THE SEPARATION OF GASEOUS ISOTOPES BY DIFFUSION

Thesis

by

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ABSTRACT

An apparatus has been constructed, similar to that of G. Hertz[3], making use of the difference in the thermal velocities of molecules of different weight to separate the isotopes of a gas. The problems of design and their solution are discussed in detail. Data are given to show the separation and equilibrium time of apparatus of sevefal types, when used to separate mixtures of various initial concentrations of hydrogen and nitrogen, carbon dioxide and nitrogen, and carbon dioxide and argon. Mass spectrometer measurements on the end-products of a separation process performed on the neon isotopes, with an apparatus containing fourteen mercury diffusion pumps, show the separation to be the same as for mixtures of carbon dioxide and argon, for which the mass ratio, 44:40, is the same as the 22:20 ratio of the neon isotopes. Separation processes performed with an apparatus of twenty-four pumps on carbon dioxide-argon mixtures reveal that the separation factor--i. e., the ratio of the relative abundance of the heavy gas at one end of the system to its relative abundance at the other end, when equilibrium has been reached--and the equilibrium time are practically independent of the initial mixing ratio of the components.

Hertz' approximate theory of the diffusion apparatus is extended to permit the calculation of the "enrichment factor"--i. e., the ratio of the relative abundance of the heavy gas at the "heavy" end of the system, after equilibrium is reached, to its relative abundance in the gas initially admitted to the system. The effects of impurities, viscosity, pressure gradients in the system, and insufficient pumping speed are discussed quantitatively.

Work done on methane, to concentrate C^{13}, and on nitrogen, to concentrate N^{15}, is described. Photographs of the band spectra of C_2, CN, and N_2 are given which show isotope bands of sufficient intensity to make possible quantitative mass measurements on the rare isotopes C^{13} and N^{15}. Methane has been produced containing 16% of C^{13}, and nitrogen gas has been produced containing 3.3% of N^{15}, instead of the 1% and 0.3% in the respective normal gases.

I. Introduction

In the past, many attempts have been made to change the isotopic mixing ratio of gases by methods making use of the difference in the thermal velocities of molecules of different weight. Ordinarily, the apparatus devised for this purpose consisted essentially of a length of clay tubing through which could be led the gas whose isotopes were to be separated. The region outside the tubing was kept evacuated so that part of the gas, while travelling along the length of the tubing, would be pulled through its porous walls. Due to the greater ease with which the lighter isotopes diffuse through porous material, the gas which traversed the length of the tubing without passing through its walls would be somewhat richer in the heavier isotopes than the gas which was originally led into the tubing. This method was used by Aston and Lindemann[1], in an attempt to separate the isotopes of neon, and by Harkins and co-workers[2], who wished to increase the relative abundance ofthe heavier isotope of chlorine. It is easy to show[1] that, when there are only two isotopes, the ratio of the numbers of heavy and light isotopes is increased by this process by a factor

$$E = \sqrt[1-\mu]{\frac{\text{Volume of gas led into tubing}}{\text{Volume led out of tubing, without diffusing through walls}}}$$

where μ -- $\sqrt{\frac{M_l}{M_H}}$

M_l --molecular weight of lighter isotope

M_H --molecular weight of heavier isotope

This notation will be preserved throughout this paper. E will often be referred to as the "Enrichment Factor" of the process.

For their work with neon, Aston and Lindemann led 2000cc of gas into the porous tubing for every 1cc that came out at the other end. For neon, $1-\rho=.05$. Substitution in the foregoing equation then shows that the end-product should contain, instead of the usual 10% of Ne^{22}, about 14%. Such smallness of enrichment factor must be characteristic of all diffusion methods for the separation of gaseous isotopes which employ only a single diffusion process. By repetition, greater enrichment is possible, but the amount of gas required and the work involved are so great that one would not expect to be able, by this method, ever to achieve anything approximating a real separation of isotopes.

This was the status of the subject until G. Hertz[3] devised a simple, but extremely ingenious scheme whereby, in effect, the gas may be automatically led through many successive diffusions, in a closed system, and without the use of large quantities of gas. Hertz' procedure is as follows. The usual long clay tube is divided into segments, each surrounded by its own glass jacket which is kept evacuated by its own individual mercury diffusion pump. The gas pulled by a pump through the walls of its "separation member" is not thrown away, but is led back into the system at a point in the apparatus reached earlier by the gas. In this way, the light constituent (on the average) of the gas which diffused through the wall of the nth separation member is sent back to the (n-1)st separation member. Its light constituent, in turn, passes through the wall of the (n-1)st member and is sent back to the (n-2)nd member, etc. As a result, there ensues a net transfer of light molecules towards the right end of the system (See Fig. 1), and a net transfer of heavy molecules towards the left. Eventually, of course, an equilibrium is reached, inasmuch as the system is closed, and no gas is led in or out after it has been

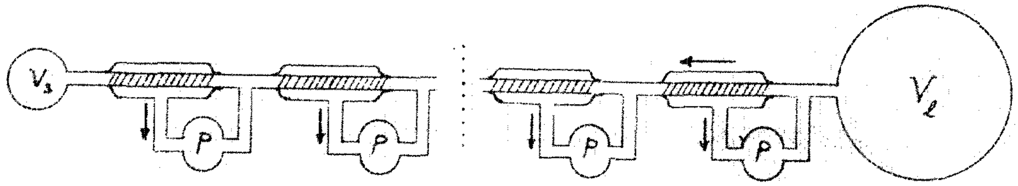


Fig. 1

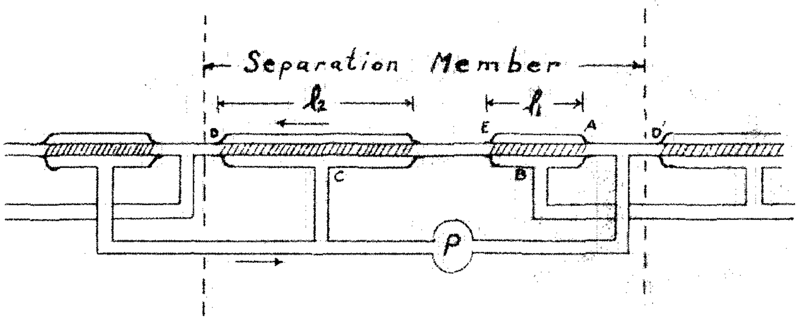


Fig. 2

initially filled. The equilibrium values of the isotopic ratios at the various points of the apparatus can be calculated for the more general method of connection depicted in Fig. 2. It is evident that the connection shown in Fig. 1 is the special case for which $l_1/l_2 = 0$.

A reproduction of the details of the calculation carried out by Hertz is given in Appendix A. His simple theory is based upon three reasonable approximations:

1. The diffusion of the gas through the walls of the tubing is not affected by its motion along the length of the tubing.
2. Diffusion along the tubing is negligible.
3. The amount of gas which diffuses through l_2 bears to the amount which diffuses through l_1 the ratio of the lengths of the tubes $l_2 : l_1$.

