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Partial Separation of the Isotopes of Chlorine by Thermal Diffusion

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The Clusius-Dickel isotope separator has been modified to allow larger scale separation of the isotopes of chlorine. The modified separator employs two coaxial Pyrex glass cylinders. A special design was necessary to allow for the heating and the resulting thermal expansion of the inner cylinder. The operation of the separator compares favorably with the operation predicted by the theory of Furry, Jones, and Onsager. The degree of isotope separation was determined directly by mass-spectrographic and spectrographic analyses. The concentration of Cl^{37} was also determined by measuring the amount of induced radioactivity resulting from deuteron bombardment of the sample to be analyzed. Sufficient chlorine gas containing 45 percent Cl^{37} was obtained for the determination by spectrographic means of the nuclear spin of Cl^{37}.

1. INTRODUCTION

THE phenomenon of thermal diffusion in which a concentration gradient is set up in a mixture of gases in the presence of a temperature gradient was first discovered by Enskog[1] in 1911 and independently by Chapman[2] in 1917. Clusius and Dickel[3] using a combination of thermal diffusion and fractionation have achieved great success in the separation of chlorine and neon into their isotopic components. Their apparatus consisted of a heated wire along the axis of a long vertical hollow tube into which was placed the gas whose isotopic components were to be separated. The combination of thermal diffusion and convective currents increased greatly the small separation produced by the temperature gradient alone. In general the light component goes to the hot wall and collects at the top while the heavy component collects at the bottom of the column.

The theory of thermal diffusion as applied to isotope separation of an element with two isotopes has been fully developed by Furry, Jones, and Onsager[4] for the case of a temperature gradient produced between two vertical plane walls at different temperatures. Corrections to the cylindrical case have been made by Furry and Jones.[5]

The separating power of such a thermal diffusion column is called the separation factor of the column which is independent of the relative proportion of the constituents of the gas to be separated. It is defined as

$$S=\frac{k_1(1-c_1)}{c_1(1-k_1)}=\exp\,(4A_Dl),$$

where C_1 is the initial concentration of component 1 and k_1 is its final equilibrium concentration at the other end of the column. Then $1-C_1$ and $1-k_1$ are the concentrations of component 2 at each end of the column. S may be obtained from the dimensions of the column and the physical properties of the gas; l is the effective length of the column; and

$$A_D=\frac{A}{(1-K_D/K)},$$

where

$$A=\frac{63}{4}\frac{\alpha\eta D}{\rho g w^4}f\left(\frac{\Delta T}{T}\right)$$

and

$$\frac{K_D}{K}=1890(T_1^2+T_1T_2+T_2^2)\left(\frac{D\eta}{w^3\rho g\Delta T}\right)^2.$$

The notation used is:

T_2, T_1 the temperatures of the hot and cold walls, $\Delta T=T_2-T_1$,
$2w$ equals the distance between walls,
D is the coefficient of ordinary diffusion,
ρ is the density of the gas,
η is the viscosity,
g is the acceleration of gravity,
$f(\Delta T/T)=1.016$ for $T_2=2T_1$, and
$f(\Delta T/T)=1.039$ for $T_2=3T_1$.

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[1] D. Enskog, Physik. Zeits. **12**, 56 and 533 (1911).

[2] S. Chapman, Phil. Trans. **A217**, 184 (1917).

[3] K. Clusius and G. Dickel, Zeits. f. physik. Chemie **B44**, 397–473 (1939).

[4] W. H. Furry, R. C. Jones, and L. Onsager, Phys. Rev. **57**, 1083 (1939).

[5] W. H. Furry and R. C. Jones, Phys. Rev. **57**, 561A (1940).

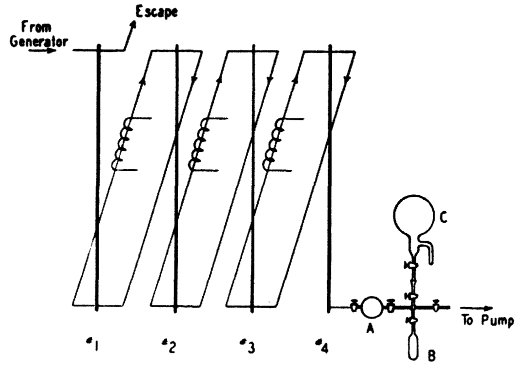

FIG. 1. Experimental arrangement.

For the case of rigid elastic spheres as applied to isotopic constituents Enskog's and Chapman's results reduce to

$$D_T/D = k_T = \alpha C_1 C_2$$

where D_T is the coefficient of thermal diffusion and

$$\alpha = 0.35(m_2 - m_1)/(m_2 + m_1),$$

the m's being the relative masses of the two constituents.

