

plaining his lower experimental result for the concentrated cathode condition.

Working with a poorer vacuum and using solid cathodes, Easton, Lucas and Creedy<sup>4</sup> have found considerably lower force values than these, though in the same order of magnitude. Two copper cathodes gave 7 and 5.5 dynes per amp. respectively and zinc gave 14. Their curves bend upward slightly.

#### SUMMARY

The horizontal component of the force at a cathode line between mercury and a vertical anchor has been measured, first roughly by the

<sup>4</sup> Easton, Lucas and Creedy, *Elec. Eng.* **53**, 1454 (1934).

depression of the meniscus edge, then more accurately by means of a torsion system.

The orientations of a magnetic field which deflected the cathode line neither one way nor the other were determined as current and anchor angle were varied.

Assuming that these neutral directions gave the directions of the resultant cathode force, this resultant was calculated from the horizontal components and was found to vary from 35 dynes amp.<sup>-1</sup> at low currents from the 1-cm wide vane to 66 dynes amp.<sup>-1</sup> at 10 amp.

Both the neutral angle experiment and this result show that the effects of concentrating emission at the cathode line are not simply additive.

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## The Separation of Gaseous Isotopes by Diffusion

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The design and use of a 34-member apparatus of the Hertzian type for the separation of gaseous isotopes by diffusion are described. Results of tests of the speed of various types and numbers of separation members are given. Tests on mixtures of carbon dioxide and argon at a few millimeters pressure give the same results as tests on the neon isotopes. The equilibrium time, from ten to fifteen hours, and the separation factor, 80, of a 24-member apparatus, working on mixtures of such gases, are found

to be independent of the initial mixing ratios. Results obtained with the 34-member apparatus on methane, to concentrate C<sup>13</sup>, and on nitrogen, to concentrate N<sup>15</sup>, are shown to be in reasonable agreement with appropriate theory. Methane containing 16 percent of C<sup>13</sup>H<sub>4</sub><sup>1</sup>, and nitrogen containing 6 percent of N<sup>14</sup>N<sup>15</sup>, instead of the normal 1 percent and 0.6 percent, respectively, have been produced.

**I**N this laboratory<sup>1</sup> an apparatus has been constructed similar to that described by Hertz,<sup>2</sup> which utilizes the difference in the thermal velocities of molecules of different weights to separate the isotopes of a gas. In principle, the apparatus works as follows. The mixture of gaseous isotopes it is desired to separate is circulated through a series of porous-walled tubes by diffusion pumps, as shown in Fig. 1. The tubes, which are alternately short and long, are surrounded by individual Pyrex jackets, connected to the low-pressure side of mercury diffusion pumps, as shown in the figure. The gas which diffuses through the wall of a long tube is pumped back

into the system at a point just to the right of the adjacent short tube. Now this gas will be a little richer in the lighter isotopes than that which passed on toward the left. Similarly, the portion of this gas which diffuses through the wall of the adjacent short tube on the right will be still lighter, and so on. Thus, on the average, there is a net transfer of the lighter isotopes toward the right, or "light" end of the apparatus, while the

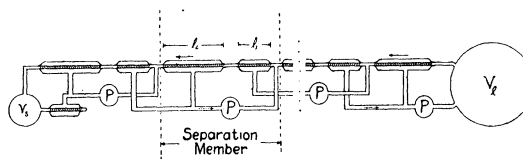


FIG. 1. Arrangement of porous walled tubes.

<sup>1</sup> Norman Bridge Laboratory of Physics, Pasadena.

<sup>2</sup> G. Hertz, *Zeits. f. Physik* **79**, 108 (1932).

heavier isotopes tend to gather in the reservoir provided at the left, or "heavy" end.

Since the system is closed, an equilibrium must eventually be reached. Hertz has treated the case of a mixture of two isotopes. He showed<sup>2</sup> that, in equilibrium, the ratio of the density of the heavy molecules to that of the light molecules increases from one separation member to the next by a factor

$$q = f^\mu / (1 - (1 - f)^\mu),$$

where  $f = 1 / (2 + l_2 / l_1)$ ;  $\mu = (m_l / m_H)^{1/2}$ .

" $q$ " he has called the "separation factor" of a single member. For an apparatus of  $m$  members, the separation factor is obviously  $q^m$ . This result was derived for the usual case, in which the relative abundance of the heavier isotope is small. He also assumed, in his derivation, that no backward diffusion occurs, either along the tubing or through its walls. If  $l_1$  is made too small, gas passes from one separation member to the next chiefly by diffusion along the tubes, and a different relation applies.<sup>3</sup> In general, the speed of separation is less for an apparatus with  $l_1 = 0$ , but it has been thought to give a higher separation factor.

