Thermal Separation of Isotopes

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The performance of a simple, multi-stage apparatus for the separation of isotopes by thermal diffusion is discussed. All parts are built of copper pipe, each unit being based on a $\frac{1}{2}$-inch G.E. Calrod heater of 2 meters effective heating length. Tests with a CH_4-N_2 mixture show that convective coupling of the bottom of one unit with the top of the next functions well. In the case of CH_4, with two units preceded by a scrubber which maintains economically normal CH_4 at the "light" end, and with $\Delta T=370°C$ between the two surfaces, the C^{13} content at the "heavy" end at equilibrium is 2.77 times the normal amount. A single unit with $\Delta T=400°C$ filled with neon at $1.5-1$ atmosphere gives a separation factor of 8 for Ne^{22}/Ne^{20}. The relative separations produced in CH_4 and Ne are shown to be in agreement with the theory.

THE theory of the separation of isotopes by the thermal diffusion process has been discussed in detail by Furry, Jones and Onsager,[1] Debye,[2] and Waldmann.[3] Comparison of experimental results with theoretical expectations has been made by Clusius and Dickel[4] in the report of their original work on the separation of N_2-O_2 mixtures and Cl isotopes with long hot-wire columns. Using a column with methane between concentric cylinders, Nier[5] has shown that the separation factor for various pressures is in quantitative agreement with the theory of Furry, Jones and Onsager. Results with short concentric cylinder columns under various operating conditions have been reported by Bramley and Brewer.[6]

Guided by the Furry, Jones and Onsager calculations, we have been experimenting with multi-stage all-metal apparatus of the vertical concentric cylinder type. This has been used chiefly for the concentration of C^{13} in methane, but the performance of the apparatus has also been investigated with N_2-CH_4 mixtures and a single 2-meter column has been employed in the separation of the neon isotopes. The multi-stage feature has been used from the start in these experiments not only as a matter of convenience, since the total length of column needed for a considerable concentration of the C^{13} isotope is large, but also because of the possibility of decreasing the gap space between the hot and cold cylindrical surfaces in successive stages. In this way one can obtain in the first stages a transport of the heavy carbon comparable to that in the last stage, thereby increasing the speed of production.

APPARATUS

All surfaces are copper both because of its good heat conductivity and because radiation losses are minimized, copper retaining its polish in the methane atmosphere. The bottom of a column is connected to the top of the next one in the series by means of two $\frac{1}{2}$-inch or $\frac{3}{4}$-inch pipes, one of which is heated in order to set up convective circulation. In our first model[7] two one-meter units were followed by a three-meter column, each unit consisting of a $\frac{1}{2}$-inch O.D. pipe concentrically mounted by means of fine centering pins inside a 1-inch I.D. pipe. The two shorter units had their inner surfaces heated by means of inside spiral Chromel ribbon heaters, while the three-meter unit was heated on the outside. With methane gas at atmospheric pressure circulating in this apparatus 2 kw of power were consumed to maintain the hot surfaces at 330°C with one gallon of water per minute to cool the other surfaces. As reported, this apparatus doubled the C^{13} content of the methane, although the calculations of Furry, Jones and Onsager would lead one to expect at least three

[1] W. Furry, R. Jones and L. Onsager, Phys. Rev. **55**, 1083 (1939).

[2] P. Debye, Ann. d. Physik **56**, 284 (1939).

[3] L. Waldmann, Zeits. f. Physik **114**, 53 (1939).

[4] K. Clusius and G. Dickel, Zeits. f. physik. Chemie **B44**, 397 (1939).

[5] A. O. Nier, Phys. Rev. **57**, 30 (1940).

[6] A. Bramley and A. K. Brewer, Science **90**, 165 (1939).

[7] W. W. Watson, Phys. Rev. **56**, 703(L) (1939).
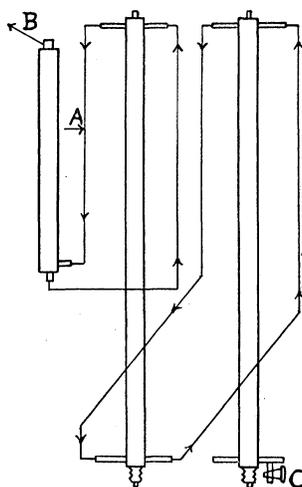
FIG. 1. Schematic drawing showing assembly and operation of two-stage apparatus for thermal separation of isotopes.

times this concentration. The lowered coefficient of thermal diffusion measured for methane by Nier[8] accounts well for the discrepancy.