The coefficient of thermal diffusion vanishes for Maxwellian molecules. For molecules such that the forces vary as an inverse power of the separation which is less than five the lighter molecules accumulate in the colder part of the gas. Actual molecules in general lie between the case of hard spheres and Maxwellian molecules. The ratio, R_T, of α for hard spheres for which it is a maximum, to α for actual molecules has been calculated by Jones[6] and by Brown[7] on the basis of various molecular models. These values of R_T run from less than 0.10 for HCl and Cl_2 to over 0.6 for neon and the other noble gases.

2. EXPERIMENTAL

The experimental arrangement is shown in Fig. 1. The separation column consists of four stages which are convectively coupled together as shown. The first stage consists of two concentric glass Pyrex tubes, 1.3 and 2.2 cm in diameter. The inner cylinder is heated to 370°C by a spiral Nichrome ribbon heater while the outer cylinder is kept at room temperature by means of tap water flowing through the condensor surrounding the column. This stage is 3.5 m in over-all length with a gap space of 4.5 mm.

The construction of the three very effective last stages is shown in Figs. 2 and 3. The diameters of the two concentric tubes are 0.6 cm and 1.55 cm giving a gap space of 4.75 mm. The inner cylinder is heated to 375°C by a twenty-mil tungsten wire heated to incandescence which is suspended along the axis of the inner tube. The differential expansion of the tubes is taken up by a sylphon bellows prepared inside with Bakelite varnish to withstand the action of the corrosive HCl gas.

The HCl gas used in the separation was prepared by dropping chemically pure concentrated hydrochloric acid into concentrated sulphuric acid. The rate of production of the hydrogen chloride gas was governed by a dropping funnel equipped with a capillary tip. The gas was dried by passing it through, first, a tube containing glass wool, and second, through a sulphuric drying tower. The tower was double, allowing the gas to go either way thus preventing the possibility of blowing the acid back through the system. It is important to have pure and dry HCl since both Cl_2 and the associated molecule formed of HCl and H_2O will go to the "heavy" end of the tube and interrupt its action. A flow of 250 cm^3 an hour of HCl through the "light"

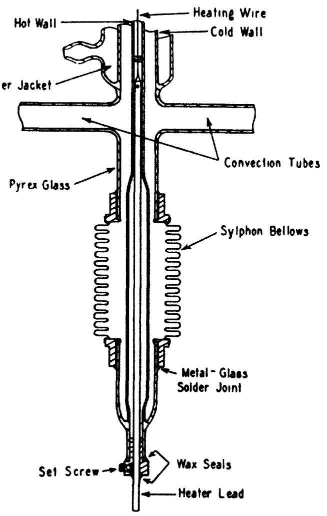

FIG. 2. Detail of lower end of last three stages.

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[6] R. C. Jones, Phys. Rev. **58**, 111 (1940).

[7] Harrison Brown, Phys. Rev. **57**, 242L (1940).

end was maintained to insure that the gas at that point did not become enriched in the light isotope.

A 20-cm^3 container placed between two stopcocks placed at the heavy end of the column allowed 20-cm^3 portions of the enriched HCl to be removed from the column without disturbing the equilibrium since the effective end volume of the tube is around 100 cm^3. The gas thus withdrawn could then be frozen down by the use of liquid air into appropriate containers for testing and further use. When the HCl was not needed in gaseous form, it was allowed to condense on ice at liquid air temperature.

The column was placed in operation by first evacuating it and then filling it to slightly over atmospheric pressure with gas from the generator. The tubes were then heated and the column allowed to come to equilibrium for 20 days without withdrawal of gas. After this time a total of 600 cm^3 of gas were withdrawn in 100-cm^3 portions over a period of 18 days. The column was then allowed to run for an additional ten days after which four 100-cm^3 portions were withdrawn at intervals of five days. Satisfactory proton bombardment analyses were obtained of each of these latter samples. The total gas withdrawn was made into one portion and converted into Cl_2 by oxidation of NaCl by means of MnO_2 and concentrated H_2SO_4. The chlorine formed was used for spectroscopic studies.

3. ANALYSES

When chlorine is bombarded with deuterons there results a radioactive product whose half-life is 37 minutes. It has been established that the radioactive product is Cl^{38} from the reaction

$$Cl^{37}+H^2 \rightarrow Cl^{38*}+H'.^8$$

Two equal portions of HCl gas, one being a normal sample and the other being an enriched sample, were given equal deuteron bombardments from the 28″ Sloane Laboratory cyclotron. The resulting radioactivity was measured by means of a calibrated Lauritson electroscope. The relative strengths of the two samples gives the relative concentration of Cl^{37}. A five-minute bombardment of 2 cm^3 of HCl at atmospheric pressure by a 0.5-microampere beam of 3.2 Mev deuterons was quite sufficient for measurement.