In our preliminary tests of various types of separation members, an apparatus with two pumps was constructed. Unglazed pyrometer tubing, obtained from the Stupakoff Laboratories in Pittsburgh, Pa. has been used throughout the work done here; it can be sealed directly to Pyrex. The circulating pumps were, initially, ordinary first-stage mercury diffusion pumps. The apparatus had end volumes of 3 liters and 200 cc at the light and heavy end, respectively. Mixtures of nitrogen and carbon dioxide, at pressures of from 3 to 15 mm, were used in this early work. The composition of the gas in  $V_s$  was followed continuously during the diffusion process by means of a Pirani gauge, which had been calibrated previously at various pressures by known nitrogen-carbon dioxide mixtures. More precise single analyses were made by measuring the pressure before and after freezing out the carbon dioxide in liquid air.

We found, early in this work, that ordinary high vacuum mercury pumps are not suitable for circulating gas at pressures of several milli-

eters of mercury. Tests of several pump designs led to the adoption of a single-stage pump having a flat boiler, to prevent bumping, a condenser of length 6 inches and I.D.  $\frac{3}{8}$ ", and a jet of O.D.  $\frac{9}{32}$ ", set  $\frac{1}{16}$ " down into the condenser. With such a pump, the pressure outside a porous tube in the diffusion apparatus can be maintained at less than  $\frac{3}{4}$  mm when that inside is 12 mm. This requires a mercury vapor pressure of 6 cm in the boiler of the pump. In operation, enough heat is supplied to the pumps, by Bunsen burners, to maintain a mercury column in each of about 8 cm.

The care taken to develop adequate pumps was justified, not only by the attainment of greater speed of separation, but by the elimination of the surprisingly large decrease in the separation factor caused by failure of the pumps to maintain a negligible pressure outside the porous tubes. If  $y$  represents the ratio of this pressure to that inside the tube, the usual expression for  $q$  must be modified by replacing  $\mu$  by  $\mu'$ , where

$$\mu' = \mu [1 + y(1 - \mu)].$$

Since  $q$  is quite sensitive to small changes in  $\mu$ , this correction may be quite appreciable, even if  $y$  is only about 0.1.

Separation members were constructed and tested for which:

1. I.D. = 5.0 mm; O.D. = 7.0 mm
  - a.  $l_1 = 12''$ ;  $l_2 = 12''$
  - b. 6 12
  - c. 4 12
  - d. 2 12
  - e. 0 12
2. I.D. = 5.5 mm; O.D. = 8.0 mm
  - a.  $l_1 = 1''$ ;  $l_2 = 12''$
  - b. 1 18
  - c.  $1\frac{1}{3}$  12
  - d.  $1\frac{1}{3}$  18
  - e. 2 24
3. I.D. = 2.95 mm; O.D. = 4.32 mm
  - a.  $l_1 = 1\frac{1}{3}''$ ;  $l_2 = 12''$

All tubes were made of the same material (Stupakoff E-42 tubing).

The measurements showed that, when running on a carbon dioxide-argon mixture (of initially equal proportions) at 6 mm pressure, the apparatus required an equilibrium time not measurably greater for case 1d than for 1a, whereas for

<sup>3</sup> Harmsden, Zeits. f. Physik 82, 589 (1933).

TABLE I. Comparison of the experimental results with theory in the case of a mixture of carbon dioxide and argon.

$t$  is the time the diffusion has been in progress.  $R_s$  is the ratio of the pressure of carbon dioxide and argon in the sample removed from  $V_s$ .  $R_l$  is the ratio of the pressures of argon and carbon dioxide in the sample removed from  $V_l$ .  $Q (= R_s R_l)$  is the separation factor of the apparatus.

	$t$	$R_s$	$R_l$	$Q$
Run 1: $p = 6.9$ mm				
	0	1/2.7	2.7	1
	6.5 hrs.	10.0	5.0	50
	26	14.8	5.75	85
Run 2: $p = 6.80$ mm				
	0	1/10	10	1
	8	1.57	48	75
	30	1.50	59	88
The gas of this run was then allowed to stand in the system for 15 hours, then circulation was recommenced:				
	0	?	?	
	10	1.11	70	78
	28	1.04	72	75
Run 3: $p = 6.60$ mm				
	0	1/50	50.0	1
	11	0.21	350	74

case 1e it was four times as great. This led to the use of separation members having a low, but not actually zero, value of  $f$ . In its final form the apparatus has units of all five types listed under "2" in the foregoing. These units have almost identical characteristics.

