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SUMMARY

ISOTOPE SEPARATION

Carbon-13 Various thermal diffusion column configurations for carbon-13 separation using methane or carbon monoxide as feed are being used to study separation efficiency. The first five stages of a seven-stage cascade system of hot wire and concentric tube columns are enriching natural methane to about 32 per cent carbon-13 while coming to steady state conditions. The concentric tube columns enriched methane from 60 per cent to over 90 per cent carbon-13. About two grams of methane were accumulated which contain about 10 per cent impurities.

Xenon Chromatography is being used to separate krypton-85 from xenon. The krypton-85 content in xenon was reduced from 10^{-5} to $10^{-6}\%$. The efficiency of the separation increased as the column temperature decreased.

RADIOELEMENTS

Resolution Time Counting In the variational method for determining a half-life and the resolution time of a proportional counting system, it was found that the assumption of a constant resolving time is valid if the dead time losses are described by a Poisson time distribution function.

Preparation of Polonium Compounds The reaction between lanthanum and tellurium was studied. Lanthanum tellurides prepared in aqueous media yield solid solutions, or amorphous substances convertible to solid solutions.

Polonium-208 and Polonium-209 The half-life of polonium-208, as determined by alpha counting, was found to be 1056^{+42}_{-34} days. Counting measurements indicated that the half-life of polonium-209 has a lower limit of 55 years.

ISOTOPE SEPARATION

Processes are being developed for separating and purifying the isotopes of a number of elements including hydrogen, the noble gases, carbon and uranium. Potential sources of supply of these materials are being evaluated.

CARBON ISOTOPE SEPARATION

Thermal Diffusion A five-stage cascaded thermal diffusion system consisting of six hot-wire columns and one concentric tube column for enriching the carbon-13 in natural methane accumulated a mass-17 enrichment of 31.9 per cent in methane of 64.4 per cent purity.

Seven liters of 60 per cent enriched methane were processed in two concentric tube thermal diffusion columns. The yield was approximately two liters of gas containing methane enriched to 90 per cent carbon-13.

Measurements of Carbon Monoxide Transport Coefficients A series of static separation experiments were made at a wire temperature of 500°C. At low pressure (150 mm Hg) the results agree with theoretical predictions from Lennard-Jones shape factors. At higher pressures (250 mm Hg and above) the logarithms of the experimental separation factors are 20 to 25 per cent less than the predicted values. More data are being accumulated in the pressure region between 150 and 250 mm Hg.

Carbon Monoxide Distillation The relative volatility, α , for the $C^{12}O - C^{13}O$ system was used as a guide for selection of column operating conditions. Where α is close to 1.0, the theoretical number of plates for a given separation are directly proportional to $\alpha - 1$.

The minimum theoretical plate requirements were calculated as a function of $C^{13}O$ concentration in the bottom product and of $C^{13}O$ recovery from the carbon monoxide feed. Because of the very small relative volatility ($\alpha \approx 1.01$) of the $C^{12}O - C^{13}O$ system, graphical methods for determining theoretical plate requirements were impractical. Since relative volatility can be considered relatively constant at all concentrations, the Fenske equation for theoretical plates at total reflux was used:

$$N = \frac{\log \left(\frac{X_L}{X_H} \right)_n \left(\frac{X_H}{X_L} \right)_W}{\log \alpha_{AV}}$$

where N is the number of theoretical plates, X is the molar concentration in liquid phase, α_{AV} is the average relative volatility, the subscripts L and H indicate the light ($C^{12}O$) and heavy ($C^{13}O$) components, respectively, n is the top of section (n th tray) and W is the bottom of Section.

The calculations were based on an average relative volatility of 1.01 and 1.1 per cent $C^{13}O$ (natural abundance) in the feed and on the assumptions that molal overflows in the stripping and rectifying sections were constant and the relative volatility was constant. The results of these calculations show that, below the feed tray, the tray effectiveness is highest in the range 20% to 80% $C^{13}O$ in the bottom product and still high up to about 90% where tray requirements increase sharply. Above the feed tray the tray requirements per unit of recovery are constant to about 50-60% recovery where a sharp increase is again found.

