be the result of self-heating of the samples to temperatures above the $\alpha \rightleftharpoons \beta$ transition temperature. The kinetics of this phase transformation as a function of temperature and time are presently being studied.

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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 During most of the past year material of molecular mass 18 has steadily accumulated, as shown in Figure 1, at the product withdrawal point of the 12-column, 8-stage, methane thermal diffusion cascade. Initially this material was thought to be water vapor; however, recent experiments showed conclusively that the mass 18 fraction is $C^{13}H_3D$.¹

The first evidence that the mass 18 was not water was acquired when a Drierite trap, inserted between columns 11 and 12, failed to affect the mass spectrographically determined mass 18 content. Samples were taken of a product bottle containing approximately 1.5 liters of methane of greater than 90% mass 17 enrichment. The product bottle had been removed from the thermal diffusion system just before installation of the Drierite trap. One sample was submitted for mass spectrographic analysis, the other for infrared analysis. The results are given in Table I. The mass spectrographic results are computed on the assumption that the mass 18 fraction is $C^{13}H_3D$. (The mass spectrograph is considerably less sensitive to H_2O than to $C^{13}H_3D$; hence, there is a large difference between mass 18 content calculated as $C^{13}H_3D$ and mass 18 content calculated as H_2O .) It is quite clear from the infrared results that the mass 18 fraction is indeed $C^{13}H_3D$. Moreover, both instruments give essentially the same result for mass 18. A composite isotopic analysis can be constructed from the two sets of results. This is also given in Table I.

Figure 1 Accumulation of material of molecular mass 18 in the methane thermal diffusion cascade.

The $C^{12}H_3D$ in the product material is expected on the basis of the natural abundance of this species in the feed gas, and it was unexpected that samples taken from the system previously showed only traces of $C^{12}H_3D$. The amount of $C^{13}H_3D$, however, cannot be accounted for in this way because the natural abundance of this species is small. It appears, therefore, that exchange is taking place in the thermal diffusion cascade, and that the exchange results in the transfer of deuterium from $C^{12}H_3D$ to $C^{13}H_3D$. The details of this process are at present unknown.

¹MLM-1254.

Table I

Infrared and Mass Spectrographic Analyses of Methane Product

Mass Spectrographic Analysis	%
Mass 16	6.1
Mass 17	90.5
Mass 18	1.1
Mass 28 (nitrogen)	2.3
<i>Infrared Analysis</i>	
C ¹² H ₃ D	0.9
C ¹³ H ₃ D	0.9
<i>Composite Analysis</i>	
C ¹² H ₄	6.1
C ¹² H ₃ D	0.9
C ¹³ H ₄	89.6
C ¹³ H ₃ D	1.1
N ₂	2.3

Chemical Exchange The apparatus for the carbon dioxide-carbamate chemical exchange system was modified to include a new boiler-decomposer so that the decomposition efficiency would be maintained at high amine solution flow rates. The new boiler incorporates a longer decomposer section which allows for more complete dissociation of the carbamate.

Two reaction runs were performed in the modified apparatus using a mixed amine solution. The solution was two molar in monoethanolamine and 0.1 molar in diethanolamine with methanol as the solvent. The results were compared with runs carried out under similar conditions using the monoethanolamine alone. There was evidence of incomplete carbamate dissociation in the mixed amine runs; therefore, further investigation is necessary before any definite conclusion can be reached regarding the effectiveness of mixed amines.

Another type of experiment was also initiated in the modified apparatus. A two molar solution of N-(3-aminopropyl) cyclohexylamine in methanol was prepared and used as the exchanger in two separate runs. The first reaction run resulted in the crystallization

of the carbamate in the column; therefore, no isotope separation was observed. The second run was performed at a one molar concentration in methanol. Again some carbamate crystallized. Some isotopic separation was observed, however. It was concluded, therefore, that either a different solvent was required or that lower concentrations are necessary for the successful investigation of this amine.

STABLE GASEOUS ISOTOPES

Helium A short, cylindrical charcoal trap, 1 in. in diameter by 12 in. long, was used to remove trace quantities of tritium from product helium-3. The initial tritium content was $2.5 \times 10^{-9}\%$. After the gas passed through the charcoal trap, which was maintained at liquid nitrogen temperature, the contamination was reduced to $6.4 \times 10^{-11}\%$ tritium.

Neon The piping on the three-column neon tube bundle has been completed. The system has been leak checked and is being pumped down. Shortly, the system will be started up, and experiments will be run to accumulate data to plot separation vs. pressure. In this manner, the proper operating pressure of the new system can be determined, and these data can be compared to similar data calculated theoretically. The three-column tube bundle is expected to enrich neon-21 to 70-80% using 10-11% neon-21 feed from the present four-stage system. Figure 2 shows how the new system will be connected to the existing one. The end streams from the new columns will be recycled periodically to the original cascade.

Argon After 29 days of running time with the five-stage argon cascade, 1100 ml (the contents of an entire column) of argon with an average argon-38 concentration of 17.0% was removed from the system. The argon-38 in this column will be enriched further. The argon-36 product withdrawal rate was 2-2.5 ml/hr, with the concentration gradually dropping to 99.0%. The argon-38 column profile is shown in Figure 3. The peak

Figure 2. Complete neon system including the present four-column system on the left and the new three-column bundle on the right.

Figure 3. Argon-38 concentration as a function of column length in the 7-1-1-1-1 argon cascade.

concentration of 28% was estimated by drawing a profile similar to a profile from previous data. The peak concentration of 28% should have an accuracy of $28 \pm 3\%$. The argon-38 of over 25% concentration will be drawn off after the peak shifts to a location close to a gas port.

Krypton In a two-column, two-stage thermal diffusion cascade, the third pass was completed for enriching krypton-84 and -86. This pass enriched the krypton to 72% krypton-86. The fourth pass was equilibrated and flow started at about 3 ml/hr with the drawoff containing 89% krypton-86. The fourth pass feed was reduced to 63% krypton-86 in withdrawing 100 milliliters of fourth pass product of 88.9% krypton-86. This product also contained 4% xenon. In order to enrich the krypton-86 to 95% instead of 90%, raffinate material is being reprocessed to obtain intermediate feed of 80% krypton-86, which will be used as feed for the final pass. Figure 4 shows the revised calculated final concentrations expected for initial concentrations in the circulating feed reservoir for various flow rates.