Combining with these assumptions some simple equations expressing the fact that the total number of molecules of each kind entering any portion of the apparatus in any time interval must equal the number leaving that portion (when equilibrium has been reached), it is easy to derive the result (when there are only two isotopes):

$$q = \frac{f^{\mu}}{1-(1-f)^{\mu}} ; \quad \frac{1}{f} = \left(\frac{1}{2+\frac{l_2}{l_1}}\right)^{-1}$$

where q, the "separation factor" of each separation member, is the factor by which the ratio of the number of heavy to the number of light molecules at a given point in the nth separation member exceeds that ratio at the corresponding point in the (n-1)st separation member. For an apparatus consisting of m such members connected in series, the separation factor is obviously q^m. All experiment so far recorded indicates that this is strictly true;

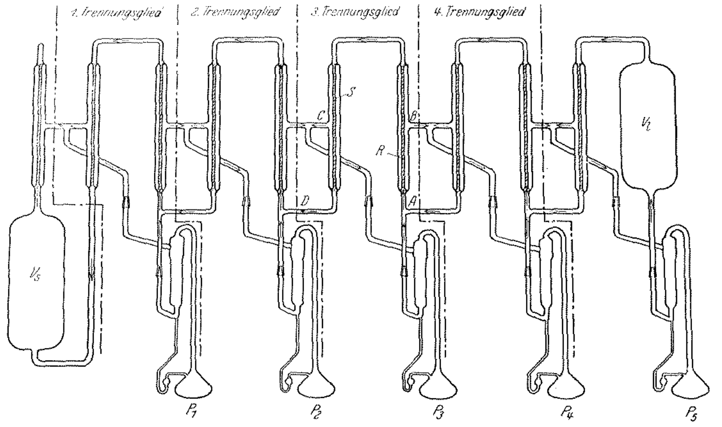
there is no decrease in efficiency as m increases.

It might seem that an apparatus of only a few members might be made to yield a large separation, simply by making $\ell_1 << \ell_2$, so that $f \rightarrow 0$. Although it is true that q may be increased in this way, at the same time the speed of the apparatus is diminished (See Appendix A), so that the equilibrium time is apt to become prohibitive. Further, if ℓ_1 becomes too small, so that the hook-up approaches that of Fig. 1, the transfer of gas from member to member takes place chiefly by diffusion, in violation of Hertz' third assumption, so that a modified theory[4] must be used, which shows that both q and the equilibrium time are limited in this case also.

In Hertz' original apparatus there were twenty-four separation members, for each of which ℓ_1 and ℓ_2 were equal. The apparatus was first tested on neon, for which case the calculation just indicated yields a value of 1.092 for q, which corresponds to a predicted separation factor for the entire apparatus of 8.32. Fabry-Perot interferometer intensity measurements on the fine structure components of the spectra of neon at the two ends of the apparatus (as well as mass-spectrometer measurements) showed that the separation factor actually achieved was at least 80% of this predicted value.

Since this early work, Hertz has built a 48-member apparatus, employing principally the method of connection shown in Fig. 1, with which he has produced spectroscopically pure Ne^{22} and H^2 [5,6]. The theoretical separation factor for the isotopes of neon for this apparatus he has reported to be about 1600. A single run requires 20 liters of gas at a pressure of 7 or 8 mm of mercury, and produces an enriched sample of a few hundred cc.

Plate I



From one of Hertz' papers[3]

II. Development of Apparatus

In setting out to construct a similar apparatus for the separation of gaseous isotopes by diffusion, one is first confronted with the necessity of determining what sort of porous tubes are required for the process. If it is found possible to obtain material porous enough to enable diffusion to occur, but not porous enough to swamp the mercury pumps available for the circulation of the gas, one may feel some confidence in the outcome of his work, and set about to attempt to embody, in his apparatus, as many specific improvements as possible. One has at his disposal, as adjustable parameters of the apparatus: the porosity, internal and external diameters, and lengths of the porous tubing; the diameter of the connecting tubing; the volumes of the reservoirs V_ℓ and V_s (See Plate I); and the pressure at which the system is to operate.

The logical method of procedure is first to design a practical mercury diffusion pump which will circulate as much gas as possible (consistent with reasonable simplicity of construction) at a pressure of about 1 cm of mercury (It will be seen later that, at higher pressures, viscosity effects diminish the separation factor). This, then, will serve to determine the overall porosity of the clay tubes used--they should pass just as much gas as the pump can handle, when the pressure inside the tubing is 1 cm of mercury, and that outside is negligible. It is essential that the tubing be not too porous, as in this case the pressure on the outside of the tubing will not be negligible, and reverse diffusion will diminish the separation factor (See Appendix A).

The internal diameter of the diffusion and connecting tubing must be chosen on the basis of several divergent considerations. In order to keep down the volume of the system, as well as to reduce the effect of diffusion along the tubes, this diameter should be made small; in order to keep down the pressure drop between the two ends of the system, this diameter should be made large.

Once the internal diameter is fixed, one must adjust the external diameter, ℓ_1 and ℓ_2 simultaneously, by experiment, to determine how large a value of q can be used consistent with reasonable speed of separation. In any event, ℓ_1, ℓ_2 and the external diameter of the tubing must be such as to satisfy the pump condition previously stated.

Finally, V_ℓ and V_s must be selected. In most of the work done with this type of apparatus, the heavier isotope is the rarer and, therefore, the one which the experiment seeks to concentrate. For such work, it is clear that the choice of a value for V_s is dictated by the amount of enriched gas one wishes to produce in a single run. Increasing V_s increases the yield per run of the system, but it also increases the equilibrium time. V_ℓ, on the other hand, should be made large--if possible, large enough that the removal from it of enough of the heavier molecules to fill V_s will not materially alter the isotopic mixing ratio in V_ℓ. Otherwise, the operation of the system will be to increase the relative abundance of the lighter isotope in V_ℓ, as well as to increase the relative abundance of the heavier isotope in V_s, so that the actual "enrichment factor", E, of the apparatus may be appreciably less than the "separation factor", Q. This effect is treated in detail in Appendix B.

In order to investigate the feasibility of the Hertzian method here, an apparatus with two pumps was first constructed. Ordinary first stage, single-jet, mercury diffusion pumps were used for the circulation of the gas, while unglazed pyrometer tubing (I.D. 5.0 mm, O.D. 7.0 mm) was employed in the construction of the separation tubes. This type of tubing[7] has been found satisfactory throughout the work done here. It is unique in that it can be sealed directly to pyrex, with ease and permanence. This is a great convenience in an apparatus of this type.

In the construction of the separation tubes a method of assembly was used which made it possible to vary the f ratio of the apparatus. The tube ℓ_2 (Fig. 2) was made twelve inches in length, but ℓ_1 consisted of two six-inch tubes, connected by pressure tubing in such a way that, by closing off the tubes in various combinations, ℓ_1 could be made 12, 6, or 0 inches in length. The results of the tests thus made will be described in the following pages.

Evidently, for such a small apparatus, the separation factor is negligibly low except for a mixture of gases of widely different molecular weights. Therefore mixtures of hydrogen and nitrogen and, later, nitrogen and carbon dioxide gases were used to test the apparatus. Two methods of analyzing the compositions of the mixtures suggested themselves. The first involved the matching of intensities of the H_α line and the red bands of nitrogen, observed spectroscopically in discharge tubes in the two ends of the system. For this type of measurement there was employed a direct vision spectroscope equipped with a prism and neutral wedge arranged in such a way that half of the slit could be directly illuminated, and the other half illuminated by light which had passed through the prism and neutral wedge. By angular adjustment of the prism, the H_α line of one half the field of view could be made to overlap an adjacent nitrogen band on the other half; by adjustment of the neutral wedge, the intensity of the H_α line could be cut to match that of the nitrogen band.

Measurement of relative percentages by such a spectroscopic method, of course, must depend on an empirical calibration of the measuring device. Hydrogen-nitrogen mixtures of various known compositions were first admitted to one of the discharge tubes at the pressures at which the apparatus was to be run (2 to 10 mm of mercury). For each pressure, the readings of the neutral wedge were then plotted as a function of the compositions, and the resulting curves were used in the measurement of unknown compositions.

This method, at the very best, was only semi-quantitative, since, for this observer at least, the visual intensity matching was always a doubtful process. Also, the calibration depended to such an extent on the pressure of the gas in the discharge tube that it was often hard to know whether to ascribe a change in the relative intensities of the H_α line and the nitrogen band to an actual change in gaseous composition or to a pressure gradient in the system. As a result, this method was useful only in showing that a detectable separation of hydrogen and nitrogen gas was affected by the two-member apparatus. Quantitative measurements required a different technique.