To increase the efficiency and separation factor it was decided to abandon heating of the outer cylindrical surface and to have the inner surfaces heated as uniformly and economically as possible. In the next model, therefore, two columns based on $\frac{1}{2}$-inch G.E. Calrod heaters of 2 meters effective heating length were constructed. The heater is mounted concentrically in a water-cooled 1-inch I.D. copper pipe, the differential extension of the two surfaces being taken up by a sylphon bellows at the lower end. Every 50 cm along the length of the heaters narrow copper fins are silver-soldered on to insure centering within the larger pipes. The two columns are connected together convectively and ahead of the first one is placed one of the 1-meter units as a scrubbing column. A schematic drawing of the assembly is given in Fig. 1. Fresh methane gas is introduced into a coupling pipe at the bottom of the scrubber and gas slightly enriched in C^{12} is valved-off at the top.

Tank methane (92 percent in these experiments) is purified by the method of Storch and Golden[9] and stored in a water-sealed gasometer

of 30 liters capacity from which it is introduced, thoroughly dried, into the apparatus at a pressure about 2 mm above that of the atmosphere. We have recently begun using tank methane $99\frac{1}{2}$ percent pure, and can thus be assured, with treatment, of 100 percent CH_4 in quantities for a larger apparatus with more stages. The flow of fresh gas into the apparatus is controlled by the rate of valving-off at the top of the scrubber, somewhat less than 100 cc/hr. The gas at the top of the first Calrod unit is thus maintained at normal composition and the separation factor of the apparatus gives the maximum enrichment in C^{13} at the "heavy" end.

NITROGEN-METHANE SEPARATION

To test the relative performance under several different operating conditions a 50 percent-50 percent mixture of N_2 and CH_4 was introduced into the apparatus. At the end of a column where the degree of separation was to be measured the gas mixture circulated convectively through a glass volume of about 130 cc in the manner indicated in Fig. 4 below. Additional convective circulation was maintained through a liquid-air trap attached to this end volume. The procedure was to close off this volume from the column, freeze down the CH_4 with liquid air, and read the residual pressure with a Hg manometer. The liquid air was then removed and the stopcocks opened, thus returning the trapped gas to the circulation with the end of the column. Each such measurement required 20 minutes. A calibration curve was obtained for each end volume from
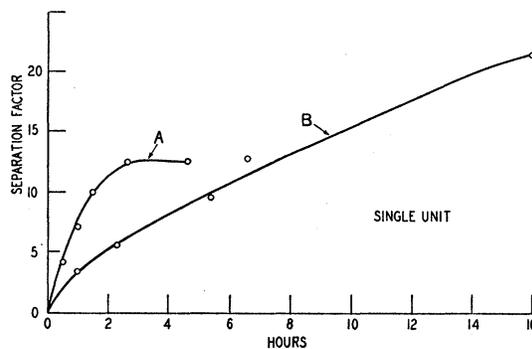
FIG. 2. Separation factor vs. time for N_2-CH_4 mixture in single 2-meter unit, A, without valving-off gas at top, B, with valving-off.

[8] A. O. Nier, Phys. Rev. 56, 1009 (1939).
[9] H. H. Storch and P. L. Golden, J. Am. Chem. Soc. 54, 4662 (1932).

determinations of the residual pressures for different known N_2-CH_4 mixtures. The temperature difference between the two surfaces was kept at 300°C.

In Fig. 2 is plotted the separation factor (ratio of the N_2/CH_4 ratio at the bottom to that at the top) for a single Calrod unit, A, without valving-off gas at the top and B, with valving-off at the top, i.e., maintainance of a 50/50 ratio at the top throughout the run. Despite the lack of high accuracy in these determinations, the approximate exponential rise of the factor to its equilibrium value and the relative slowness of the rise under the condition of valving-off gas at the top are evident. These facts are quite in agreement with the theory.

With the two units connected convectively the separation of this gas mixture was tested simultaneously at both ends at 50 minute intervals after introduction of the gas into the already heated apparatus. The results are shown in Fig. 3. Quite apparently disturbing influences are affecting the measured values, but it is evident that the factor is approximately the square of that found for a single column. It is to be concluded that this method of coupling units together works well.

This same separation experiment was performed at $\frac{1}{2}$ and $\frac{1}{4}$ atmos. pressure in the apparatus. As compared to the factors at atmos. pressure those at $\frac{1}{4}$ atmos. were considerably lower, while at $\frac{1}{2}$ atmos. the separation was found to rise at a slightly faster rate, with an equilibrium value a little above that at atmospheric pressure. Now Nier[5] has found that for a column with a gap space $d = 0.712$ cm using methane the maximum equilibrium separation factor occurs at a pressure of 0.6 atmosphere. Since according to the Furry, Jones and Onsager theory p^2d^3 should be approximately constant for maximum factor, all other variables remaining fixed, for our $d = 0.61$ cm this optimum pressure for methane should be 0.76 atmosphere. However, in view of the convenience of using atmospheric pressure and being able to maintain normal isotope concentration at the "light" end by simply valving-off, it was decided to continue operating at the higher pressure. The resulting lowering of the factor may be offset by merely increasing the length of the column slightly.