Figure 4. Calculated krypton-86 concentrations for various flow rates at $K_c/K_d = 10$; $P = 0.405$ atm.

Xenon

Thermal Diffusion Leak checking of the 24-column, six-stage thermal diffusion cascade, having tube bundle construction with 18 columns in one shell and six columns in the second shell was completed. The columns, see Figure 5, are 12 ft long and have an 0.568-in. (1.44-cm) cold-wall diameter and an 0.315-in. (0.8-cm) hot-wall diameter. The system was filled with natural xenon in preparation for enriching the lightest stable xenon isotope, xenon-124. The operating conditions were set as follows:

Feed pressure $\approx$ 4500 torr

Column pressure $\approx$ 1000 torr (stage 1); 1050 torr (stage 6)

Tubular heater temperature $\approx$ 750°C - 780°C (10 amps)

Interstage flow rate (circulation) $\approx$ 260 ml/min

Figure 5. Top and bottom sections of a xenon tube bundle column (dimensions in inches).

A concentration profile of xenon-124 is being built up in the system prior to drawing off the product. After two weeks, including two interruptions, the xenon-124 has been enriched from 0.096% to 0.67% at the top of the fifth stage. The top of the cascade contained hydrogen. Analysis of gas at the top of each stage is shown in Table 3.

A calcium trap is being installed to remove the hydrogen which is accumulating in the product. Hydrogen has been taken out of the last column twice, only to reappear shortly afterward.

Prior to initial startup, the tube bundle was calibrated to determine the STP liters of gas in each stage at operating conditions (Table 2).

Table 2

Volume of Gas at Each Stage in Tube Bundle

Stage	(liters)	Stage	(liters)
1	4.15	4	3.51
2	3.90	5	3.23
3	3.77	6	0.79

A large interstage circulation rate is being used to achieve adequate mixing at the ends of the column. Figure 5 shows the location of the gas ports on a column. At the top of each column, the hot section of the tubular heater is adjacent to one of the gas ports, and the other port is opposite the tubular heater cold section. The circulation at the top should not be critical. At the bottom, the hot section does not extend below a gas port; thus the circulation will have to rely on ordinary diffusion in order to get the circulating gas up to the hot section of the tubular heater, approximately 3 in. The increased circulating flow rate should help since the larger stream of gas should force mixing in the bottom of the column.

Table 3

Xenon Tube Bundle Analytical Data After 10 Days of Operation

Xenon Isotope	Analysis (%)						
	Feed	Stage 1 Top	Stage 2 Top	Stage 3 Top	Stage 4 Top	Stage 5 Top	Stage 6 (product) Top
Total							
Xenon	99.80	99.51	99.37	99.21	99.16	60.83	0.00
124	0.06 ^a	0.09	0.10	0.11	0.16	0.45	0.00
126	0.07	0.09	0.10	0.10	0.14	0.29	0.00
128	1.75	2.38	2.64	2.47	3.38	4.92	0.00
129	23.71	27.40	29.74	30.09	34.73	45.08	0.00
130	3.87	4.27	4.52	4.53	4.91	5.43	0.00
131	21.22	22.06	22.27	22.32	22.28	20.41	0.00
132	27.57	26.94	26.15	26.11	24.17	18.46	0.00
134	11.42	9.53	8.51	8.49	6.57	3.55	0.00
136	10.33	7.26	5.98	5.78	3.66	1.40	0.00
H ₂	0.00	0.18	0.29	0.53	0.53	38.08	99.83
Other	0.20	0.49	0.34	0.26	0.31	1.10	0.27

^aXenon-124 should have been 0.09%; the lower concentration was a result of poor circulation in the 100-liter feed tank.

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 at further reducing the krypton-85 level while at the same time increasing the product output.

The series of separations using the synthetic Zeolite, Linde Molecular Sieve 5A, 50/60 mesh, with a nitrogen carrier gas was completed.²The retention times of krypton and xenon were measured at 166°, 200°, and 243°K. The calculated heats were -1208 and -1901 cal/mole for krypton and xenon, respectively. When helium was used as the carrier gas, the values obtained were -3091 and -5127 cal/mole. It is estimated that in this temperature range 0.6 of a monolayer or more of nitrogen is adsorbed on the Zeolite. As a result, the measured heats of the krypton and xenon are probably more closely related to the heats of solution

²MLM-1266.

of these gases in nitrogen than to their heats of adsorption. This would account for their values with a nitrogen carrier gas being much lower than those obtained with helium, which is negligibly adsorbed.

Some work has been done with Molecular Sieve 13X, 50/60 mesh, using nitrogen for the carrier gas. The work so far has been done at 166° and 243°K. The preliminary values for the heats calculated from these two temperatures are -1240 and -1969 cal/mole for krypton and xenon, respectively. These values are in close agreement with those found with Molecular Sieve 5A.³ Unlike Molecular Sieve 5A, however, Molecular Sieve 13X exhibited far less tailing. As a result, Molecular Sieve 13X appears to be a promising candidate for use in a large-scale chromatographic column.

THERMAL DIFFUSION RESEARCH

Transport Coefficients Consistently large deviations from theory have been observed in separation experiments involving neon and helium in the four 12-ft, experimental, hot-wire thermal diffusion columns.⁴ The deviations are observed in flow experiments only. Static separation data are in good agreement with theory.

For the flow experiments with neon, gas is circulated at a high rate across the top of the column while gas is withdrawn at a measured slow rate from the bottom of the column. In an effort to find a possible experimental explanation for the deviation from theory, it was postulated that a stagnant diffusion barrier was present at the top of the column as indicated in Figure 6. Calculations were made on the basis of the experimental data from column EI to find, for each experiment, the barrier thickness required to account for the discrepancy between theory and experiment. The results of these calculations are given in Table 4.

Table 4

Thickness of Postulated Stagnant Gas Barrier
for Thermal Diffusion Experiments

Product Flow (STP ml/hr)	Thickness of Stagnant Gas Layer Necessary to Account for Experimental Result (cm)
65	4.2
160	1.6
191	1.4
245	1.7
444	2.2
461	1.7
535	1.7
623	1.5
713	1.7
919	2.0
1197	2.7
1627	2.0

Average = 1.8, excluding
first point

Figure 6. Postulated
stagnant gas barrier
in thermal diffusion
experiment.