The second, and more satisfactory device used for measuring the composition of gaseous mixtures was simply a Pirani gauge.

This instrument consisted of a tungsten filament of about 15 cm length and 10 ohms resistance, suspended in a glass tube of about 5 mm internal diameter. It was used in connection with the usual Wheatstone Bridge circuit, with a potential difference of 1.5 to 2 volts across the gauge.

Again, of course, an empirical calibration had to be used in connection with the measurement of the composition of gaseous mixtures. A set of curves was obtained for different pressures of gas, the voltage across the bridge for the balanced condition being plotted against the percentage of hydrogen in the hydrogen-nitrogen mixture. More or less reproducible, quantitative measurements were found possible by this method, provided that frequent calibrations of the gauge were made. Apparently letting air into the system was often sufficient to alter the calibration of the instrument appreciably. Also, care had to be taken to keep water vapor out of the system as this disturbed the measurements greatly. Because of these difficulties, this method of gas analysis was discarded as soon as the enlargement of the apparatus made possible a different, simpler technique (described later). However, the Pirani gauge continuedto be useful in studies of speeds of separation, since it made it possible to make continuous observations of changing compositions.

In the tests of this preliminary apparatus, the Pirani gauge was sealed into a 200cc bulb which constituted one of the end-reservoirs of the system. The other reservoir was a bulb of 3 liters capacity. Each reservoir was equipped with a manometer. By means of ground glass connections, the two bulbs could be interchanged. Inasmuch as most of the rarer gaseous isotopes are the heavier ones, most of the measurements were made with V_ℓ = 3 liters and V_s = 200cc.

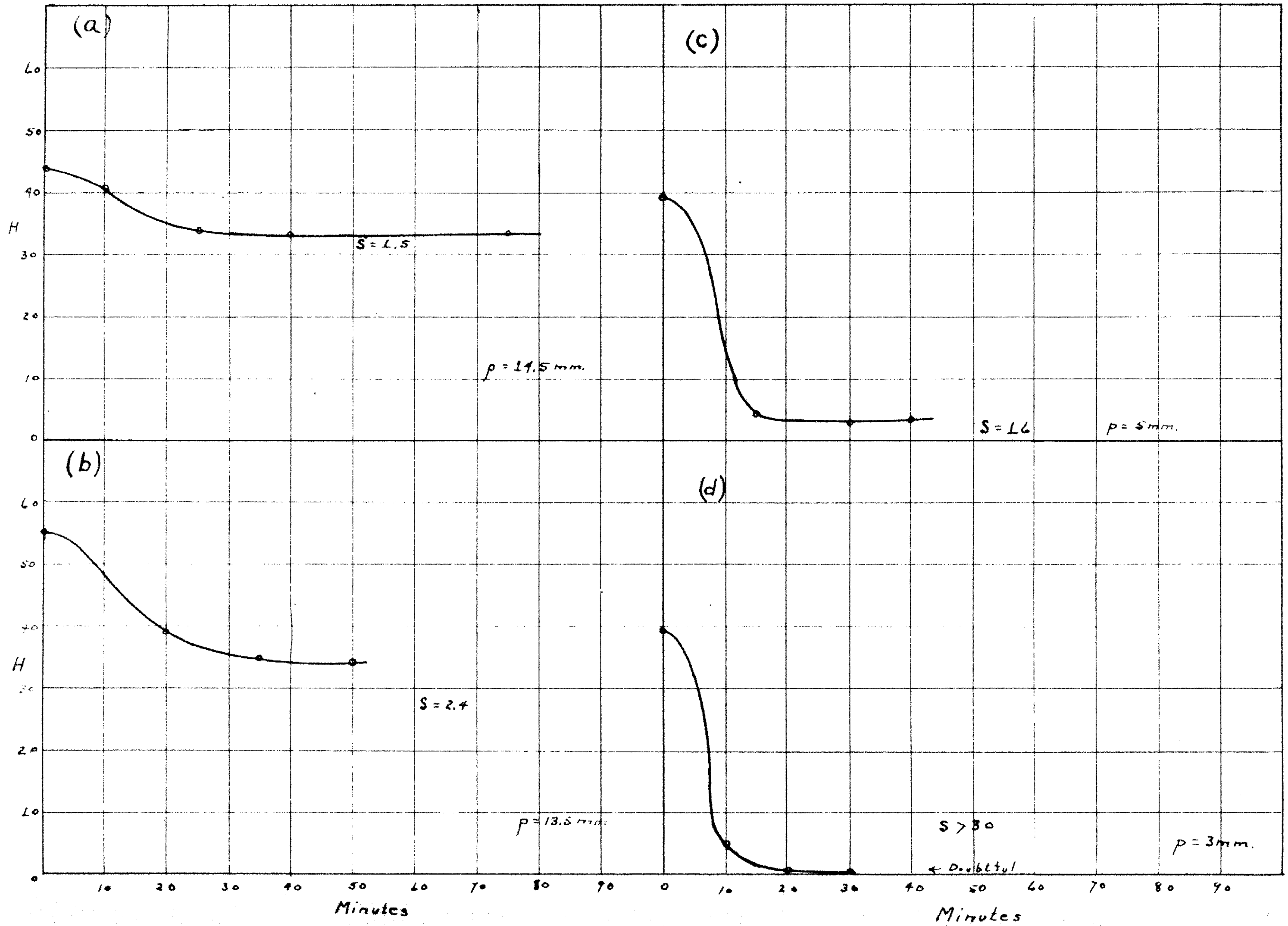
It soon became evident, with this two member apparatus, that appreciable separation of hydrogen and nitrogen was possible only at low pressures and for high pump speeds. Curves a, b, c, and d are typical of the many curves obtained. These curves represent the operation of the system at pressures of 14.5, 13.5, 5 and 3 mm, respectively. The final enrichment factors reached, as measured by the Pirani gauge, were 1.5, 2.4, 16, and 30. Although these figures are not too reliable, the data leave no doubt as to the value of low pressure in these early experiments.

In this work, the mercury pumps were being run with about a 2 or 3 cm head of mercury pressure. It was found that the enrichment attained was affected very materially by slight alterations in the "speed" of the pumps, as indicated by this vapor pressure. Curves e1, f1, and g1 show this effect unmistakably. Therefore the first conclusion drawn from these preliminary tests was that a better type of diffusion pump had to be devised, especially if work at high pressure was to be possible. In the absence of such a pump, the only data which could mean anything would be those for "fast" runs at pressures of only a few mm of mercury. Hence, although in the subsequent tests both low and high-pressure runs were made, only the results of the former will be given detailed consideration here.

