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Partial Separation of the Oxygen Isotopes by Thermal Diffusion and the Deuteron Bombardment of O^{17} *,**

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With an eighteen-meter column, O^{18} has been enriched from the ordinary concentration of 0.2 percent to 17 percent and O^{17} from 0.04 percent to 0.8 percent. The former increase was determined by the mass spectrometer, the latter by the increased activity of F^{18} produced in the nuclear reaction $O^{17}(d, n)F^{18}$. The time rate of increase of the concentration of O^{18} was characterized by a step-wise nature, which arises from the staggering of the six three-meter tubes convectively coupled in series. A qualitative discussion of staggering is given.

THE apparatus consisted of six three-meter columns. The first three were constructed and used by E. F. Shrader for the separation of the chlorine isotopes.[1] They were all of the same dimensions, and consisted of an outer cold tube (I.D. 15.5 mm), cooled by a water jacket, and an inner hot tube (O.D. 6 mm). These tubes were of Pyrex glass and were kept concentric by means of groups of three, accurately ground, glass pins attached to the inner tube. The space between the tubes was 4.75 mm.

The inner tube was heated by means of a tungsten wire. This filament was centered by Lavite spacers at 15-cm intervals, and was kept under tension by a steel spring. The temperature of the inner tube was 373°C when 11.5 amperes were flowing through a 20-mil wire. About 770 watts are expended for each three-meter column. The tungsten filaments were at a temperature of 800°C and were in an atmosphere of nitrogen to afford good heat conduction and to prevent oxidation. An all-glass system for this was added to the original tubes and in five months of running no wire burned out. The differential expansion between the hot and cold tubes, which amounts to 2.5 mm, was taken care of by a thin brass sylphon bellows soldered in one end of the outer tube.

The other three tubes were of the Clusius and Dickel type.[2] In the first two, the inner diameter of the cold tube was 1 cm, and in the third it was 8 mm. The hot surface was a 15-mil platinum wire which was centered by cross wires attached by spot-welding. The wire was fastened to a 50-mil tungsten lead in a removable ground-glass joint fitting into the top of the tube. A copper weight, suspended from the end of the platinum wire, kept it straight and afforded electrical contact with a pool of mercury contained in a removable bottom. The expansion of the wire on heating was thus taken up by the lowering of the weight into the mercury. As there was no appreciable heating of the ground joints, they were kept tight with stopcock grease. About 300 watts per tube were required to keep the wire at a temperature of 700°C.

The columns were connected in series by convective coupling which produces the equivalent of a single column having a length equal to the sum of the effective lengths of each of the six tubes, i.e., 18 meters. Between the bottom of each column and the top of the next one are two connecting tubes, one at room temperature and the other heated to about 100°C. This procedure keeps the concentration at the top of one tube equal to that at the bottom of the preceding one. The oxygen was generated electrolytically at the rate of a half a liter per hour by passing a current of one ampere through five parts of distilled water and one part of concentrated sulphuric acid. Cylinders of platinum foil were used as electrodes. The gas was dried by being

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[1] E. F. Shrader and E. Pollard, Phys. Rev. **59**, 277 (1941).

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

passed through glass wool, calcium chloride, sodium hydroxide, and phosphorous pentoxide. The oxygen passes continually through the "top" of the first column, and keeps the concentration of O^{18} there at a constant value. An end volume of 300 cc was connected convectively to the "bottom" of the last column. Gas could be removed from there for the purpose of testing the separation factor during the period of operation. It is exploded with pure methane in a bulb provided with electrodes to form CO_2 which can be frozen down into a break-seal tube. This tube is then sealed off and can be connected to the mass spectrometer.

Each sample drawn off into the explosion bulb had a volume of 6 cc at N.T.P.; with this a little more than 3 cc of CH_4 was mixed by heating a convective return tube. The amount of CO_2 obtained was of the order of 2 cc, which gave a satisfactory pressure in the reservoir of the mass-spectrometer. Because of the oxidizing effect on the filament of the ion source of the mass spectrometer when O_2 is introduced, it was necessary to use CO_2. This introduces a peak at mass 45 owing to $C^{13}O^{16}O^{16}$ whose intensity is 1 percent of the normal $C^{12}O^{16}O^{16}$. Hence $C^{13}O^{16}O^{16}$ mask $C^{12}O^{16}O^{17}$ whose intensity is only 0.08 percent for unenriched oxygen. Because of the instability of the mass spectrometer when measuring on full sensitivity, it was impossible to estimate the increase of peak owing to mass 45 as the concentration of O^{17} increased. Figure 1 gives the separation factor of $O^{16}O^{18}$ from $O^{16}O^{16}$ as a function of the time.

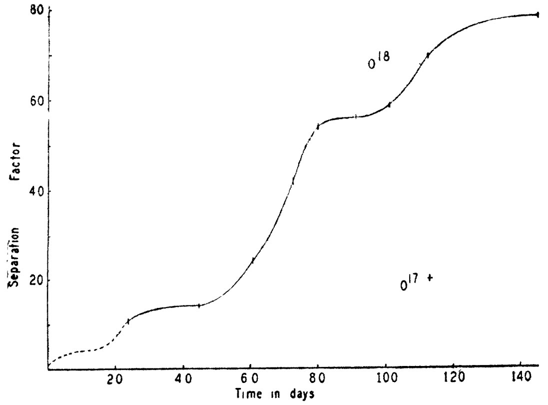

FIG. 1. Separation factor of O^{18} as a function of the time of operation.