³MLM-1268.

⁴Dimensions and other characteristics of these columns are given in MLM-1254.

Over an extremely wide range of flow rates the observed results can be explained by the presence of a layer of stagnant gas of 1.8 cm thickness at the top of the experimental column. The gas ports on the column in question are very close to the top. From the dimensions of the column it does not appear that the gas is completely stagnant at the port location, however, it seems quite likely that the convective circulation rate is inadequate at this point.

Experiments are in progress to check this hypothesis. In these experiments gas samples will be taken at several points along the column.

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. Calculation of collision integrals for more flexible potential functions are needed for this purpose. There is also a need for the calculation of collision integrals 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.

The collision integrals are defined by the equation,

$$\Omega^{(l,s)}(T) = \left(\frac{h I}{2\pi\mu} \right)^{1/2} \int_0^\infty e^{-\gamma^2} x^{(2s+3)} Q^l_g d\gamma$$

where h is Boltzman's constant μ is the reduced mass of the system of two interacting particles, $\gamma^2 = E/kT - 1/2 \mu g^2/kt$, and E is the total energy of the system. The cross section $Q^l(E)$ is given by

$$Q^l(E) = 2\pi \int_0^\infty b(1 - \cos^l \chi) db,$$

where b is the impact parameter and χ is the angle of deflection in the center of mass coordinate system:

$$\chi = \pi - 2b \int_{r_m}^\infty \frac{dr}{r^2 F(r)},$$

where r_m , the distance of closest approach, is the larger of the two roots of $F(r_m) = 0$ of

$$F(r) = \left[1 - \frac{\phi(r)}{E} - \frac{b^2}{r^2} \right]^{1/2},$$

and $\phi(r)$ is the interaction potential between the two particles.

Figure 7. Region of integration for collision integrals, shown as shaded areas; r_c is curve maximum.

Figure 8. Interaction potential.

are applicable to any potential of the form shown in Figure 8. In this figure r_1 is the zero of the potential, r_2 is the minimum, and r_3 is an inflection point. These three quantities are useful in calculating the boundary curve and a subprogram has been written to calculate them by the Newton-Raphson method. This subprogram also calculates the quantity r_c by the same method, where r_3 is used as an initial estimate to r_c .

A second subprogram has been written to calculate the boundary curve, $E_o = F(r_m)$, from the above set of equations. For a given energy, the value of $r_m > r_o$ is calculated by the Newton-Raphson method from the first equation. This value is then used in the second equation to calculate b_o . The value of $r_1 < r_m < r_c$ is calculated by the Newton-Raphson method from the third equation. Finally, the value of $r_m < r_1$ is calculated by the same method from the equation $E_o - \phi(r_m) = 0$. The initial estimates used are: r_c for $r_m > r_c$, r_1 for $r_1 < r_m < r_c$, and r_1 for $r_m < r_1$. These estimates are used for the first energy; for subsequent energies the values for the preceding energy are used as initial estimates.

T-0138 The equation $F(r_m) = 0$ can be used to change the variable of integration from b to r_m in the equation for $Q^l(E)$. With this change in variable the region of integration for the collision integrals can be represented as shown in Figure 7. The portion of the boundary from $r_m = 0$ to r_1 corresponds to the repulsive portion of the potential. The portion of the boundary from $r_m = r_1$ to ∞ is defined by the equations,

$$E_o - \phi(r_m) - \frac{1}{2}r_m\phi'(r_m) = 0 \quad r_m > r_c,$$

$$b_o = r_m\sqrt{1 - \phi(r_m)/E_o} \quad r_m > r_c,$$

$$E_o(b_o^2 - r_m^2) + r_m^2\phi(r_m) = 0 \quad r_1 < r_m < r_c, \text{ and}$$

$$3\phi'(r_c) + r_c\phi''(r_c) = 0.$$

The angle of deflection, which is a function of E and r_m , is defined at every point in this region except on the portion of the boundary curve lying to the right of r_1 . It is a continuous function of E and r_m and goes to $-\infty$ along this portion of the boundary curve. The cross section is defined as an integral with respect to r_m at constant energy. For energies less than E_c , where E_c is the value of the boundary curve at r_c , this integral must be broken into two parts. Finally, $\Omega^{l,s}$ is defined as an integral over the cross sections, which are functions of the energy.

The numerical techniques used in the program which has been written to calculate the collision integrals

Smith and Munn have discussed the evaluation of the integrals for χ , $Q^l(F)$, and $\Omega^{(l,s)}(T)$ by Gaussian quadrature.⁵ The integrals are evaluated in basically the same manner in this new program. The range of energies that are needed to calculate the integral for $\Omega^{(l,s)}(T)$ by the Gauss-Laguerre quadrature formula is first found from the equations,

$$E_{max} = kT_{max} \gamma_N, \text{ and } E_{min} = kT_{min} \gamma_i,$$

where T_{max} and T_{min} are the maximum and minimum temperatures for which the collision integrals are to be evaluated, and γ_N and γ_i are the largest and smallest Gauss-Laguerre abscissas. Energies are then chosen at equal logarithmic intervals in the ranges E_{min} to E_c , E_c to $2E_c$, and $2E_c$ to E_{max} , and $Q^l(E)$ is calculated at each of these energies. This table of cross sections versus energy is used in evaluating the integral for $\Omega^{(l,s)}(T)$. The cross sections that are needed in the evaluation of this integral are found by interpolation of $\log Q^l$ versus $\log E$. Aitken's method of interpolation is used for this purpose.

The accuracy of several of the numerical methods used in the calculation of the collision integrals has been investigated. Because it is one of the simplest potentials having the form shown in Figure 8, the Lennard-Jones (12-6) potential has been used in most of these studies. The boundary curve for this potential has been calculated to 1 ppm. For the first energy, where r_1 and r_c were used as the initial estimates, approximately 10 iterations were required for each of the three boundary values. For subsequent energies, where the values for the preceding energy were used as initial estimates, approximately five iterations were required for each of the three boundary values.

Figure 9. Number of points necessary in the Gauss-Mehler quadrature formula to calculate χ .