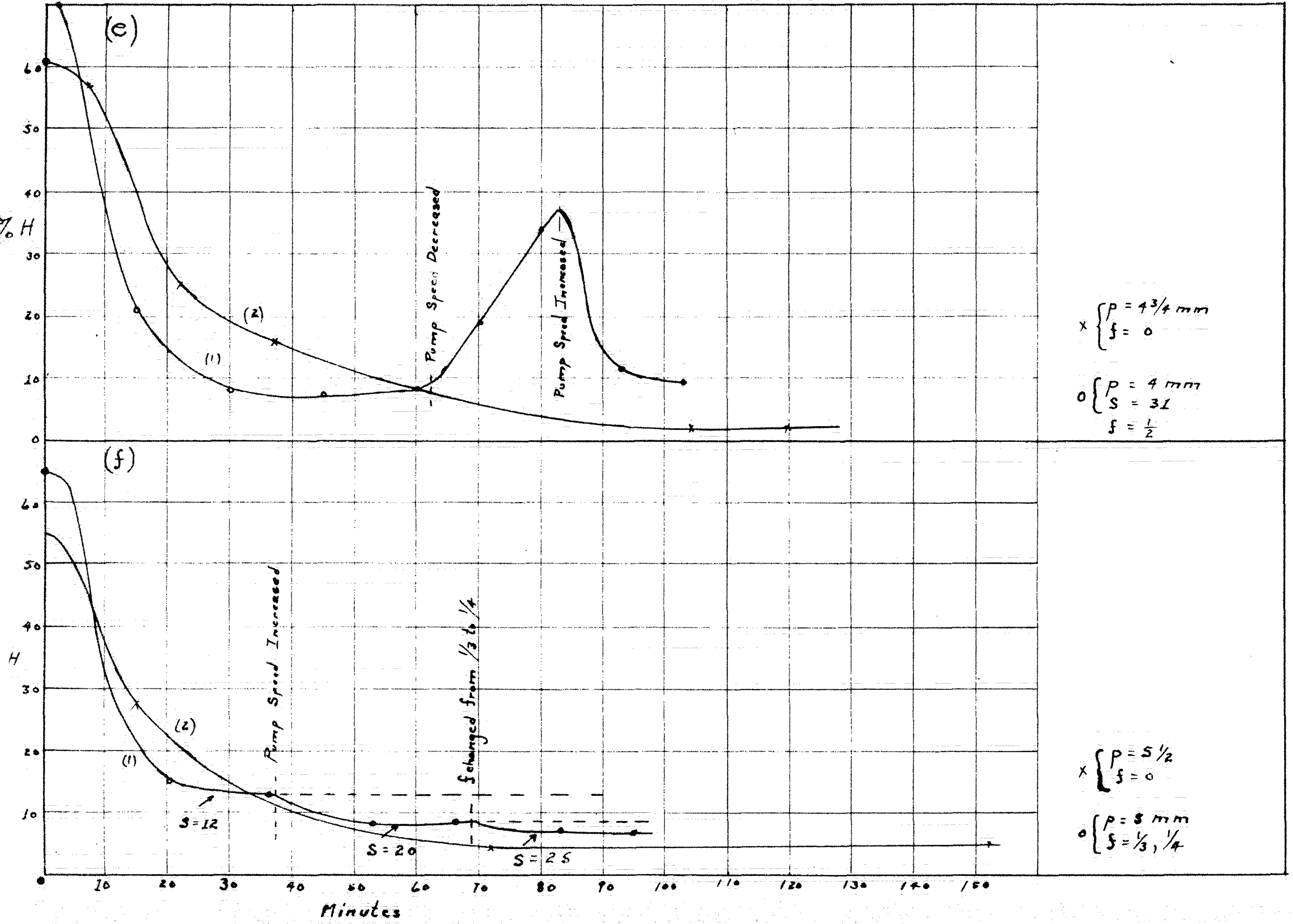
In his work with the diffusion apparatus, Hertz had built and used separation members having f = 1/3 and f = 0. His work had convinced him that, on the whole, the latter style of separation member was the best. This was the next point to be investigated here. Curves e, f, and g should be referred to in this connection. In each figure, two curves are shown; curve 1 was taken with $f = 1/3$ (except in f1, in which f was changed from 1/3 to 1/4 during the run); curve 2 was taken with $f = 0$. Curves 2 were always taken shortly after curves 1, so that the gas, at the start, was not completely mixed. This accounts for the apparent difference between the initial mixing ratios of the two sets of curves. It also results in showing the equilibrium time of separation for $f = 0$ to be lower than it really is. Nevertheless, definite conclusions could be drawn.

From figures e and f, representing hydrogen-nitrogen separations, it appears that $f = 0$ eventually gives a somewhat greater separation, but the process is considerably slower than when f is 1/3. While the equilibrium time for the latter case is only 25 or 30 minutes, about an hour is required for the separation with $f = 0$ to catch up with the separation for $f = 1/3$. 40 minutes more are then required for equilibrium to be established. Furthermore, f1 shows that a decrease in f from 1/3 to 1/4 serves to diminish appreciably the final amount by which the separation factor is increased by setting $f = 0$, while other data, not given here, have shown that the equilibrium time is not appreciably increased by decreasing f still more than this, provided that it is not actually put to zero. Further, curve g shows that the relative slowness of separation for $f = 0$ is greater when the weights of the two gases are more nearly the same. (The rise in the curve near the start was often observed; it is attributed to imperfect mixing of the gases initially, dispelled by commencing the circulation of the gas)

2 members H-N mixtures

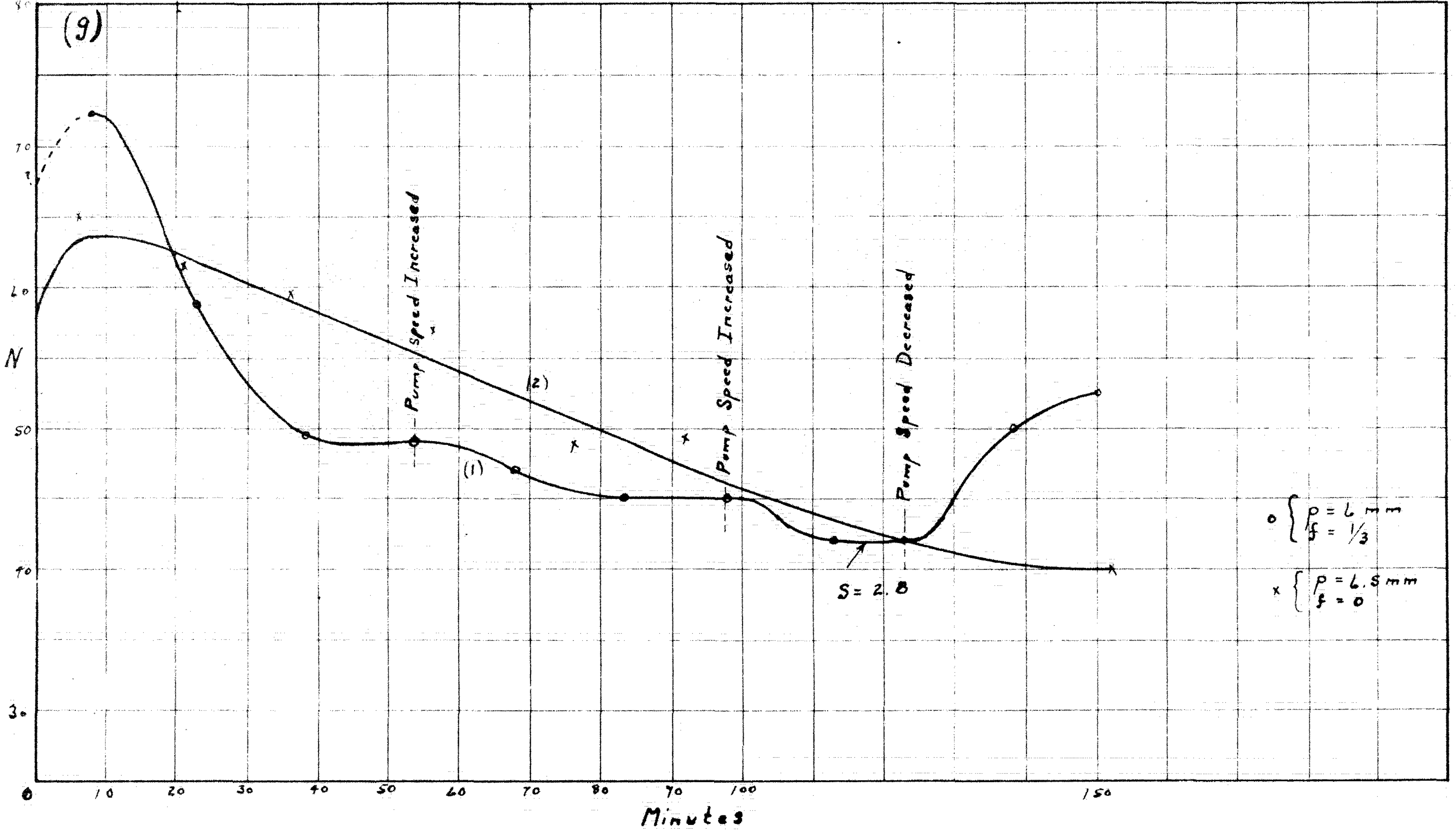


2 members H-N Mixtures



2 members CO₂-N mixtures

(9)



For all these reasons, it was decided to use a value for f less than 1/4, but greater than 0. Somewhat arbitrarily, it was decided to replace the separation tubes by new ones for which $\ell_2 = 12"$, $\ell_1 = 1\ 1/3"$, making f = 1/11. As was hoped, runs with carbon dioxide-nitrogen mixtures required no measurably longer time for equilibrium than they did when f was 1/3. Hence in the immediately succeeding tests, these new values of ℓ_1 and ℓ_2 were always used.