Minimum reflux ratios were calculated by the method of Robinson and Gilliland, which is based on the determination of the slope of the operating line which connects the feed condition on the equilibrium curve with the overhead composition on the line $x = y$.

$$\left(\frac{O_R}{D} \right)_{\text{minimum}} = \frac{x_D - y_C}{y_C - x_C}$$

where x = molar concentration of more volatile component in liquid phase, y = molar concentration of more volatile component in vapor phase, O_R = liquid overflow rate in section above feed, D = distillate rate, and subscripts D = in distillate and C = at feed tray.

The ratio $(O_R/D)_{\min}$ represents the reflux ratio that would require an infinite number of trays to perform a given separation. Because the relative volatility is nearly one, the minimum reflux ratio is numerically close to the $C^{13}O$ recovery.

Having determined minimum trays and minimum reflux, the correlations of Gilliland and of Erbar and Maddox were used to evaluate actual tray requirements at reflux ratios higher than minimum. These are both based on the fact that the ratio of actual to minimum trays varies from infinity to 1.0 as reflux ratio varies from minimum to total reflux. Because of the 1:1 relationship between $C^{13}O$ recovery and minimum reflux ratio, the ratio of actual trays to minimum trays is found to be independent of $C^{13}O$ recovery and a function only of boil-up for a given product rate. In this case the basis for the calculation was 1.0 gram per day carbon-13 as $C^{13}O$ in the bottom product. The two methods agreed closely and showed that the optimum value for boil-up is about 1700 gram per hour of carbon monoxide. This will reduce actual tray requirements to 1.1 times minimum trays and little would be gained by further increase.

Chemical Exchange The carbon dioxide-carbamate system for the enrichment of carbon-13 was studied to improve the enrichment capabilities of the system. The purpose of this study to find ways of increasing the reaction rate of the carbon dioxide-carbamate system and to determine the most efficient way to separate carbon-13 by this method. If the reaction rate can be increased sufficiently, the method offers a simple, economical way of enriching carbon-13.

When carbon dioxide is absorbed by primary and secondary amines, carbamates are formed. Isotope enrichment occurs because $C^{13}O_2$ reacts faster with the amine molecules than $C^{12}O_2$. This degree of preference is the separation factor, and is inversely proportional to the temperature of the reaction rate.

An apparatus is being constructed for the chemical exchange studies. A glass column, eight feet long, 3/4-inch in diameter, was filled with Helipak stainless steel helices. A glass water jacket is provided to maintain a constant temperature for the exchange reaction. The carbon dioxide is fed from a cylinder to the top of the column. Above the column is a reactor filled with Helipak, where the carbamate is formed. Below the column, boiler and condenser serve to dissociate the carbamate into the amine and the carbon dioxide. To the right of the boiler, a condenser cools the amine and a pump returns the amine to the top of the column. Sample ports are located at a feed, waste, and product points.

In a typical run, the amine solution in methanol is pumped to the top of the reactor and allowed to flow through the packing in the reactor. At the same time, carbon dioxide is fed in the bottom of the reactor, rises, and reacts with downflowing amine to form the carbamate. Any excess carbon dioxide passes through the waste port. The carbamate flows down through the column and the condenser into the boiler. The boiler is operated at the boiling point of methanol (about 65°C). This causes the carbamate to dissociate to carbon dioxide and amine; the carbon dioxide rises with the methanol to the condenser and the methanol returns to the boiler. The carbon dioxide passes into the column. In the column this enriched carbon dioxide exchanges with the absorbed carbon dioxide of the carbamates which further enriches the carbamate. The spent amine solution in the boiler passes through the cooler to be used again.

Initially, runs will be made using a two molar solution of monoethanolamine in methanol as a solvent. The runs will be made at room temperature and the liquid and gas flow rates will be varied to give maximum enrichment.

XENON ISOTOPE SEPARATION AND PURIFICATION

Experimental Chromatography Chromatography is being used as one method for the separation of krypton and xenon. A new column with a cross sectional area of 5.067 cm² a length of 19 cm and coconut charcoal adsorbent of 50/60 mesh was used in five experiments. Two of these runs had a sample feed of 500 ml, adsorbent column temperature of 243°K and elutrient flow rate of 3.4 liters/per minute, with pre-cooled helium as the carrier gas. The average of these two runs was as follows:

	<u>Averaged Run 03 + 04</u>
Retention time for krypton, t_{kr}	4.75 minutes
Retention time for xenon, t_{Xe}	34.75 minutes
Counting Analyses (%Kr-85)	
Feed	$2.38 \times 10^{-3}\%$
Xe Trap	$1.27 \times 10^{-4}\%$
Kr Trap	$1.16 \times 10^{-4}\%$
Degree of clean-up Feed/Xe trap	18.74
Recovery in Xe Trap	79.5%
Total Recovery	88 %

Comparison of these runs with Runs 01 and 02 (MLM-1170) showed that the amount of separation is dependent on the sample volume, and that higher efficiencies can be obtained with smaller feeds.