An analysis of the integrand for Q^l has shown that an error of 0.1% in χ introduces an error of 0.05% or less, in the integrand for $(1-\cos^l \chi)$ equal to, or greater than, 0.1. For $(1-\cos^l \chi)$ less than 0.1 the error is greater, but it has little effect since $(1-\cos^l \chi)$ is so small. The number of points necessary in the Gauss-Mehler quadrature formula to calculate χ accurate to 0.05% has been determined. It was found that this number depended upon the energy and distance of closest approach. The number of points as a function of the fractional distance from the repulsive portion of the potential to the portion of the boundary curve $r_1 < r_m < r_c$ is shown in Figure 9 for several energies less than E_c (≈ 0.8). For energies greater than 1.0 it was found that less than 15 points were required at all distances of closest approach.

⁵F. J. Smith and R. J. Munn, *J. Chem. Phys.*, **41**, 3560 (1964).

The accuracy of the interpolation technique used to obtain cross sections at arbitrary energies from a table of cross sections versus energy was checked in the following manner. Cross sections were calculated at equal logarithmic intervals in the energy: 10 cross sections per decade for E less than E_c , 10 between E_c and $2E_c$, and 10 per decade for E greater than $2E_c$. Aitken's interpolation scheme was then used to calculate cross sections at a large number of arbitrary energies. Interpolation of both Q^I versus E and $\log Q^I$ versus $\log E$ was used. The accuracy of the interpolated values was determined by the difference in the last two diagonal elements of the interpolation array. On the average the interpolation of $\log Q^I$ versus $\log E$ gave significantly better results than that of Q^I versus E . It was found that four points in the interpolation scheme were sufficient to calculate cross sections accurate to better than 0.2% at all energies. For a few energies, cross sections were calculated directly and compared with the interpolated values. It was found that the difference in the last two diagonal elements gave a good estimate of the error between the interpolated value and the actual value; in general, it tended to overestimate the error.

It has already been demonstrated that the computer program calculates collision integrals which are in agreement with published values.⁶ This work on the accuracy of the numerical techniques used in the program indicates that it will be possible to calculate values accurate to 0.1% with this program. This is more accurate than any of the experimental data on the transport properties.

Molecular Beam Scattering A velocity selector has been proposed for use in obtaining a monoenergetic beam of particles in a molecular beam scattering system. Previous designs have incorporated either the multiple slotted disc⁷ or a radial drum selector with helical grooves.^{8,9} The best velocity spread has been given as between 3 and 4% with an effective open time of 34.8% obtained with the slotted disc type selector.¹⁰

The proposed design uses a single rotor disc which is placed in the path of the beam with its axis of rotation perpendicular to the beam axis. The rotor can then be conveniently driven from outside the vacuum system by means of a magnetic drive. A solenoid may be used to raise and lower the rotor from the beam. This type of rotor offers relatively simple construction and convenient drive with no moving feedthroughs. This design offers a total velocity spread of less than 1.5% with an open time of 38.2%, somewhat better than those mentioned above.

The design of the rotor is shown in Figure 10. Five circular grooves are machined in the face of the disc and the center is bored out to the groove depth. The material to be used is 7075-T6 aluminum for its high ratio of tensile strength to density. One hundred and eighty slits are milled across the face of the disc equally spaced through the six lands produced by the grooves and the center bore. This gives 360 radial slits with a one-degree angular spacing which intersect at the center of the rotor.

The slit spacing and the outside diameter of the disc d_o determine the rotation ϕ and, hence, the angular speed ω necessary for transit of a molecule of the selected velocity v_o across the rotor. Table 5 gives the rotor specifications.

⁶MLM-1274.

⁷H. A. Hostettler and R. B. Bernstein, *Rev. Sci. Instr.*, **31**, 872 (1960).

⁸A. E. Grosser, R. P. Iczkowski and J. L. Margrave, *Rev. Sci. Instr.*, **34**, 116 (1963).

⁹S. O. Colgate, Private Communication.

¹⁰S. M. Trujillo, P. K. and E. W. Rothe, *Rev. Sci. Instr.*, **33**, 841 (1962).

Figure 10. Rotor design (dimensions in inches).

Sideband velocities are attenuated due to the multiple lands since the slit spacing decreases with diameter, giving a nonuniform slit location as seen from the transit particle.

Figure 11 shows the representation of the maximum and minimum transmitted velocities $v_2(max)$ and $v_1(min)$ with respect to the selected velocity v_0 . The entry and exit slits are shown where a is the slit width and l the land thickness, θ_1 and θ_2 are the angles subtended by the outside and inside edges of the slits with r_1 and r_2 their respective radii.

T-0141

Table 5

Rotor Specifications

Rotor OD, d_o	6.000 in. (15.240 cm)
Rotor ID	4.062 in.
Slit Width, a	0.020 in. (.0508 cm)
Number of Lands	6
Land Thickness, l	0.0312 in. (.0794 cm)
Land Spacing	0.1562 in.
Number of Slits per Land	360
Angular Spacing of Slits	1 degree
Minimum Distance Between Slits	0.0154 in.
Maximum Distance Between Slits	0.0324
Fractional Open Time	0.382
Rotation for One Transit, ϕ	32 deg. (0.5585 rad.)
Resolution (Total Velocity Spread), R_T	0.0135

Figure 11. Representation of transmitted velocities.

For transmission of $v_2(max)$ a molecule must travel the distance $(d_0 - 2l)$ while the rotor rotates through the angle $(\phi - \theta_2)$ in the time $(\phi - a/r_2)/\omega$ where $\theta_2 \approx a/r_2$ and ω is the angular speed of the rotor. Then,

$$v_2(max) = \frac{\omega(d_0 - 2l)}{(\phi - a/r_2)}.$$

Similarly, with $\phi_1 \approx a/r_1$: $v_1(min) = \omega d_0 / (\phi + a/r_1)$. A molecule traveling at the selected velocity v_0 must traverse the distance $(d_0 - l)$ while the rotor rotates through the angle ϕ in time ϕ/a ; hence, for $\omega(rpm)$: $v_0 = [\omega(d_0 - l)]/\phi = 2.843 \omega \text{ cm/sec.}$

$$v_1(min) = \frac{\omega d_0}{(\phi + a/r_1)}.$$

The velocity resolution R is given as the fractional spread in velocity,

$$R_T = \frac{v_2(max) - v_1(min)}{v_0} = \frac{\phi}{(d_0 - l)} \frac{(d_0 - 2l)}{(\phi - a/r_2)} - \frac{d_0}{(\phi + a/r_1)}.$$

The resolution corresponding to the half intensity width R , which is referred to in the literature is given as,

$$R = \frac{R_T}{2},$$

Figure 12. Velocity as a function of rotor speed for rotor design shown in Figure 10.