So far only one size of porous tubing had been used--I.D. 5.0, O.D. 7.0 mm. It was thought worth while to investigate the effect of a smaller bore. If diffusion along the length of the tubing was cutting the separation down, it was believed that tubing of smaller cross-section would yield better results. Consequently, tubes of I.D. 2.95, O.D. 4.32 mm were assembled, and carbon-dioxide-nitrogen tests made. There was no observable difference in the results, so small bore tubing was not again considered.

Finally, tubing of somewhat thicker walls than the first used (I.D. 5.5, O.D. 8.0 mm) was tried and found to yield the usual results. Hoping that this slightly less porous material might help to prevent the overloading of the pumps, this style of tubing was used thenceforth.

At this stage of development, it was considered desirable to attempt to obtain more accurate measurements of the enrichment factor of the apparatus. With mixtures of carbon dioxide and nitrogen, accurate analyses could be made by measuring pressures before and after freezing out the carbon dioxide in liquid air. For measuring pressures, a simple mercury manometer was not sufficiently accurate, while an ordinary McLeod gauge could not easily be used, on account of its large volume (It must be remembered that the volume of the gas being analyzed was only about 200cc). However, it was found sufficient to construct a miniature McLeod gauge, of total volume about two cubic centimeters. By such means, three measurements of separation factors (involving analyses of the gas in both V_ℓ and V_s, of course) attained in 5 mm, "fast" runs, yielded

$$Q = 2.16,\ 2.08,\ 2.08$$

The theoretical calculation would predict a separation factor

$$Q_{th.} \sim 2.8$$

That the experimentally measured Q is less than the theoretically calculated value is not to be regarded as alarming, since the calculation has not taken sufficient account of the smallness of ρ, which considerably weakens some of the assumptions made in the derivation of the theory. This effect, it must be pointed out, is entirely inappreciable except for mixtures of gases of widely different molecular weights. Thus, the agreement between theory and experiment was found to be much better when mixtures of carbon dioxide and argon gases were worked with. For pressures of from 5 to 8 mm of mercury, the separation factor for such mixtures was measured to lie between 1.23 and 1.28. The theoretical calculation here would give Q = 1.30. The time required for equilibrium was not measured, but it was less than two hours.

The deleterious effect of high pressure may again be noted in the measurements made on carbon dioxide-nitrogen mixtures. Runs at 13 mm pressure yielded for Q values between 1.4 and 1.7, depending on the speed of pumping, as compared with the values of over 2 always obtained in 5 mm runs with the same gases.

The results of this group of preliminary experiments seemed to justify the continuation of the problem. Therefore plans were made for the construction of a diffusion apparatus of enough members to effect a useful enrichment of the rarer isotopes of some of the light gases. It was decided to build the apparatus up gradually, in units of five separation members each; each unit being mounted and assembled on its own iron framework. While these were being constructed, some investigations were carried out on various styles of mercury diffusion pumps, in order to eliminate the inadequacy of the earlier methods of circulating the gas.

The investigation of the circulation of the gas was carried out in the obvious way. A pump was connected to one of the separation tubes to be used in the diffusion apparatus, so that it circulated gas in the same fashion in which gas was circulated in that apparatus. Manometers indicated the pressures inside and outside the walls of the porous tubing. A three liter reservoir served to maintain steady the pressure inside the tubing (See Fig. 3). This system was filled with air at a pressure of a few mm of mercury, the pump was started, and the behaviour of the system was followed by the pressure indications of the manometers. As was expected, the pressure on the high-vacuum side of the porous wall was not zero, but was an appreciable fraction of that on the high-pressure side. For example, when the pressure inside the tubing was 9.8 mm, that outside could not be gotten below 2.5 mm. For higher pressures, the percentage effect was worse. Part of the difficulty, it was soon found, lay in the fact that the tubing from the high-vacuum side of the pump to the outside of the porous walls offered sufficient resistance to the flow of the gas to

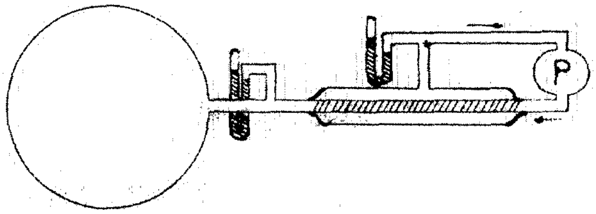
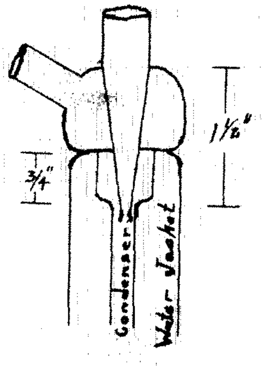


Fig. 3



Length of Condenser
= 6"

I.D. of Condenser
= 3/8"

O.D. of Jet
= 9/32"

Fig. 4

result in an appreciable pressure drop. This situation was corrected in all subsequently constructed separation members by the use of wider and shorter leads.

But the use of less-resistant leads was not in itself sufficient to make possible satisfactory pumping; it appeared that the mercury pump would have to be redesigned, if circulation at several mm pressure was to be feasible. This was not surprising, inasmuch as the pump being used was built for evacuation purposes, and not for high-pressure circulation.

Nevertheless, it was found that reasonably low pressures could be maintained on the high-vacuum side of the porous member if enough heat was supplied to the pump, so that the mercury vapor pressure was several centimeters of mercury. This necessitated the use of a flat boiler, so as to eliminate the violent bumbing which took place when the deep column of mercury of the usual pump was heated rapidly. Further, it was found impossible, in any reasonable way, to construct electric heating units for the pumps which would supply enough heat to them without burning out. Gas heating was tried and found quite satisfactory. In all the subsequently constructed apparatus, each mercury pump has been heated by its own Bunsen burner (of a special improved type).

Experiments were also performed to determine the best dimensions of jet, jet clearance, etc., for a pump such as was required for the diffusion apparatus. The general construction of the single-stage pumps tried is drawn roughly to scale in Fig. 4. The maximum speed of which the pump is capable is limited by the clearance between jet and condenser. To attain this maximum speed of circulation at a pressure of several mm of mercury, however, it is necessary to drive the mercury very rapidly through the jet. If the jet is small, the mercury vapor pressure at which the pump operates must be large so as to overcome the resistance in the jet. However, this seems to make for stability in pumping, so that the irregularities in the evaporation of the mercury that always occur do not appreciably affect the circulation of the gas. With a wide jet, on the other hand, the vapor pressure required for maximum pumping is much less, but slight fluctuations in boiling are apt to result in temporary lapses in the circulation. Probably the heat required by the pump is about the same for both cases.

When a small jet is used, pumping begins almost discontinuously when the mercury vapor pressure passes through a value characteristic of the gas pressure in the system. With the pump design finally adopted, this "critical pressure" is about 60 mm, for a gas pressure of 12 mm in the system. For a given pump, measurements of the critical pressure made under similar conditions can be duplicated to within 2 or 3 mm, while this is about the range over which pumping sets in.