Two runs had a sample feed of 1,000 milliliters, column temperature of 232°K, and elutrient flow rate of 3.4 liters per minute using precooled helium as the carrier gas. The results were as follows:

	<u>Run # 1</u>	<u>Run # 2</u>
Retention time for krypton, t_{Kr}	7.25 minutes	7 minutes
Retention time for xenon, t_{Xe}	32 minutes	33.5 minutes
Counting Analysis (% Kr-85)		
Feed	$2.26 \times 10^{-3}\%$	$2.22 \times 10^{-3}\%$
Xe trap	$1.21 \times 10^{-4}\%$	$1.80 \times 10^{-4}\%$
Kr trap	$1.47 \times 10^{-3}\%$	$1.23 \times 10^{-4}\%$
Degree of clean-up Feed/Xe trap	1,868	1,233
Recovery in Xe trap	84%	86%
Total Recovery	98%	100%

Despite the increased peak tailing of krypton in the last two runs, the efficiency of the separation increased as the temperature of the column decreased.

RADIOELEMENTS

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

DETERMINATION OF COINCIDENCE CORRECTION

In the report for June 1, 1963 (MLM-1160), it was shown that the computed value of a half-life ($T_{1/2}$) varies in a linear fashion according to the value of the resolving time (τ) used in the computation. Conversely, the value of the resolving time computed from different half-life values varies linearly with the half-life selected for a given set of data. In neither case is the variation reflected in the probable error computed by the method of least squares.

Furthermore, the slope of the line derived from $T_{1/2} = f(\tau)$ is significantly different from the slope of $\tau = F(T_{1/2})$ when no consideration is given to the relative weights of the individual observations or to the change of weight implied by a change in variable.¹ When the same data are assigned weights inversely proportional to the squares of the probable errors of the individual observations, *and corrected for changes in functional relationships*, the lines representing half-life as a function of resolving time and resolving time as a function of half-life become more nearly congruent.

The equations used in the computations are:

$$N = n(1 - n\tau)^{-1} = N_0 e^{-\lambda t} \quad (1)$$

$$\log_e N = \log_e n(1 - n\tau)^{-1} = \log_e N_0 e^{-\lambda t} \quad (2)$$

$$\tau = \frac{1}{n} - \frac{e^{\lambda t}}{N_0} \quad (3)$$

where N = the true count at time, t ;

N_0 = the true count at time, $t = 0$;

τ = the resolving time of the counter;

and λ = the decay constant of lead-211.

It is evident that Equations (2) and (3) are merely different versions of Equation (1) and should yield the same slopes for any given set of parameters. That they do not is shown in Figure 1. The most widely divergent lines are those in which the data were equally weighted and no compensation was made for the implicit change in weights due to the change in variable. When the data are equally weighted, but corrected for implicit changes, the lines become more nearly, although not perfectly, congruent. With weighted data, corrected for change in variable, the lines again become slightly more divergent.

In addition, as seen in Table 1, the three methods of treating the same data lead to three significantly different results when the data are analyzed by the variational procedure. (In the variational procedure, as applied to the present problem, several values of τ are assumed, and the half-life is determined from equation (2) for each value of τ . The solution yielding the smallest sum of the squares of the deviations is assumed to yield the best value of the half-life. To determine the best value of τ , equation (3) is treated in the same manner, with several values of the half-life assumed.)

¹Worthing, A. G. and Geffner, J., "Treatment of Experimental Data," New York, John Wiley & Sons (1943), pp. 247-9.