Later, runs were made with systems of five and ten members, to compare their equilibrium times. For these comparisons types 2c and 2d were used. A  $10\frac{1}{2}$  mm run on a carbon dioxide-nitrogen mixture (of initially equal proportions) was completed in 30 minutes using five members, and in 90 minutes using ten. The final separation factors were at least 7.5 and 50, respectively. For these tests,  $V_l$  was 5 liters and  $V_s$  was 200 cc.

Apparatus of more than ten separation members was tested with mixtures of carbon dioxide and argon. Analyses were made by pressure measurements before and after freezing out the carbon dioxide. The mass ratio 40 : 44 for mixtures of such gases is exactly that of the neon isotopes. Before using the results of tests made with this mixture, it seemed advisable to see if this separation factor was the same as that obtained with the neon isotopes. With 14 members, 11 mm runs on carbon dioxide-argon mixtures (of initially equal proportions) gave a separation factor of 8 or 9. Similar runs on neon gas were made and four analyses of the end-products, us-

ing a mass-spectrometer,<sup>4</sup> agreed in assigning a value of between 6 and 10 to the separation factor, the average being 7. The agreement between these results seemed to justify the simpler method of testing. It should be remarked here that the results obtained with carbon dioxide-argon mixtures are always consistent with those obtained in the actual separation of isotopes, provided that the pressure of the carbon dioxide-argon runs is not over 10 or 11 mm. At higher pressures the separation factor drops rapidly, probably because of the setting in of viscosity effects which invalidate the simple diffusion ideas on which the theory of the apparatus has been founded. It seems likely that similar viscosity effects should appear in actual isotope separations, but so far no evidence for this has been found, for pressures up to 12 mm.

Table I affords a comparison of the experimental results with theory, and gives an idea of the time of equilibrium of the apparatus, for various initial mixing ratios of the component gases. These data were obtained with carbon dioxide and argon in an apparatus of 24 separation members, for which  $V_l$  was 5 liters and  $V_s$  was 300 cc. The apparatus contained five members of type 2a, five of type 2b, five of type 2c, five of type 2d, and four of type 2e. In Table I " $t$ " shows the length of time the diffusion has been in progress; " $R_s$ " denotes the ratio of the pressures of carbon dioxide and argon in the sample removed from  $V_s$  and analyzed; " $R_l$ " is the ratio of the pressures of argon and carbon dioxide in the sample removed from  $V_l$  and analyzed; " $Q$ " is the separation factor of the apparatus, i.e.,  $Q = R_s R_l$ . Each analysis of  $R_s$  and  $R_l$  involved the removal from each end of the system of enough gas to fill a 600 cc volume to a pressure of from 0.5 to 1.0 mm of mercury.

Such data clearly show that neither the separation factor nor the equilibrium time depends appreciably on the initial mixing ratio of the gases, for carbon dioxide-argon mixtures in the 24 member apparatus. These measurements give the separation factor to be about 80, and the time of equilibrium to be of the order of 10 to 15 hours. The calculated separation factor for this apparatus is 73. The apparent greater than 100

<sup>4</sup> D. D. Taylor, Phys. Rev. **47**, 666 (1935).

percent efficiency signifies little, since small errors in the lengths of some of the porous tubes could easily account for this difference, if indeed it is real.

But one is ordinarily interested, not in  $Q$ , but in the enrichment factor,  $E$ , which is the ratio of the relative abundance of the heavier isotope in  $V_s$ , after equilibrium is reached, to that in the gas initially admitted to the system. If  $E$  is to approach  $Q$ , it is evident that  $V_l$  should be large compared with the volume of the rest of the system, so that  $R_l$  is nearly constant. Even though  $V_l$  is 22 liters in the final diffusion apparatus,  $E$  is always quite appreciably less than  $Q$ . It can be shown that, when equilibrium has been reached:

$$x_0/P = (-b + (b^2 - 4ac)^{1/2})/2a,$$

where  $a = q^{m+1} - 1$ ;  $b = r q^{m+1} + 1 - (p_0/P)t(q^{m+1} - 1)$ ;

$$c = -(p_0/P)t$$

and  $r = (V_s + V_e)\rho^{m+1}/V_l$ ;

$$t = [V_l + \rho^{m+1}V_s + v(1 - \rho^m)/(1 - \rho)]/V_l,$$

while

$$V_e = v \frac{[(q^{m+1} - 1)/(P/x_0) + 1]}{(\rho q)^{m+1}} \sum_{n=1}^m \frac{(\rho q)^n}{(q^n - 1)/(P/x_0) + 1}$$

where  $x_0$  is pressure of heavy isotope in  $V_l$ ;  $P$  is total pressure in  $V_l$ ;  $p_0$  is pressure of heavy isotope in gas when separation was started;  $m$  is number of separation members;  $q$  is separation factor for one member;  $\rho$  is factor by which total pressure in  $n$ th separation member from  $V_l$  exceeds that in  $(n-1)$ st member (always less than 1);  $v$  is volume of a separation member.