In order to obtain the foregoing information, measurements were made with single-stage pumps of seven different designs. In addition to what has just been reported, it was found that the tolerance in dimensions of jet, jet clearance, and condenser was surprisingly small if the pump was to work at all at 10 mm of gas pressure or thereabouts. Although a test of only seven pump styles cannot be considered exhaustive, when there are three or more parameters capable of independent variation, it can nevertheless be asserted that, unless values completely different from those tested here are used, the dimensions of the working parts of the pump should be within about 50% of those finally adopted as a result of these tests. These values are given in Fig. 4.

Of course, these considerations do not apply to two-stage pumps; probably something might be gained by going to a more complicated construction. Experiments were made with two or three designs of two-stage pumps, but the results were not better than those finally obtained with the simpler construction of Fig. 4.

With the pump finally adopted, tests under normal working conditions, as duplicated in the arrangement of Fig. 3, revealed that a pressure of 3/4 mm could be maintained on the high-vacuum side of the porous tubing, when the pressure inside the tubing was 12 mm. Such pumping required about a 60 mm column of mercury in the pump. In the diffusion apparatus, the pumps are normally operated at a vapor pressure of 7 or 8 cm of mercury.

III. Final Diffusion Apparatus

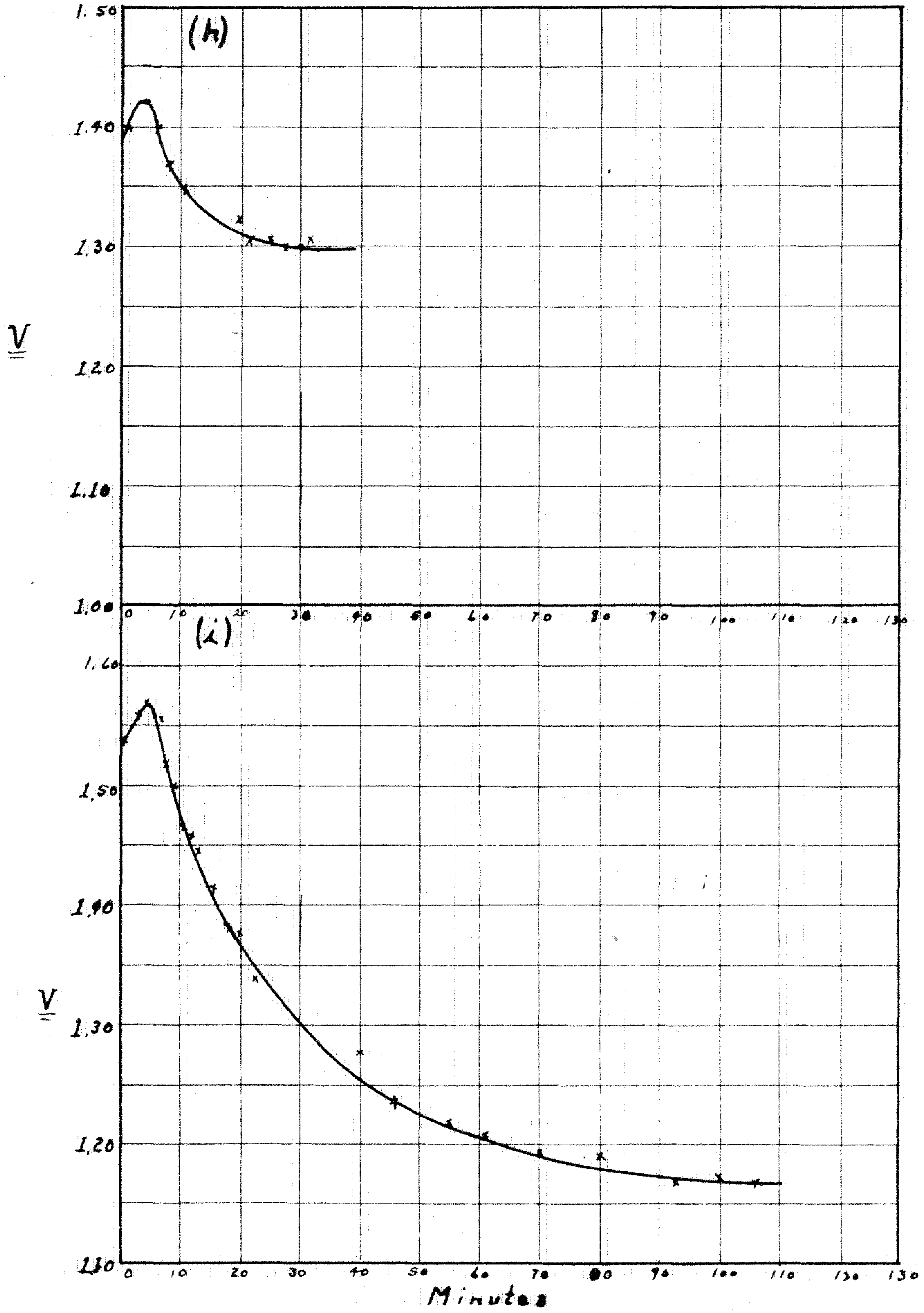
The apparatus has been built up until now it contains seven units, each unit consisting of five separation members. The circulating pumps are according to the design worked out in the preceding pages; the porous tubing is all of the type described in the foregoing. The mounting for the separation members has been designed so as to make the leads as short as possible. The low-pressure leads from the pumps to the porous members are about 2 cm in diameter (this was found large enough to eliminate any sensible pressure gradient), while the rest of the connecting tubing is about 6 or 7 mm in diameter. The construction varies from unit to unit only in the lengths of the porous tubes. There are

Unit A, for which	$\ell_2 = 24''$,	$\ell_1 = 2''$,	$1/f = 14$
B	18	1	20
C	18	1 1/3	15.5
D	18	1	20
E	18	1 1/3	15.5
F	12	1	14
G	12	1 1/3	11

The units are arranged in alphabetical order from V_ℓ to V_s. The ordering of the units in the system is dictated by two considerations. First, the volume at the "heavy" end of the system must be kept as small as possible, when the apparatus is used to collect heavy isotopes, as has thus far been the case (See Appendix B). This suggests putting the units with long tubes and consequently relatively large volumes at the "light" end of the system. If any arbitrariness remains, an arrangement should be selected which will make for the maximum speed (See Appendix A). This suggests putting the units with the highest f-ratios closest to the "heavy" end of the system. Both these conditions were met, within limits, by the ordering adopted.

In the earlier stages of development, of course, each unit was tested before being put into the system. All units behaved about alike, however, their separation factors being also about the same, within the accuracy of measurement, which was not sufficient to distinguish with certainty between the different f-ratios, in a five member apparatus being tested with carbon dioxide-argon mixtures. Typical test results are those obtained with Unit E. 1 2/3 hours of circulation witha pressure of 9.5 mm of a mixture of carbon dioxide and argon in the system resulted in a separation factor of 1.90. 2 hours of circulation with 6.5 mm pressure yielded a separation of 1.92. The calculated factor for this sytem is 2.2. More reliable measurements on two two-hour runs with Unit A gave values for Q of 2.10 and 2.16, as compared with the calculated factor of 2.16 for this case. In general, the agreement was thought to be reasonably good. However, a run with Unit E at 14 mm pressure yielded a value for Q of only 1.69. Runs with carbon dioxide-argon mixtures at pressures greater than 8 or 9 mm have been found to result in low separation factors, with all units and combinations of units tried. This effect is worse with mixtures of carbon dioxide and nitrogen. With Unit E, for example, two 11 mm runs on this type of mixture yielded values for Q of 7.5 and 8.0, whereas the calculated factor is greater than 16. There seems little doubt that this is due to viscosity effects, which would be expected to set in at pressures of this order of magnitude. This pressure effect must be distinguished from that found due to the inadequacy of the earlier style of pumps, which has been corrected by the improved pump design. For the present considerations it is sufficient to realize that only measurements of carbon dioxide-argon separations at pressures of less than 8 or 9 mm can have any quantitative significance in checking the operation of the apparatus against the theory.