Figure 1

Table 1

HALF-LIFE AND RESOLVING TIME AS FUNCTION OF WEIGHTING PROCEDURE

Weighting	Half-Life (Minutes)	Resolving Time (Minutes X 10 ³)
None	36.075 ± 0.007	1.212 ± 0.172
Readings Equal ^a	35.707 ± 0.011	1.392 ± 0.003
Readings Weighted ^{a,b}	35.941 ± 0.008	1.305 ± 0.004

^a Corrected for change in weight implied by change in variable

^b Weights proportional to reciprocal of probable error squared

It was also shown (MLM-1160, p 15 and 16) that, when various segments of the decay curve were analyzed variationally, there was a trend in both the computed half-life and the computed resolving time; the half-life tended to increase with decreasing counting rate, while the resolving time tended in the opposite direction.

In view of these discrepancies, it became necessary to re-examine the assumptions on which the equations (1-3) used in the computations were based. These are:

1. The radioactive decay constant, λ , is perfectly constant.
2. The resolving time, τ , is effectively constant over the counting range, and under the conditions, of the experiment.
3. The counter cannot be reactivated during the effective period of its dead time.
4. The number of pulses lost during the dead time of the counter is given by: $nN\tau$, the product of the number of dead time intervals, the average true counting rate, and the resolving time.

The first "assumption" is axiomatic; it has been repeatedly verified theoretically and experimentally that the half-life of a pure radioisotope, and consequently, the value of λ , is perfectly constant.

The proportional counter system used in this work was a Nuclear Measurements Corporation Model PC-3A alpha-beta-gamma counter, consisting of a hemispherical flowing gas chamber with a 0.001-inch diameter pear-shaped center wire electrode, a transistorized amplifier-discriminator, a vacuum tube one-shot multivibrator circuit, a three-decade vacuum tube scaler, and a Veeder-Root electro-magnetic register. The mechanical register with a 10^3 scaling factor was found to be accurate at counting rates up to approximately 1.4×10^6 counts per minute. The limiting resolving time of the counting system is, therefore, that of the one-shot multivibrator, and this resolving time is fixed by the values of the circuit components.

To determine if there was a significant change in the dead time of the multivibrator, the output plate circuit of the 5963 vacuum tube was monitored with an oscilloscope. The rise time was approximately 0.8 microsecond, and the overall dead time, to 90 per cent recovery, was seven microseconds. When the output grid circuit was examined, the same dead time was measured. There was no significant change in overall dead time whether the pulse was of fixed frequency (60 cycles per second) or random at counting rates between 10^3 and 2×10^6 counts per minute. The only observable difference in pulse shape was a slight decrease in the rise time, of the order of 0.08 microsecond, when higher repetition rates were used. The overall recovery time, however, remained the same at all counting rates, confirming the validity of the second and third assumptions.

The ability of the scaler, as distinct from the mechanical register, to follow the output pulses of the multivibrator was checked by feeding the same output pulse simultaneously to the vacuum tube scaler and to an

Figure 2

external transistorized scaler through an amplifier and discriminator. An additional decade of scaling was introduced between the third decade of the vacuum tube scaler and a mechanical register. At rates up to 2×10^6 recorded counts per minute, there was no significant difference in the counts recorded by the transistorized scaler and those of the vacuum tube scaler. At 2.4×10^6 counts per minute, the transistorized scaler recorded 148 counts more than did the vacuum tube scaler, or 0.006 per cent.

The fourth assumption, regarding the number of counts lost during a dead time interval, is recognized to be an approximation, because the time distribution of the random pulses is assumed to be uniform regardless of the time interval. A more precise description, based on the Poisson distribution function, is given by²

$$n = Ne^{-Nr}; \quad (4)$$

To test the validity of equation (3) the value of r was computed for each point, based on a half-life value of 36.075 minutes and N_0 equal to 1.7×10^6 counts per minute. Equation (4) was rearranged to yield

$$r = \frac{1}{N} (\log_e N - \log_e n) \quad (5)$$

The same values for $T_{1/2}$ and N_0 were then used to compute r from Equation (5). The results, shown in Figure 2, clearly show that the values of r computed from Equation (5) are more nearly constant than those computed from Equation (3).

The program for the IBM 1620 computer has been rewritten to permit the use of Equation (4) and other time distribution functions in the variational method for determining the half-life and the resolving time. It is expected that the results will be available for comparison in the near future.

PREPARATION OF POLONIUM COMPOUNDS

Further attempts to prepare the lanthanum tellurides (primarily La_2Te_3) were partially successful. The procedure was a modification of the one used to prepare the transition metal chalcogenides.