Figure 12 shows a plot of the selected velocity v_0 against the rotor speed for this design. An increase in v_0 may be obtained by omitting some lands with the same angular slit spacing but sideband elimination will suffer.

In molecular beam work narrow band velocity selection is useful in studying elastic and inelastic scattering, chemical reaction kinetics and the velocity distributions of various types of beam configurations using neutral particles.

The present application is a crossed beam experiment with two thermal energy beams of neutral particles. Effusive and supersonic nozzle jet beams are to be investigated. Two such selectors will be used, one in each beam. These will be driven from a common variable phase sensitive power supply. This will allow control over the phase relation between the two beams. Each beam will be pulsed for detector synchronization.

HELIUM RESEARCH

Low-Temperature Distillation Techniques have been developed for transferring liquid helium to a pumped helium bath. These techniques will be used in an automatic liquid helium level control in the helium still being designed for the separation of helium-3 and helium-4. The helium flow to the bath was controlled by a valve mounted on the cryostat end of the helium transfer tube. The handle of this valve could be operated from outside the cryostat. It was found that a valve with reasonably smooth seating surfaces could completely stop a flow of normal liquid helium. Superfluid helium could leak through the closed valve, but the amount

was negligible. A flow of liquid helium could be restarted with relative ease after the valve had been closed. Even after the transfer tube warmed up for 10 min a flow of liquid helium could be started in less than 1 min. However, if the valve was below the level of the helium bath, the incoming helium gas at the start of a transfer would boil away all the helium above the valve. Thus the only practical arrangement is to have the valve above the surface of the helium bath. Similarly, the incoming stream of warm gas or liquid should not be directed toward the surface of the bath as this also causes excessive evaporation of the bath liquid.

When the valve is first opened, the relatively warm gas which comes through the valve causes some liquid helium to evaporate. If the bath is being pumped to below the lambda point, the pump can easily carry away this evaporated helium. But, in the case of a bath not being pumped this hard, the helium gas can build up an excessive pressure in the cryostat. For this reason a pressure regulator will be needed which can quickly open the pumping line to handle the intermittent large volumes of gas.

In order to continuously supply such a system with liquid helium, it appears that an intermediate dewar between the standard storage dewar and the cryostat will be necessary. Thus, it would be possible to change storage dewars without interrupting the supply of helium to the cryostat to flush out the helium transfer lines. The intermediate dewar would probably consist of a storage dewar modified to accept a transfer tube from another storage dewar, the transfer tube to the cryostat, and some sort of liquid level indicating device.

Vapor Pressure Thermometry The thermomolecular pressure corrections necessary for precise vapor pressure thermometry are being investigated both theoretically and experimentally.

An alternative method of obtaining an equation describing the thermomolecular pressure has been considered previously.¹¹ The molecules passing a given cross section of the tube were considered in two classes. The pressure gradient due to molecules making their last collision in the gas and those making their last collision with the wall were determined separately. The mass flow for each component was set equal to zero and then the components were added together giving

$$\frac{dP}{dT} = \frac{N_u}{N} \left(\frac{1}{2} \frac{P}{T} \right) + \frac{N_i}{N} \left(\frac{1}{2} \frac{P}{T} \right) \left[\frac{12\eta^2}{\rho P} \frac{1}{r^2 + 4K\gamma r} \right]. \quad (1)$$

This equation was shown to reduce to the differential form of the Weber-Schmidt equation both in the low pressure and high pressure limits.

Further consideration has shown that if the mass flow for the two components are added together before they are set to zero, an equation results which is identical in form to the Weber-Schmidt equation. In this rearrangement of steps, certain factors are retained which were divided out in the first considerations. Following Kennard,¹² the mass flow in the free molecule case is given by

$$Q'_\omega = \frac{2-f}{f} \frac{4}{3} \sqrt{\frac{2\pi M}{R}} r^3 \frac{d}{dx} \left(\frac{P}{\sqrt{T}} \right), \quad (2)$$

where f is the fraction of molecules diffusely reflected from the tube wall, i.e., the accommodation coefficient, R is the gas constant per mole, r the tube radius and x the coordinate of the tube axis. In the case where the velocity distribution function is not maxwellian, the average velocity may be represented by $v = \beta'_v v(\text{maxwellian})$. Consideration of equation (2) in this light shows that $Q_\omega = \beta_\omega Q'_\omega$.

¹¹MLM-1266.

¹²E. H. Kennard, *Kinetic Theory of Gases*, New York, McGraw-Hill, 1938, pp. 291-333.

The mass flow in the viscous flow case is

$$Q_v = \frac{\pi}{8} \frac{Pr^4 M}{\eta RT} \frac{dP}{dx} - \frac{3\pi}{4} \frac{\eta r^2}{T} \frac{dT}{dx}. \quad (3)$$

Now when λ approaches r , but $r \geq \lambda$, the viscosity can be approximated to first order in λ/r by¹³

$$\eta = \eta_0 \frac{1}{1 + 4K(\lambda/r)} \approx \frac{(\frac{1}{2})\rho \bar{v}_v \lambda}{1 + 4K(\lambda/r)} \quad (4)$$

where now $K = (2 - f)/f$. The factor of 4 in the denominator comes from the use of cylindrical boundary conditions.¹² To be consistent with the free molecule case, $\bar{v}_v = \beta_v \bar{v}_{max}$. The term $\bar{v}_v$ appears in a rather complicated way in deriving the dT/dx term of equation (3). Therefore, the non-maxwellian behavior in calculating this term will be represented by a multiplicative factor β'_v . In the absence of an explicit distribution function, the β terms will be taken as undetermined constants for the time being.

Defining N_w and N_v as the number of molecules passing through a given cross section of the tube, making their last collision with the wall and in the gas respectively, the ratio N_v/N_w is

$$\frac{N_v}{N_w} = \frac{\int \pi r^2 dv (n \bar{v}_v / \lambda)}{\int 2\pi r ds (\frac{1}{4} n \bar{v}_w)} = \frac{\Omega_1}{\Omega_2} \frac{\beta_v}{\beta_w} \frac{2r}{\lambda}, \quad (5)$$

where Ω_1 and Ω_2 are geometry factors, and $\alpha = \Omega_1/\Omega_2$ will be taken as an undetermined constant. An attempt is being made to calculate α .