Some idea as to the equilibrium time of a single unit may be obtained from curve h, in which the voltage across the bridge of the usual Pirani gauge set-up is plotted against the length of time the gas circulated. This curve was taken on a run of car-


(h)
1.50
1.40
1.30
1.20
1.10
1.00
V
0
10
20
30
40
50
60
70
80
90
100
110
120
130
(i)
1.60
1.50
1.40
1.30
1.20
1.10
V
0
10
20
30
40
50
60
70
80
90
100
110
120
130
Minutes

bon dioxide-nitrogen in Unit E, at a pressure of 11 mm of mercury. The equilibrium time for carbon dioxide-argon mixtures is probably somewhat greater, but the Pirani gauge was not sensitive enough to be used on such mixtures.

A comparison of curves h and i shows the influence of the number of separation members on the equilibrium time. Curve i was taken when Units E and G were run in series. The gas in the system was 10.5 mm of carbon dioxide-nitrogen mixture. For this case, the curve shows that the equilibrium was reached after about 1½ hours of circulation, whereas only about one-half hour was required for one unit alone. The implication is that the time required for equilibrium to be reached increases more rapidly than the number of separation members, everything else being equal. The separation factor finally attained in the run represented by curve i was about 50, as compared with 7.5 or 8.0 for Unit E alone.

In all the measurements thus far described the initial mixing ratio of the gases used was 1:1, roughly. In the work with apparatus of five or more members, V_ℓ has been 5 liters, and V_s 200cc.

For comparison with work later to be described, it will be of interest to note the results of measurements made on the separation factorof the fifteen-member apparatus composed of Units A, E, and G. Three runs on carbon dioxide-argon mixtures at a pressure (measured in V_ℓ) of 11 mm gave values for Q of 4.3, 7.8 and 9.6. The durations of the circulations were 3½, 4½, and 3 hours, respectively. In each case the initial mixing ratio was about 1:1. Later work has strengthened the belief that the value 4.3 was probably spurious. If it is neglected, the separation factor for this apparatus for carbon dioxide-argon mixtures at 11 mm pressure is seen to be between 8 and 9, probably. The theoretical value, for 100% efficiency, would be 11.5.

The last group of measurements which need to be considered here are those made on carbon dioxide-argon mixtures with an apparatus of twenty-five members--Units A, B, E, F, and G. In these measurements, V_ℓ was 5000cc, V_s was 300cc. With an apparatus of this size, there is found to occur an appreciable pressure drop between V_ℓ and V_s. The fractional drop increases with decreasing pressure; for the twenty-five member system, a p_ℓ of 10 mm would correspond to a p_s of about 8 mm, while a p_ℓ of 7 mm would accompany a p_s of $4\frac{1}{2}$ or 5 mm. These values are very rough, inasmuch as they were measured on ordinary mercury manometers sealed into the two ends of the system. It was possible, in these experiments, to determine p_ℓ as accurately as desired, by keeping the 5 liter volume of V_ℓ open to an ordinary McLeod gauge at the beginning of the run, but p_s could never be measured accurately, since obviously V_s could not be opened to the large volume of an ordinary McLeod gauge, and the method of analysis involving the use of the previously mentioned miniature McLeod gauge had been supplanted, for work on larger assemblies, by a method wherein the gas to be analyzed was pumped out of the system and worked on with ordinary, full-scale instruments.

Quite a large number of runs were made at pressures of 9 to 12 mm of mercury (p_ℓ), but the results seemed to point to no conclusion except that previously noted--that high pressure runs always result in low separation factors (sometimes not over one-third or one-fourth the calculated value). Also, the results were not all in quantitative agreement; there always seems to be some uncertainty in runs on carbon dioxide-argon mixtures at pressures of over about 8 mm.

However, the results obtained in a group of runs at pressures (p_ℓ) of about 7 mm were entirely consistent and satisfactory. It will be worth while to record the data for these runs in some detail, inasmuch as these data provide material for the evaluation of some of the constants of the apparatus, as discussed in Appendix B. In the following table are recorded: p_ℓ; the length of time the system has run, t; the ratio of the pressures of carbon dioxide and argon in the sample removed from V_s and analyzed, R_s; the ratio of the pressures of argon and carbon dioxide in the sample removed from V_ℓ and analyzed, R_ℓ; and the separation factor, $Q = R_sR_\ell$.

<u>t</u>	<u>R_s</u>	<u>R_ℓ</u>	<u>Q</u>
<u>Run</u> <u>I</u>: p_ℓ = 6.9 mm			
0	1/2.7	2.7	1
6.5 hrs	10.0	5.0	50
26	14.8	5.75	85
<u>Run</u> <u>II</u>: p_ℓ = 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 hrs, when circulation was recommenced:

<u>t</u>	<u>R_s</u>	<u>R_ℓ</u>	<u>Q</u>
0	?	?	1
10	1.11	70	78
28	1.04	72	75

The gas of this run was then allowed to stand in the system for 3 days, at the end of which time a sample of V_ℓ gave R_ℓ = 22.

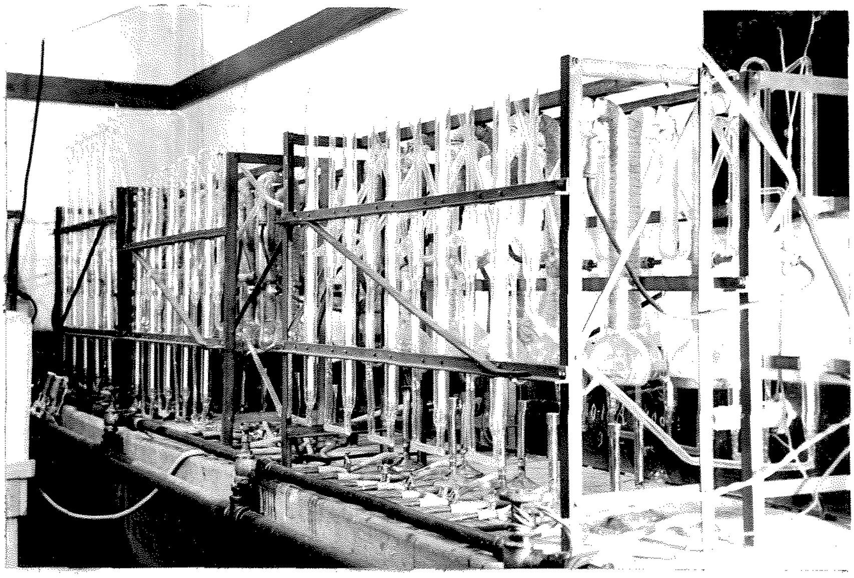
	t	R_s	R_ℓ	Q
Run III: p_ℓ = 6.60 mm.				
	0	1/50	50.0	1
	11	0.21	350	73.5

It will be useful, for the considerations which are to follow, to note that each analysis of R_s and R_ℓ involved the removal from each end of the system of enough gas to fill a 600cc volume to a pressure of from 0.5 to 1 mm of mercury. The exact amounts of gas removed in each case were recorded, but are of no interest at this point.

A casual inspection of the foregoing data suffices to establish two important points: the separation factor of the apparatus tested does not depend appreciably on the initial mixing ratio of the gases; the time required for equilibrium to be reached is not affected very much by the initial mixing ratio. From these measurements, the separation factor is about 80, and the time of equilibrium is of the order of 10 to 15 hours, for carbon dioxide-argon mixtures. The extensive interpretation of these data and their theoretical significance is taken up in Appendix B. For the purposes of this section it is sufficient to point out that the calculated separation factor for this apparatus is 73. The apparent greater than 100% efficiency is not considered significant, since small errors in the lengths of some of the porous tubes could easily account for this difference, if indeed it is real.