The effects of pH and temperature on the reactions were studied. Four different pH levels (6.5, 7.0, 7.5, 8.5) were used; the pH was held constant during a reaction period of 30 minutes. Three temperature variations were employed at each pH, as follows:

1. temperature raised from 20 to 90°C in 30 minutes;
2. temperature raised from 20 to 60°C in 30 minutes; and
3. temperature maintained at about 27°C.

The reaction products were identified by x-ray powder photography. The following substances were identified in one or more samples and in amounts up to 20%: tellurium metal, alpha lanthanum, tellurium dioxide, LaTe , La_2Te_3 , La_3Te_4 , and possibly LaTe_2 and La_2Te_4 . All of the listed materials were not found in every sample. All the x-ray patterns were indicative of solid solutions and/or amorphous substances; the principal constituents of these solid solutions and amorphous materials remain unidentified. Trends in the nature and composition of the reaction products as a function of pH and temperature were not discernable. From visual observations of the color changes during the course of the reactions (usually from white to either gray or black), the rates of the reactions appear to increase with increasing temperature gradient and decreasing pH.

²Volz, Helmut, *Z. Physik* 93, pp. 539-52 (1935)

The color changes could easily correspond to the reduction of tellurium(IV) to tellurium metal. The rate of reduction also increases with increasing temperature and decreasing pH.

One portion of the material was heated to 800° to 100°C in air for ten minutes. The resulting yellow compound contained the alpha form of lanthanum (as determined by x-ray analysis), and 5 to 20% La₂Te. Two other portions of the starting material were heated in sealed Pyrex tubes in a furnace at 450° and 700°C, respectively, for 20 minutes at about one micron pressure. The x-ray patterns indicated solid solutions. La₂Te(20% or less) was formed in the sample heated to 450°, and possibly La₂Te and LaTe₂ in the sample heated to 700°. Black film deposits of tellurium metal were found on the sides of the crucible and tubes after heating.

The lanthanum tellurides prepared in aqueous media yield solid solutions (or amorphous substances convertible to solid solutions) of unknown character and composition. However, lanthanum and tellurium appear to be present in several different forms and oxidation states.

POLONIUM-208 AND POLONIUM-209 STUDIES

Two samples of polonium-208-polonium-209 which were prepared in the 1950's by proton bombardment of bismuth metal were studied. One sample contained approximately 70 microcuries plated on a platinum foil. The other source had less than one microcurie; the activity in the smaller source was in about 50 ml of dilute hydrochloric acid. The polonium in the one microcurie source was purified, and the alpha activity ratio ($R_\alpha \text{Po}^{208}/\text{Po}^{209}$) was determined by alpha pulse height analysis. The ratio was found to be 24.29 ± 0.24 . This value is about 30 per cent greater than that of the polonium-208-polonium-209 which was recently returned from Argonne National Laboratory ($R_\alpha \text{Po}^{208}/\text{Po}^{209} = 18.98 \pm 0.43$).

Sources with different $R_\alpha \text{Po}^{208}/\text{Po}^{209}$ values are important for the decay schemes studies of polonium-208 and polonium-209, since a given decay mode can be assigned to one or the other of the isotopes by comparison of the relative abundances of disintegrations in different samples.

Several sources of polonium-208-polonium-209 have been prepared for a study of the internal conversion electron spectra of these isotopes. The resolution of semiconductor electron detectors is about an order of magnitude better than that of gamma scintillation crystals. Thus, the fine structure in the decay of polonium-208 and polonium-209 may be observed. Several runs with a source of about 100 microcuries of mixed polonium-208-polonium-209 were made; the data obtained are still being analyzed.

A moderately good value for the half life of polonium-208 was obtained by a counting method in which the decay of polonium-208 was compared with the decay of polonium-210 in a sample containing both isotopes. Based on only two counting experiments, 173 days apart, the experimental half-life was found to be 1056^{+42}_{-34} days, in good agreement with the value of about 1055 days recently reported by K. C. Jordan (MLM-1157). More accuracy is expected as further data are accumulated.

An attempt to measure the half life of polonium-209 by the same counting technique was not conclusive. In a sample containing only polonium-209 and polonium-210, polonium-209 decay was not observed (within experimental error) over a period of 291 days. Assuming that a one per cent decrease in the polonium-209 alpha activity could be observed in these experiments, a lower limit of 55 years can be assigned to the half-life of polonium-209.