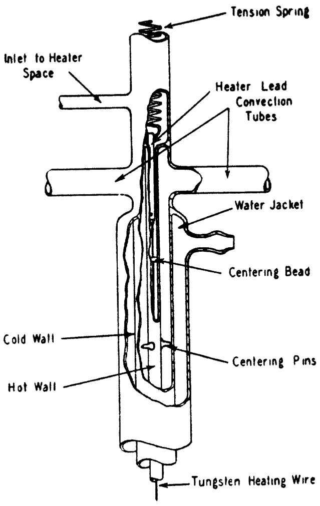

FIG. 3. Detail of upper end of last three stages.

Analyses of three of the last 100-cm^3 portions of HCl gas withdrawn gave an average concentration of 53.3 percent Cl^{37}.

If an atomic mixture consists of two isotopes, the relative abundance of various diatomic molecules which can be formed is given by the expression

$$(C_1a+C_2b)^2=C_1^2aa+2C_1C_2ab+C_2^2bb,$$

where a and b represent the two isotopes and C_1 and C_2 their relative abundances hence

$$\frac{I_{aa}}{I_{bb}}=\frac{C_1{}^2}{C_2} \quad \text{or} \quad \frac{C_1}{C_2}=\left(\frac{I_{aa}}{I_{bb}}\right)^{\frac{1}{2}},$$

where I_{aa} and I_{bb} are the intensities of lines due to the molecules aa and bb in the spectrum of the diatomic molecules.

A spectroscopic determination of the isotope abundance was made from the absorption spectrum of Cl_2 obtained from the total operation of the column. This determination showed a trifle over 45 percent of Cl^{37} present as compared to 24.28 percent of Cl^{37} in normal Cl_2.

4. DISCUSSION OF RESULTS

It is now a well-known fact that any degree of isotopic purity may be obtained if one is willing to build a thermal diffusion column that is long

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[8] E. F. Shrader and E. Pollard Phys. Rev. 59, 277–280 (1941).

enough. There is also sufficient evidence that the relatively simple theory outlined by Furry, Jones, and Onsager is fairly adequate in predicting the performance of such a column. Therefore, the main emphasis in this work was put on the production of a large amount of chlorine enriched in the heavy isotope for later spectroscopic study. In spite of the fact that the column was not run in a manner which best permitted a comparison with the theoretical predictions, it is interesting to make this comparison on the basis of the data available.

Column No. 1 was studied independently before the construction of the later column. After allowing the column to come to equilibrium a mass-spectroscopic analysis was made of a sample through the courtesy of Professor Urey of Columbia University. This analysis showed a concentration of 28.3 percent of Cl^{37} as compared to the original 24.28 percent Cl^{37}. This gives 1.18 as the maximum separation factor of the column.

The proton bombardment analyses of these last three samples taken show an average concentration of 53.3 percent Cl^{37}. This is with a transport of 0.80 cm^3/hr., S.T.P., of HCl with the assumption, of course, that a state of quasi-equilibrium has been established. For the last three columns, therefore, the separation factor is 2.89, or 1.42 for a single stage. For continuous operation with a transport $\tau = nH$ Furry, Jones, and Onsager give for the case of C_1 between 0.3 and 0.7 that

$$k - C_1{}^0 = (1 - \exp[-4{}_nA_dI])/4n.$$

From the transport the separation factor for true equilibrium may be obtained. This raises the separation factor for each of the columns to 1.45.

Before any calculations as to separation factors can be made a suitable value of R_t must be found. Brown calculates, from viscosity data, a value of $R_t = 0.12$ for chlorine, while Jones does not give any value, but indicates that it is small. For the purpose of this calculation a value of $R_t = 0.10$ was chosen.

For column No. 1 the actual performance fell far short of the theoretical predicted performance which was calculated to have a separation factor of 1.70. This fact indicated the necessity that any other columns built should be of different design. The theoretically predicted separation factors of columns No. 2–No. 4 were each 1.46. While it is impossible to compare the theoretically predicted performance with actual performance due to the approximations involved, it may be said that the last three columns outperform column No. 1. This is probably caused by the fact that their construction allows a higher degree of mechanical and temperature symmetry. The peripheral distance enters as the fourth power into the terms giving the remixing due to temperature asymmetry and this is quite important. The calculations show that the value R_t chosen is the right order of magnitude.

In conclusion the author wishes to thank Professor L. Onsager for his valuable suggestions and Professor E. Pollard for his help and advice in making determinations of the isotope concentrations by deuteron bombardment. The author is especially indebted to Professor W. W. Watson for his interest and guidance in this problem.