

Plants which are starred in Table 1 gave extracts colored by anthocyanins. These were removed by treating with a small quantity of Lloyd's reagent (hydrated aluminum silicate) and centrifuging. This also removes a little of the ascorbic acid but was the most satisfactory reagent for the decolorization that could be found out of a great many that were tested. It is also realized that certain other substances besides ascorbic acid can reduce the dye and that in cooking,

particularly when the liquid is discarded, there may be large losses of vitamin C. The values as determined for the fresh samples are given in Table 1.

For comparison, the average of several samples of fresh spinach by the same method was 0.812 milligrams of ascorbic acid per gram of fresh weight.

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SCIENTIFIC APPARATUS AND LABORATORY METHODS

A THERMAL METHOD FOR THE SEPARATION OF GASES AND ISOTOPES

Two methods are available for the separation of isotopes in quantity; one is the chemical, the other the physical. The chemical method, which will not be discussed in this paper, has been developed to a high degree of perfection by Professor Urey, of Columbia University. The physical method depends for its operation on the difference in the thermal behavior of the isotopes. As early as 1917 Chapman and Dootson¹ observed that when a gas consisting of two isotopes is placed in a tube heated at one end a slight concentration of the light component is induced in the heated portion of the tube by thermal diffusion. The effect in itself, however, is too small to serve as an efficient device for separating gases or isotopes. Within the last year processes have been developed which put the physical method on a practical basis. Clusius and Dickel² observed that, in an apparatus consisting of a cooled vertical tube with a heated wire down the center, an appreciable concentration of the heavy component of the gas is obtained at the bottom, while the light component rises to the top. The details given of the apparatus are so meager that an accurate description is impossible; it is stated, however, that the tubes vary in height from one to thirty meters and that the temperatures of the central wire range from 300 to 600° C. With the thirty-meter tube several liters of HCl³⁷, 99.4 per cent. pure, have been separated. These investigators describe the mechanism of operation as one arising from the combined action of thermal diffusion (the Chapman effect) which concentrates the light component at the heated wire, and to an overall convection current action which causes the gas to move upward along the heated wire and down along the cold wall. In this process the light gas is transported to the top of the tube and the heavy to the bottom.

Another modification of the thermal method has been developed in this laboratory.³ The mechanism of separation depends on the combined action of the

Chapman effect and an internal diffusion which results from the fact that molecules of different mass have different velocities when in thermal equilibrium. The basic principles involved in internal diffusion have been described in detail by Mulliken and Harkins.⁴ The most effective design of apparatus so far constructed here consists of two vertical concentric glass tubes, the outer one water-cooled, while the inner one is heated electrically. In a device of this type the heat is transferred from the hot wall to the cold by a series of swirls in the intervening gas and not by an overall convection current up the hot wall and down the cold. Direct transference of heat by conduction occurs only in a thin layer adjacent to the walls. It is a well-known fact that if two molecules, one light, the other heavy, impinge on a heated plate they receive the same amount of energy, except for a slight difference due to their accommodation coefficients. In the case of isotopes the accommodation coefficients are obviously the same. In consequence, the lighter molecules, on coming in contact with the heated inner tube, rebound with the greater average velocity and hence go ahead to enrich the front rank of the expanding gas. The reverse process occurs at the cold wall. This effect is still further enhanced by thermal diffusion, which tends to concentrate the light gas at the hot surface. As a consequence of this enrichment more light than heavy molecules are trapped by the overlying gas swirl, the net result being that the light gas moves upward and the heavy downward.

The operation of the apparatus is illustrated by the following experimental results. The object of these experiments was to determine the most efficient design of instrument and not the separation of large quantities of material. The tubes were all one meter in length and the outside diameter of the inner cylinder was 1 cm. A 50-50 mixture of methane and ammonia was used, because analysis could be made quickly by freezing out the ammonia with liquid air. The effect of wall

Bramley and Brewer, *Am. Chem. Soc. Abs.*, Baltimore meeting, April, 1939.

⁴ Mulliken and Harkins, *Jour. Am. Chem. Soc.*, 44: 37, 1922.

¹ Chapman and Dootson, *Phil. Mag.*, 34: 248, 1917.

² Clusius and Dickel, *Naturwiss.*, 26: 546, 1938.