Now, letting the mass flow of gas passing a cross section perpendicular to the tube wall be represented by $(N_w/N)Q_w + (N_v/N)Q_v$, and setting the total flow to zero,

$$Q_w + \frac{N_v}{N_w} Q_v = 0, \quad (6)$$

or

$$\begin{aligned} & \frac{4}{3} \sqrt{\frac{2\pi M}{R}} \beta_w^3 \frac{d}{dx} \left(\frac{P}{\sqrt{T}} \right) \\ & + \frac{\beta_v}{\beta_w} \frac{2\alpha}{K} \frac{r}{\lambda} \frac{\pi}{8} \frac{r^4 MP}{RT \eta_0} \left(1 + 4K \frac{\lambda}{r} \right) \frac{dP}{dx} - \beta'_v \frac{3\pi}{4} \frac{r^2 \eta_0}{T} \frac{1}{1 + 4K(\lambda/r)} \frac{dT}{dx} = 0 \end{aligned}$$

Assuming that $\eta_0 = \frac{1}{2} \beta_v \rho \bar{v} \lambda$ and $Pr/\eta_0 = \pi/4(1/\beta_v)(r/\lambda)$, the following algebraic steps will reduce equation (6) to the form of the Weber-Schmidt equation.

Taking the derivative indicated in the first term of equation (6) and dividing through by $4/3 \sqrt{2\pi M}/R \beta_f r^3$,

$$\begin{aligned} & \frac{dP}{dx} - \frac{1}{2} \frac{P}{T} \frac{dT}{dx} \\ & + \frac{3}{4} \frac{\beta_v}{\beta_w^2} \sqrt{\frac{RT}{2\pi M}} \frac{2\alpha}{K} \frac{r}{\lambda} \left[\frac{\pi M}{8RT} \frac{Pr}{\eta_0} \left(1 + 4K \frac{\lambda}{r} \right) \frac{dP}{dx} - \frac{1}{2} \frac{P}{T} \frac{3\pi}{2} \frac{\beta'_v \eta_0}{Pr} \left(\frac{1}{1 + 4K(\lambda/r)} \right) \frac{dT}{dx} \right] = 0 \end{aligned}$$

¹³S. Chapman and T. C. Cowling, *Mathematical Theory of Non-uniform Gases*, Cambridge University Press, 1953, pp. 101-03.

Using the relation

$$\frac{Pr}{\eta_0} = \frac{\pi}{4} \frac{\bar{v}}{\beta_v} \frac{r}{\lambda} = \frac{l}{\beta_v} \sqrt{\frac{\pi RT}{2M}} \frac{r}{\lambda},$$

it becomes,

$$\frac{dP}{dx} - \frac{1}{2} \frac{P}{T} \frac{dT}{dx} + \frac{\beta_v}{\beta_\omega} \left[\frac{3}{4} \frac{a}{K} \frac{r}{\lambda} \left[\frac{\pi}{8} \frac{l}{\beta} \frac{r}{\lambda} \left(l + 4K \frac{\lambda}{r} \right) \frac{dP}{dx} - \frac{3}{2} \frac{P}{T} \beta_v' \frac{\lambda}{r} \left(\frac{l}{l + 4K \lambda/r} \right) \frac{dT}{dx} \right] \right] = 0$$

or

$$\left[l + \frac{3\pi}{32} \frac{a}{K} \frac{l}{\beta_f^2} \frac{r^2}{\lambda^2} \left(l + 4K \frac{\lambda}{r} \right) \right] \frac{dP}{dx} = \frac{1}{2} \frac{P}{T} \left[l + \frac{9}{4} \frac{a}{K} \frac{\beta_v' \beta_v}{\beta_\omega^2} \left(\frac{l}{l + 4K \lambda/r} \right) \frac{dT}{dx} \right].$$

On the right side of the above equation, using the fact,

$$l + a \left(\frac{l}{l + bx} \right) = (l + a) \frac{l + b/(l + a)x}{l + bx},$$

and forming dP/dT ,

$$\frac{dP}{dT} = \frac{1}{2} \frac{P}{T} \frac{\left[l + \frac{9}{4} \frac{a \beta_v' \beta_v}{K \beta_\omega^2} \left(\frac{l + \frac{4K}{l + \frac{9a \beta_v' \beta_v}{4K \beta_\omega^2}} \frac{\lambda}{r}}{l + 4K \frac{\lambda}{r}} \right) \right]}{\left[l + \frac{3\pi}{32} \frac{a}{K} \frac{l}{\beta_\omega^2} \frac{r^2}{\lambda^2} \left(l + 4K \frac{\lambda}{r} \right) \right]}. \quad (7)$$

Since the combinations $9/4 a/\beta_f^2$ and $\beta_v \beta_v'$ always appear together, they will be denoted by γ and β , respectively. These two combinations have separate physical meanings. Thus, equation (7) becomes

$$\frac{dP}{dT} = \frac{1}{2} \frac{P}{T} \frac{l}{\frac{\pi}{24} \left[\frac{\gamma}{K} \frac{l}{l + \frac{\gamma \beta}{K}} \right] \frac{r^2}{\lambda^2} \left(\frac{\left(l + 4K \frac{\lambda}{r} \right)^2}{l + \frac{4K}{l + \frac{\gamma \beta}{K}} \frac{\lambda}{r}} \right) + \frac{l}{l + \frac{\gamma \beta}{K}} \left(\frac{l + 4K \frac{\lambda}{r}}{l + \frac{\gamma \beta}{K} \frac{\lambda}{r}} \right)}. \quad (8)$$

This equation can be put into the differential form of the Weber-Schmidt equation by performing the division indicated in the first term of the denominator:

$$\frac{\left(l + 4K \frac{\lambda}{r} \right)^2}{l + \frac{4K}{l + \frac{\gamma \beta}{K}} \frac{\lambda}{r}} = l + 4K \left(\frac{l + 2 \frac{\gamma \beta}{K}}{l + \frac{\gamma \beta}{K}} \right) \frac{\lambda}{r} + \frac{16K^2 \left(\frac{\gamma \beta}{K} \right)^2 \frac{\lambda^2}{r^2}}{l + \frac{4K}{l + \frac{\gamma \beta}{K}} \frac{\lambda}{r}}.$$