C^{13} CONCENTRATION

The two-columns plus scrubber with convective coupling were operated with methane for four days after which samples were withdrawn at the "heavy" end through a variable metal-taper leak at the rate of 3 cc per hour. The temperature difference was 370°C. Mass spectrographic analysis of CO_2 made from one of these samples showed a C^{13} content 2.77 times the normal amount. The other samples have been used in a
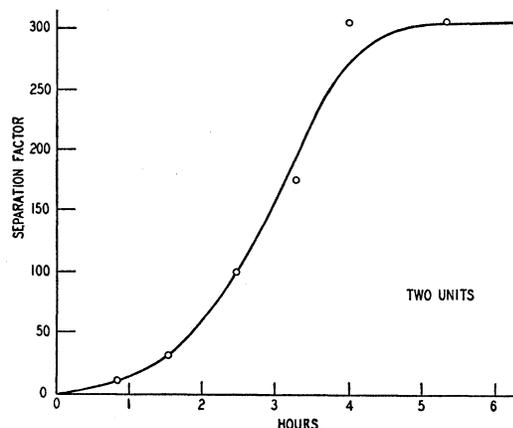
FIG. 3. Separation factor $vs.$ time for N_2-CH_4 mixture in two 2-meter units connected convectively.

gas target of our cyclotron for the purpose of enhancing activities arising from C^{13} bombardment.

The power consumption in this carbon isotope separation was 1300 watts. Now according to Eq. (67) of reference 1, the power expended because of conduction in the methane gas should be 800 watts in the two Calrod columns and the scrubber. About 100 watts are taken by the coupling pipe heaters and probably some 200 watts would be the radiation loss, the latter being relatively small because of the fact that the copper walls retain their polish in this reducing atmosphere. The remainder of the power input is apparently being lost by conduction through the copper and brass end plates silver-soldered on to the heaters. This loss is now being minimized by end-connectors made of four inches of stainless steel tubing.

For an apparatus made of six of these identical 2-meter Calrod columns this 2.77 factor should be cubed, a factor of 21. In collaboration with Professor Onsager, the writer has designed such a

six-unit model, but with decreasing gap spaces and coupling pipe sizes for successive units. It is to be hoped that its factor is better than this 21 estimate. We expect to have this apparatus in operation soon.

SEPARATION OF NEON ISOTOPES

One of these Calrod units has been used very successfully in separating the neon isotopes. The manner of operation is indicated schematically in
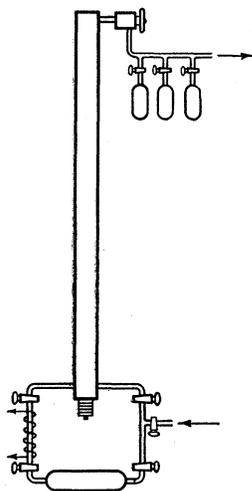
FIG. 4. Diagram illustrating operation of single unit for separating neon isotopes.

Fig. 4. Two liters of pure neon gas were pumped into the column with a Toeppler pump to a pressure of $1\frac{1}{2}$ atmospheres. The gas was circulated convectively through the lower end volume of about 300 cc. Between the hot and cold surfaces a temperature difference of 400°C was maintained. After two days, gas was bled off at the top at the rate of about 20 cc an hour into several glass containers until the pressure in the column had dropped to atmospheric. The lower end volume was then cut off and, with little

waste, the contents of the column pumped back into the original flask. Mass-spectrographic analyses of the heavy and light samples gave the following results:

	HEAVY	LIGHT	RATIO
Ne^{20}	84%	97.6%	0.86
Ne^{21}	0.43%	0.163%	2.64
Ne^{22}	15.7%	2.28%	6.88

The factor for Ne^{22}/Ne^{20} separation is thus about 8. It is of interest to compare this with the C^{13} enrichment produced by the same apparatus. Our factor for methane in a single column would be $2.77^{\frac{1}{2}}=1.67$, with ΔT lower by 30°C than that used for neon. Nier[10] has recently measured the coefficient of thermal diffusion for neon. He finds that for end temperatures close to those used here this quantity is 0.71 times the value computed from Enskog's equation for elastic spheres, whereas for methane it is 0.3 of the hard sphere value. The $(m_2-m_1)/(m_2+m_1)$ factor is 1/33 for CH_4 and 2/42 for Ne, the ratio being 11/7 in favor of Ne. Thus although the varying pressure in the neon experiments makes exact calculation impossible, it is evident that the relative performance of the apparatus for these two gases is about that to be expected. These neon samples have been used in deuteron bombardment experiments by Professor Pollard and the writer. There is an indication that a subsequent separation of the neon isotopes was even better than the values just mentioned.

10 A. O. Nier, Phys. Rev. 57, 338 (1940).