The step-wise increase of the concentration of the rare isotope in the end volume may be explained quantitatively by setting up the equations of transport for each tube and introducing the effect of the convective coupling tubes which act as reservoirs between the diffusion tubes.[3] The phenomenon may also be explained from a graphical consideration. In Fig. 2 the rectangles at the bottom indicate the transport of each of two tubes. The transport T_2 of the heavy isotope is given by the expression

$$T_2 = H\left\{c_2(1-c_2) - \frac{1}{2A}\frac{\partial c_1}{\partial z}\right\},$$

where H and A are constant in time and along the tube (the z direction) and c_2 is the relative concentration of the heavy isotope.[4] If c_2 is small and there is no concentration gradient, then the transport is equal to Hc_2. After the tubes have been in operation for a period of time, the concentration in the second tube will be larger than that in the first so the transports will be approximately equal only if the value of H for the second tube is proportionally smaller than that for the first tube. With these values of H, then at the beginning of operation, the transport of the first column will be greater than that of the second.

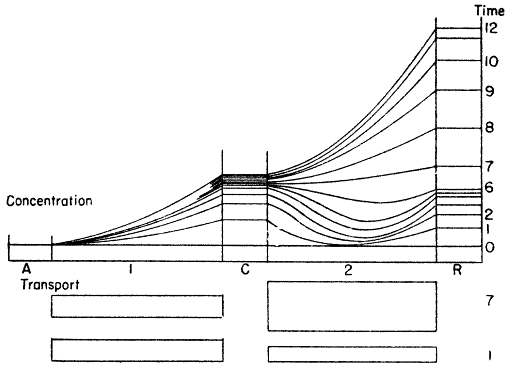

FIG. 2. Distribution of the concentration of a rare isotope in two thermal diffusion columns (1) and (2), connected by convective coupling pipes *C*. The time interval between successive curves is always the same. The step-wise rate of increase of concentration in the end volume reservoir (*R*) is apparent.

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[3] L. Onsager, by private communication.

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

Above the transport rectangles in Fig. 2 is plotted the concentration c_2 against the length down the tubes. Each curve is for a particular time, and the time interval between adjacent curves is the same. The concentration at A is kept constant by the continual flow of ordinary oxygen through the top of the apparatus. At time t_1, the concentration in the convective tube C will be greater than that in the reservoir R, because the transport of 1 is greater than that of 2, assuming the volumes of C and R are the same. The concentration of 2 near C will be larger than that near the middle, because of diffusion and convection from C. The rate of increase of the concentration in C will decrease because of the diffusion and convective flow into 2. There is no effect of this concentration wave on the transport of 2 until it reaches the end of 2. Until this time, the concentration of the end volume rises exponentially with time. When the concentration wave does reach the end volume, there is a rapid increase in concentration. Now the concentration of the whole tube is much higher than at the start, and consequently the transport is larger. The two tubes now begin to act as one and there is now another exponential decrease in the rate of increase of the end volume concentration. The addition of a third tube would introduce another wave and hence a third step in the concentration-time plot. Just such an effect is noticed in the separation of oxygen.

Clusius and Dickel separated air with several columns of different gap spaces, with several temperature differences, and different pressures.[2] From the factors they obtained, a rough idea of the performance of the hot wire columns used for oxygen alone can be calculated. The separation factor for the hot tubes of Shrader can be calculated for oxygen from their performance with chlorine.[1] The difference in the constants η, ρ, D, and α must be taken into account in each case, as well as the fact that α differs slightly in form for isotopic molecules and non-isotopic ones.

The operation of the columns can also be predicted upon the theory of Furry, Jones, and Onsager for the flat wall case.[4] The theoretical separation factors are always much larger than the actual ones, both because of asymmetry effects and because the flat wall assumption is a poor approximation to the hot wire columns. There is considerable uncertainty as to the value of α that should be used; that value determined from viscosity measurements is particularly unreliable in the temperature range used.[5] In addition the separation factor is quite sensitive to the value of the average temperature used in calculating the gas constants. The mean temperature $\frac{1}{2}(T_1+T_2)$ is certainly not correct for the hot wire case.

The expected equilibrium separation factors for the hot wire columns on the basis of the results of Clusius and Dickel are 4.2 and 4.7 for the 1 cm and 8 mm (I.D. of cold tube) tubes, respectively. It is interesting to note that the plateaus of Fig. 1 come at 4.15 (unobserved), $4.15\times 3.65=15.2$, $4.15\times(3.65)^2=56.0$, etc., indicating that the separation factors of the hot wire tubes are approximately 3.65 and 4.15, respectively, about ten percent smaller than the expected values. In addition the time dependence is correct as may be seen from a calculation of the relaxation times. Thus the theory of staggering outlined above may be considered qualitatively verified.