It can be seen that (λ^2/r^2) divides out when the above expression is put into equation (8) giving

$$\frac{dP}{dT} = \frac{1}{2} \frac{P}{T} \left\{ \frac{\pi}{24} \frac{\gamma}{K} \frac{l}{1 + \frac{\gamma\beta}{K}} \frac{r^2}{\lambda^2} \left[l + 4K \left(\frac{1 + 2 \frac{\gamma\beta}{K}}{1 + \frac{\gamma\beta}{K}} \right) \frac{\lambda}{r} \right] + \frac{\left[l + \frac{\frac{2\pi}{3} K \gamma \left(\frac{\gamma\beta}{K} \right)^2}{4K \left(1 + \frac{\gamma\beta}{K} \right)^2} \right] \frac{r}{\lambda}}{\left[1 + \frac{l}{4K} \left(1 + \frac{\gamma\beta}{K} \right) \frac{r}{\lambda} \right]} \right\}^{-1} \quad (9)$$

It is now clear that equation (9) is of the same form as the differential form of the Weber-Schmidt equation,

$$\frac{dP}{dT} = \frac{1}{2} \frac{P}{T} \frac{l}{\frac{\pi}{24} \frac{l}{K_1} \frac{r^2}{\lambda^2} \left[l + 4K_2 \frac{\lambda}{r} \right] + \left[\frac{l + g \frac{r}{\lambda}}{l + h \frac{r}{\lambda}} \right]} \quad (10)$$

where now, in terms of k , γ and β , the Weber-Schmidt constants are

$$K_1 = \beta + \frac{k}{\gamma}, \quad K_2 = K \frac{l + 2\gamma\beta/K}{l + \gamma\beta/K}, \quad (11)$$

$$g = \frac{l}{4K} \frac{\frac{2\pi}{3} K \gamma \left(\frac{\gamma\beta}{K} \right)^2}{\left(1 + \frac{\gamma\beta}{K} \right)^2}, \quad \text{and} \quad h = \frac{l}{4K} \left(1 + \frac{\gamma\beta}{K} \right).$$

It is helpful here to review the physical significance of k , γ , and β . The term $K = (2 - f)/f$ is a measure of the fraction of molecules reflected diffusely from the tube wall. The term $\gamma = 9\alpha/4\beta_\omega^2$ 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 . The term $\beta = \beta'_v \beta_v$ is a measure of the deviation from the maxwellian distribution of the molecules making their last collision in the gas.

As a comparison of the present work with the Weber-Schmidt constants, values of K_1 , K_2 and g/h calculated from (11) were compared with the experimental fit to the data given by Weber and Schmidt. The results are given in Table 6.

Table 6

Comparison of Mound Values with Weber-Schmidt Constants

	K_1	K_2	g/h
Taken from Weber-Schmidt data ^a	1.36	1.68	1.25
Taken from Knudsen data ^a	1.32	1.72	1.18
Calculated ^b from equation (11)	1.33	1.74	1.14

^aS. Weber, W. H. Keesom, and G. Schmidt, Leiden Communication 246-b.

^bUsing $K = 1.0$, $\beta = 1.0$, and $\alpha/\beta^2 = 1.3$, which are physically reasonable values.

In view of the differences between the Mound data and literature values, calculations are now in progress to vary K , β , and γ to see if a fit can also be obtained with the Mound data. Then some physical insight into the differences between the thermomolecular pressures measured by different investigators may be gained.

Two simplified versions of the Weber-Schmidt differential equation have been investigated. These are applicable only to the high pressure region when the mean free path is very small compared to the dimensions of the tube. The first equation was obtained¹⁴ to test the effect of the gas viscosity on the predicted thermomolecular pressure differences since it was observed that the viscosity index ($n = 0.147$) used by Weber and Schmidt did not agree with that computed using more recent, experimentally determined viscosities.¹⁵ A least squares fit of the data indicated a value of $n = 0.155$ from 6.5°K to 300°K and $n = 0.518$ from 1°K to 6.5°K. The equation,

$$p_w = \left[\frac{12R}{Mr^2} \int_{T_c}^{T_w} \eta^2(T) dT + p_c^2 \right]^{1/2}$$

was solved using experimental values of the viscosity and the results are compared in Figure 13 to the Weber-Schmidt equation and the smoothed experimental data obtained at Mound.

Figure 13. Comparison of Mound pressure data and data obtained with the Weber-Schmidt equation.

¹⁴MLM-1231.

¹⁵D. P. Kelly and W. J. Haubach, MLM-1161.

The differential equation was also solved with the slip term included,¹⁶ (the slip term appears a second time as indicated previously) which arose from the Maxwell-Hettner expression for the "creep" velocity. A rigid sphere model was assumed to adequately represent the temperature dependence of the viscosity. The solution to this equation is

$$\ln \frac{T_2}{T} = \frac{1}{2} \ln \left(\frac{8r^2 \sigma^2 N p_1^2 / T_1^2 + 5\sqrt{2} R r p_1 / T_1 - 75R^2 / 16\pi \sigma^2 N}{8r^2 \sigma^2 N p_2^2 / T_2^2 + 5\sqrt{2} R r p_2 / T_2 - 75R^2 / 16\pi \sigma^2 N} \right) + \sqrt{\frac{\pi}{4\pi + 12}} \left[\ln \left(\frac{16r^2 \sigma^2 N p_1 / T_1 + 5(\sqrt{2} - \sqrt{2 + 6/\pi}) R r}{16r^2 \sigma^2 N p_2 / T_2 + 5(\sqrt{2} - \sqrt{2 + 6/\pi}) R r} \right) \right] - \ln \left(\frac{16r^2 \sigma^2 N p_1 / T_1 + 5(\sqrt{2} + \sqrt{2 + 6/\pi}) R r}{16r^2 \sigma^2 N p_2 / T_2 + 5(\sqrt{2} + \sqrt{2 + 6/\pi}) R r} \right) \quad (12)$$

Calculations have shown that the shape of the curve is not particularly sensitive to the power index used and the correct magnitude for the effect may be obtained by using "effective" rigid sphere collision diameters calculated from realistic collision cross sections by

$$\sigma_{eff} = \left(\frac{Q^{(l)}}{\pi} \right)^{1/2}$$

Cross sections were calculated at several temperatures for a modified-Buckingham potential with parameters reported by Mason and Rice.¹⁷ The results are shown in Table 7. The results are realistic with respect to the intermolecular potential, but they were obtained classically.