³ Brewer and Bramley, *Phys. Rev.*, 55: 590 (A), 1939;

clearance was studied in a series of tubes in which the distance between the walls was varied from 1.3 mm to 22.0 mm. The gas separation (ratio of ammonia to methane) rose sharply with increasing wall clearance to a rather broad maximum at 7 mm. The effect of gas pressure was investigated from 11 to 60 cm of Hg for the different tubes. The 7 mm tube gave a maximum gas separation of 27 per cent. at 20 cm pressure. The pressure however is not critical nor is the optimum pressure the same for all gas mixtures. In these tests the temperature difference between the walls was 350° and the average temperature of the gas close to 150° . By varying the power input it was found that the final gas separation increased with the temperature difference between the walls. The rate of separation was investigated for a wall clearance of 7 mm and a temperature difference of 350° . The separation rose to 90 per cent. of its final value in 15 minutes. The absolute rate at which gas could be removed without decreasing the separation factor was not determined with accuracy; it was observed, however, that 1 cc of gas (N. T. P.) could be removed every 15 minutes without influencing the percentage separation. This speed suggests that a continuous flow method of operation should be feasible.

A number of gas mixtures have been studied in addition to the one mentioned above. The operation of the tube can be shown in a striking manner with a uniform 50-50 mixture of helium and bromine. In the course of a few minutes the bromine completely disappears from the top of the tube and becomes concentrated at the bottom. The separation of isotopes is easily demonstrated with HCl, in which gas the ratio of Cl^{35} to Cl^{37} was changed at a pressure of 20 cm from 3.2, its normal value, to 2.8 in a few minutes. The optimum conditions of operation depend, of course, on the nature of the gas. The results obtained with different gas mixtures lead to the conclusion that the separation depends primarily on the difference in mass of the two components divided by their sum.

Experiments have been performed which throw additional light on the mechanism of operation. When the entire tube was inclined 13° from the vertical the separation was decreased from 27 per cent. to 5 per cent. In another apparatus a series of corrugations was placed every 3 cm along the inner tube in such a manner that any gas moving along the heated wall would be deflected into the intervening space. In a 50-50 methane-ammonia mixture the average temperature of the gas was reduced about 15° and the final separation enhanced about 4 per cent. The design of the tube also appears to have a marked effect on the gas separation. A tube was built along the lines described by Clusius and Dickel with a heated tungsten wire extending down the center and a 7 mm clearance. After a run of several hours a smaller final separation

of the chlorine isotope was observed with an 800° difference in temperature than was obtained in 15 minutes with the concentric glass tubes for a 350° difference in temperature. A 350° difference in temperature gave only a negligible separation. A similar tube with a 4 mm platinum ribbon down the center failed to show an appreciable separation. It is evident that separation is augmented by symmetry of the two surfaces. An all-glass apparatus in which the outer wall was heated and the inner cooled gave a separation value only slightly lower than when the inner wall was heated; the average temperature of the gas, however, was materially higher.

The rate of mixing of the separated gases has been investigated for various tubes. The results show that the rate of back diffusion increases with wall clearance and becomes very rapid for outside tubes of larger diameter.

Reviewing the above results as a whole, it is evident that conditions involving both wall symmetry and corrugations enhance swirl definition and thereby enhance separation. On the other hand, separation is materially lower in straight wire or ribbon-centered tubes as well as in tubes having small wall clearances in which swirls are either poorly defined or impossible. It appears that the mechanism of separation is different in the two cases. Under conditions where swirls are well defined the separation results from the combined action of initial and thermal diffusion within the swirls. In wire-centered tubes or glass tubes with small wall clearances where the swirls are poorly defined, the mechanism may involve thermal diffusion and an overall convection current.

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BOOKS RECEIVED

- CONWAY, EDWARD J. *Micro-diffusion Analysis and Volumetric Error*. Pp. xiii + 306. 49 figures. Crosby, Lockwood, London. 25/-.
- CUMMINGS, ALEX., CHARLES, and SNYDER A. KAY. *A Text-book of Quantitative Chemical Analysis*. Pp. xv + 496. 85 figures. Van Nostrand. \$5.00.
- Meeting the Needs of the Mentally Retarded*. Bulletin No. 420 of the Department of Public Instruction, Commonwealth of Pennsylvania. Pp. 158. Illustrated. The Department, Harrisburg.
- MILLS, CLARENCE A. *Medical Climatology*. Pp. vii + 296. Illustrated. Charles C Thomas. \$4.50.
- POPE, CLIFFORD H. *Turtles of the United States and Canada*. Pp. xviii + 342 + v. 99 plates. Knopf. \$3.75.
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