In practice, it is necessary to solve for  $x_0/P$  and  $V_e$  simultaneously, by successive approximations. All other quantities are known except  $v$ , the volume of a separation member. This cannot be determined from geometrical considerations alone because the gas pressure in the pump boilers, and its effective contribution to  $v$ , is not known. For the data in Table I, an assumed value of 110 cc for  $v$  fitted all the experimental results, so this value has been used in subsequent computations.

The present apparatus has 34 members, five more members of type 2b, and five of type 2d having been added. A 22-liter Pyrex bulb is used

for  $V_l$  and a 300 cc or 400 cc one for  $V_s$ . The pressure gradient in this apparatus depends on the pressure in  $V_l$ . When this pressure is 10 or 11 mm, the pressure in  $V_s$  is only 6 or 7 mm; when  $p_l$  is 8 mm,  $p_s$  is about 4.

The porous tubes used are somewhat hygroscopic, so that preliminary flushings to remove water and absorbed gas must usually precede a separation run. The run itself is generally performed at a pressure (in  $V_l$ ) of 10 or 11 mm. Somewhat arbitrarily, 24 hours of circulation has been fixed upon as ample and convenient for a separation process. Ordinarily, several 300 cc samples are removed from  $V_s$ , at 24-hour intervals, for each filling of the system. This removal is facilitated by using a magnetically operated mercury cut-off to shut off  $V_s$  from the diffusion system while its contents are being pumped into storage bulbs by a mercury diffusion pump like those in the diffusion apparatus.

During the separation process the spectrum in a small capillary discharge tube sealed into  $V_s$  is watched through a small pocket spectroscop<sup>e</sup> for the appearance of impurities. When any real concern is felt as to the extent of impurities in the final sample, a molecular weight determination is made by means of a quartz fiber gauge,<sup>5</sup> into which a small amount of the contents of  $V_s$  may be admitted. If, as is often the case, the gas initially admitted to the diffusion system contains several tenths of a percent of heavy impurities, it is necessary to remove this by a preliminary separation run. This, of course, decreases the enrichment factor.

Occasionally we have used multiple diffusions to increase the effective enrichment factor of the apparatus. This involves collecting gas from the heavy end of the system at the end of several diffusions and reintroducing this, together with enough ordinary gas to fill the system, for the final separation process. Another scheme tried has been that used by Hertz<sup>6</sup> in his work on heavy hydrogen. He ran a discharge tube continually in his diffusion apparatus, in order to break up the  $H^2H^1$  molecules and form, by recombination,  $H^2H^2$  molecules. This device might be useful whenever the gas being worked with is

<sup>5</sup> Haber and Kirschbaum, *Zeits. f. Elektrochemie* **20**, 296 (1914).

<sup>6</sup> Hertz, *Naturwiss.* **21**, 884 (1933).

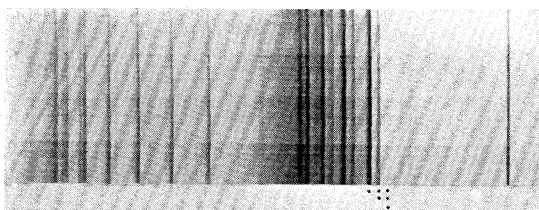


FIG. 2. Photograph of the Swann bands of  $C_2$  showing an enrichment factor of about 16 in  $C^{13}$ . The single dot marks the head of the  $\lambda 4737A$   $C^{12}C^{12}$  band; the double dot, the head of the  $\lambda 4744A$   $C^{12}C^{13}$  band; the triple dot marks the corresponding  $C^{13}C^{13}$  band head. (Photograph taken by F. A. Jenkins.)

of the form  $X_2$ —i.e.,  $H_2$ ,  $N_2$ ,  $O_2$ , etc. It can be shown that ordinarily (when the separation factor is not too high) the use of a discharge tube in this way can result in doubling the separation factor.