Table 7

Effective Rigid Sphere Diameter From Collision Cross Sections

$$r_1 = 3.135; \alpha = 12.4$$

$$\epsilon/K = 9.16; l = 2$$

T	(°K)	30	50	100	150	200	250	300
$Q^{(l)}$	(Å ²)	15.85	14.24	12.51	11.60	10.98	10.50	10.12
σ_{eff}	(Å)	2.25	2.13	2.00	1.92	1.87	1.83	1.79

It can be seen in Table 7 that a value of $\sigma_{eff} = 2.0$ Å adequately represents the experimental data. A somewhat larger value (≈ 2.1 Å) is necessary to fit the Weber-Schmidt equation. However, it is unlikely that all of the gas in the experimental system is at the very low temperature necessary to yield a large value of the collision radius, and this is impossible in the runs made at $T_c = 77^\circ\text{K}$. In addition, the most recent experimental data taken at Mound (also considered to be the most reliable) cross the Weber Schmidt curve at about 3000 microns of p_w . It appears that the experimental data in the high pressure region are in better agreement with the two previous equations than with the Weber-Schmidt calculation.

¹⁶MLM-1266.

¹⁷E. A. Mason and W. E. Rice, *J. Chem. Phys.*, **22** (1954).

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.

EMISSION SPECTROSCOPIC ANALYSIS

Beryllium in Air A new direct reader emission spectroscopic procedure was developed for the determination of beryllium in air samples. Palladium was selected as the internal standard because it was available on the direct reader and because it was probably not a contaminant in the samples.

The intensity of the palladium line increased with an increase in the concentration of beryllium in the sample. To minimize the inter-elemental effect, various buffering agents were added. A 10% BaCO₃ in graphite mix was a satisfactory suppressor. The palladium intensity did not vary significantly when the beryllium concentration was varied from 0.1 μg to 10 μg . To improve precision and increase the sensitivity of detection, an argon-oxygen atmosphere was employed. With this method it was possible to determine 1 μg of beryllium with an average deviation of $\pm 0.1 \mu\text{g}$.

Impurities in Gold A direct reader procedure for the quantitative determination of impurities in gold was also completed. The method is capable of detecting impurity levels below 0.00006 mg. The use of a 20% BaCO₃ in graphite mix and a controlled atmosphere of argon-oxygen improved the limits of detection of the impurities two- to threefold.

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ORGANIC RESEARCH

In support of other programs at Mound Laboratory, research is being conducted on filled plastics, foams and adhesives for specialized applications.

ADHESIVE SHRINKAGE STUDIES

The total shrinkage of Eastman 910 Adhesive (methyl 2-cyanoacrylate) was determined under thermal, free-radical and anionic polymerization conditions. Samples initiated thermally or by free-radical conditions were first stabilized against anionic polymerization by the addition of a boron trifluoride-2 acetic acid complex.¹⁸ The complex was prepared by bubbling boron trifluoride slowly through a layer of mercury into glacial acetic acid. The product was distilled under reduced pressure in a nitrogen atmosphere. Adhesive samples were stabilized by the addition of 0.05 ml of boron trifluoride-2 acetic acid complex for each 10 ml of sample.

The total shrinkages were evaluated by determining the densities of the uncured and cured adhesive at room temperature using a modification of the procedure of Moll and Spencer.¹⁹ This value (in percent) is given by

$$S = \frac{D_2 - D_1}{D_2} \times 100,$$

where D_1 is the density of the uncured sample at room temperature (1.098 g/cc) and D_2 is the density of the cured sample at room temperature. The volume of each sample was determined by its displacement of distilled water at a known temperature. From this value and the weight of the sample, the density D_2 was calculated.

Volumetric flasks, previously coated with 225 Mold Release, were employed as molds for the shrinkage determinations of the thermally and free-radically initiated samples. In all cases the cured samples were not of uniform texture; they contained both regions of a more dense yellow-brown material and less dense light yellow material. The bottom section of each flask, however, always consisted of uniform yellow-brown plastic and this section was used for density determinations. Anionic polymerization was accomplished by coating a thin film of the adhesive on a brass strip and allowing the water vapor present, acting as a weak base, to cure the sample. In this case the cured sample was white. Table 8 lists the same preparation, initiator used, cure temperature, density of cured sample and total shrinkage.

The values found for the total shrinkage of the adhesive did not vary with the polymerization conditions employed. Graham *et al.*¹⁸ polymerized methyl 2-cyanoacrylate of high purity under free-radical conditions obtaining polymer with a density of 1.304 g/cc at 25°C, which represents a total shrinkage of 15.6%.

¹⁸R. H. Graham *et al.*, *J. App. Poly. Sci.*, **4**, 231 (1960).

¹⁹R. E. Moll and J. B. Spencer, Sandia Corporation Report, August 9, 1962, p. 8.

Table 8

Shrinkage of Eastman 910 Adhesive on Curing

Sample Preparation	Initiator	Cure Temp. (°C)	Reaction Time (days)	Final Density (D ₂) (g/cc)	Total Shrinkage (%)
Stabilized with BF ₃ ·2CH ₃ COOH	None	70°	7	1.297	15.3
Stabilized with BF ₃ ·2CH ₃ COOH	None	70°	7	1.297	15.3
Stabilized with BF ₃ ·2CH ₃ COOH	None	70°	7	1.301	15.6
Stabilized with BF ₃ ·2CH ₃ COOH	Benzoyl peroxide	70°	3	1.304	15.8
Stabilized with BF ₃ ·2CH ₃ COOH	Benzoyl peroxide	70°	3	1.298	15.4
Stabilized with BF ₃ ·2CH ₃ COOH	α,α^1 - Azodiisobutyronitrile	60°	1.5	1.298	15.4
Stabilized with BF ₃ ·2CH ₃ COOH	α,α^1 - Azodiisobutyronitrile	60°	1.5	1.299	15.5
A thin layer of nonstabilized adhesive was coated on a brass strip.	(None) moisture	25°	~1 hr	1.300	15.5
A thin layer of nonstabilized adhesive was coated on a brass strip.	(None) moisture	25°	~1 hr	1.291	14.9