In order to have the convective coupling tubes operate effectively, the flow of gas through them must be large enough so that there is no appreciable change in concentration between the points that they connect. The flow of gas in cc per second through the tubes is given by

$$v=\frac{\pi g M p \Delta T d^4}{2.1\times 10^4 \eta T^2},$$

where M is the molecular weight of the gas, p is the pressure in atmospheres, ΔT is the difference between the temperature of the gas in the hot tube and that of the gas in the cold tube, d is the diameter of the tube, η is the viscosity, and T is the geometric mean between the temperature of the hot and cold gas.

It can easily be shown that the separation factor of the tubes is given by

$$\Delta S=\frac{c_1'}{c_1}\cdot\frac{c_2}{c_2'}=1+\frac{N_1}{Nc_1}-\frac{N_2}{Nc_2},$$

where c_1 and c_2 are the relative concentrations of species 1 and 2 in one tube and the primed

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[5] M. Trautz and R. Heberling, Ann. d. Physik **10**, 155 (1931).

quantities are for the other tube. N_1 and N_2 are the net forward transports of species 1 and 2, and $N=\rho v$, the mass of gas passing through a cross section of the tube per second. For ΔS to be less than 0.1 percent different from unity, the diameter of the convective tubes for the last columns can be as small as 5 mm for a $\Delta T=50°\text{C}$. Without departing too far from perfect coupling, the volume of the convective tubes should be as small as possible in order that the holdup of gas, and therefore the relaxation time, may be smaller.

DEUTERON BOMBARDMENT OF OXYGEN

Yasaki and Watanabe noticed a 114-minute activity from a tungsten oxide target which had been bombarded by deuterons.[6] F^{18} is known to emit positrons and the half-life is of this value.[7] There is, therefore, the question as by which isotope of oxygen the reaction is caused. There are two possibilities, either $O^{16}(d, \gamma)F^{18}$ or $O^{17}(d, n)F^{18}$. As both neutron and gamma-ray detection are difficult near the cyclotron, some other means of deciding between the two is advisable.

Yasaki and Watanabe were of the opinion that the reaction was not caused by the very rare O^{17} whose normal concentration is only 0.04 percent. W. L. Davidson[8] studied the reaction both by varying the energy of the incident deuterons and by calculating the cross section of the reaction, and found results which are characteristic of the (d, n) reaction. He concluded that the rare isotope is responsible.

A definite proof of the validity or falseness of this conclusion can be obtained by using two targets, one containing ordinary oxygen and the other containing an equal amount of oxygen enriched in the heavy isotopes. If, after bombarding each the same length of time and with the same intensity of beam, the enriched target showed an increased activity, the O^{17} is the isotope responsible. The only other reactions involving deuterons on oxygen which give radioactive products are $O^{16}(d, n)F^{17}$ (70 sec.), $O^{18}(d, p)O^{19}$ (31 sec.), and $O^{18}(d, \alpha)N^{16}$ (8 sec.). These will not interfere with the measurement of the 114-min. activity.

The tungsten targets, 1.7 cm in diameter and 1-mm thick, were cleaned by heating to a dull red and then applying sodium nitrite. After thorough washings and subsequent drying, the target was weighed. It was then placed in a quartz tube which contained oxygen at a pressure of approximately 18 cm of Hg. After two hours of heating at 700°C, the pressure had dropped to 4 cm. The increase in weight was about 40 milligrams. Each target was bombarded for 90 minutes by a 3.7-Mev deuteron beam of 0.9 microampere intensity. The activity was measured with a Lauritsen electroscope and for the enriched oxygen target was 20.4 times that for the ordinary oxygen one.

This factor is just what one would expect to obtain for the separation factor of O^{17} at the time the enriched oxygen was withdrawn. The rate of approach to equilibrium is much more rapid for O^{17} than for O^{18}, mainly because the equilibrium separation factor for the former is only the square root of that for the latter.

A careful measurement of the half-life of F^{18} gave 112 minutes. The energy of the emitted particles was in agreement with the accepted value, 0.7 Mev.[6] A magnetic analyzer checked the sign of the charge as being positive.

The Schumann-Runge bands in absorption of 17 percent (atomic) O^{18} heated to 800°C[9] failed to reveal bands caused either by the 18,18 molecule or by the 18,16 one. At this atomic concentration, the molecular concentration of 18,18 is only 4 percent of that of the 16,16 one, while the molecular concentration of 16,18 is only 10 percent. The failure to observe these bands is characteristic of work with absorption spectra, and it is estimated that a concentration of the order of 50 percent (atomic) would be necessary in order to determine (as well as detect) the alternating intensity ratio of the rotational lines of the enriched molecule.

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[6] T. Yasaki and S. Watanabe, Nature **141**, 787 (1938).

[7] A. H. Snell, Phys. Rev. **51**, 143 (1937).

[8] W. L. Davidson, Jr., Phys. Rev. **57**, 1086 (1940).

[9] C. Füchtbauer and E. Holm, Physik. Zeits. **26**, 345 (1925).