#### DESCRIPTION OF RESULTS

Results obtained in separations performed with this apparatus on methane, to concentrate  $C^{13}$ , and on nitrogen gas, to concentrate  $N^{15}$ , have been reported in recent issues of the *Physical Review*.<sup>7, 8</sup> In Fig. 2 is reproduced a photograph of an intensity plate taken by F. A. Jenkins, of the Physics Department of the University of California, of the Swann bands of  $C_2$ . The discharge was produced in argon containing some of the methane gas which had been run through the 34 member diffusion apparatus described herein. The single dot marks the head of the  $\lambda 4737A$   $C^{12}C^{12}$  band, the double dot the head of the  $\lambda 4744A$   $C^{12}C^{13}$  band, while the triple dot marks the corresponding  $C^{13}C^{13}$  band head, which can be seen in the lower steps of the photograph. Microphotometer measurements yielded a value of  $3.3 \pm 0.2$  for the relative intensities of the  $C^{12}C^{12}$  and  $C^{12}C^{13}$  bands. The intensity of the  $C^{13}C^{13}$  band (three dots), which could also be measured, was consistent with this. The relative intensity of these bands, in normal carbon, is  $53 : 1$ .<sup>9</sup> The enrichment factor of the process which produced this heavy gas was, therefore, about 16. This was an occasion on which heavy

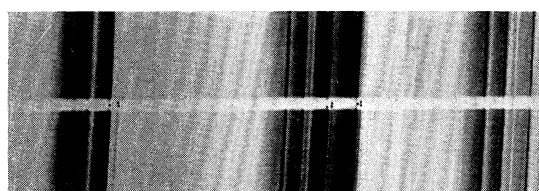


FIG. 3. Photograph of a part of the band system of  $N_2$  in the  $\lambda 3000A$  region. Upper photograph, ordinary  $N_2$ ; lower photograph, with nitrogen enriched in the  $N^{15}$  isotope.

gas was lost by preliminary purification runs, while this was compensated for by a multiple diffusion process such as described in the foregoing, wherein two preliminary runs were employed. The result is in as good agreement with the theory as could be expected, in view of the quantitative uncertainties of this method.

In Fig. 3 are shown photographs, also taken by Jenkins, of part of the band system of  $N_2$ , in the  $\lambda 3000A$  region. The upper photograph is of a discharge in gas containing ordinary  $N_2$ ; the lower is of a discharge in gas containing  $N_2$  which had been run through the diffusion apparatus. Single dots mark  $N^{14}N^{14}$  band heads, double dots the corresponding  $N^{14}N^{15}$  heads. Measurements<sup>10</sup> of the intensities of the normal and isotope bands of nitrogen have assigned a value of  $175 : 1$  to this ratio, for ordinary gas. The corresponding ratio was found by Jenkins to be  $16.5 : 1$  for the enriched gas. Three preliminary diffusions were employed in the work with nitrogen. Theory and experiment check as well as can be calculated, on the assumption that the efficiency of the diffusion process is 100 percent.

More recently, oxygen has been treated in this way, but no measurements of the results have yet been made. For the near future, work on argon is projected, to concentrate  $A^{36}$ .

Acknowledgments are due Dr. F. A. Jenkins, for the photographs and analyses of band spectra reproduced here; to Dr. D. D. Taylor, for assisting in the mass spectrometric measurements on neon; and to Drs. B. N. Sage and W. N. Lacey, of the Chemistry Department of the California Institute of Technology, for supplying us with the pure methane gas used in some of this work.

<sup>7</sup> Wooldridge and Jenkins, *Phys. Rev.* **49**, 404 (1936).

<sup>8</sup> Wooldridge and Jenkins, *Phys. Rev.* **49**, 704 (1936).

<sup>9</sup> F. A. Jenkins, *Proc. Koninklijke Akademie van Wetenschappen Te Amsterdam*, **35**, 10, 1212 (1932).

<sup>10</sup> Murphy and Urey, *Phys. Rev.* **41**, 141 (1932).

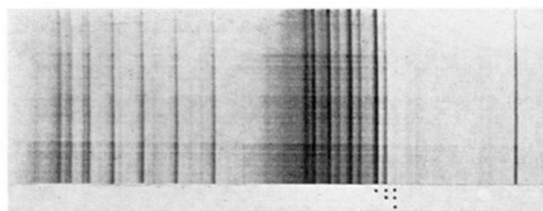


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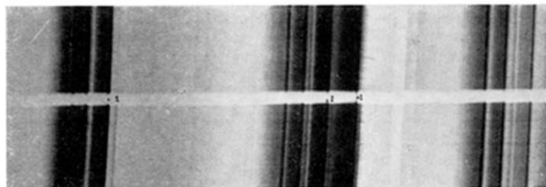


FIG. 3. Photograph of a part of the band system of  $N_2$  in the  $\lambda 3000\text{\AA}$  region. Upper photograph, ordinary  $N_2$ ; lower photograph, with nitrogen enriched in the  $N^{15}$  isotope.