This concludes the present discussion of the development and testing of the diffusion apparatus. In Plate II is reproduced a photograph of a section of the system, while Fig. 5 is a schematic diagram of the diffusion apparatus and auxiliary devices. It is important to note that V_ℓ is 22 liters. This end-volume has been

Plate II



Photograph by courtesy of Howard Griest

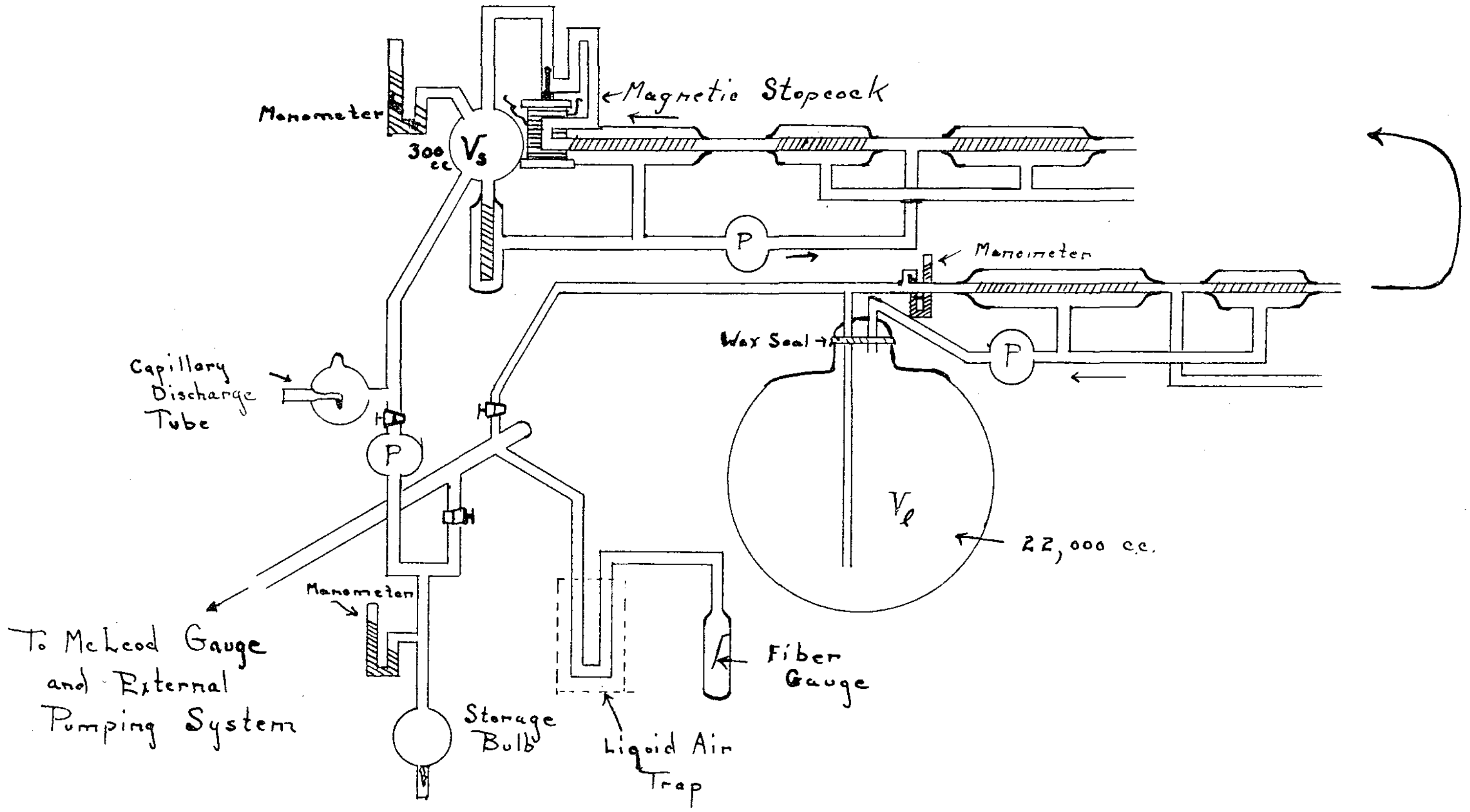

Manometer
300 cc
V_s
Magnetic Stopcock
P
Manometer
Wax Seal
P
Capillary Discharge Tube
P
V_ℓ
22,000 c.c.
Manometer
To McLeod Gauge and External Pumping System
Storage Bulb
Liquid Air Trap
Fiber Gauge

Fig. 5

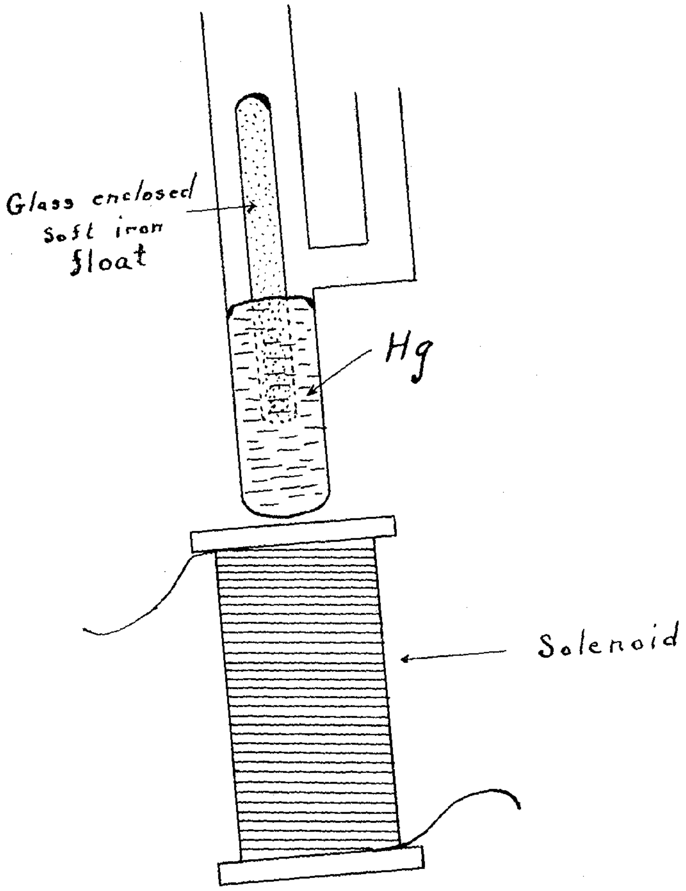


Fig. 6

used in all isotope separations with the thirty-four member apparatus. Not shown on the diagram, but of rather great practical importance, are the 18-inch fan and baffle board system designed to help keep the temperature down in the laboratory, and the safety devices which turned the gas off whenever anything went wrong with the water line, the gas line, or the vacuum system. In spite of the "cooling" system, the temperature of the room was normally well over 100° F., so that the two apiezon-lubricated stopcocks in the diffusion system had to be cooled by keeping them wet and blowing compressed air over them.

As is shown in Fig. 5, the "auxiliary apparatus" included the equipment necessary for removing and analyzing the gas, as well as means whereby the entire diffusion apparatus could be evacuated or filled with gas of the kind being studied. The diffusion pump separated from V_s by a stopcock was to enable the contents of V_s to be pumped into storage bulbs and set aside for future use. The "magnetic stopcock" shown in Fig. 5, and in detail in Fig. 6, enabled V_s to be shut off from the rest of the diffusion system when such a removal of gas took place.

The discharge tube sealed permanently into V_s makes it possible, in many cases, to watch for the appearance of impurities in the heavy specimen. The "fiber gauge" shown in the auxiliary apparatus, is a device for the measurement of gaseous molecular weights. Inasmuch as such molecular weights could be determined by means of this instrument to within about 2%, it was generally possible to obtain a fairly good idea of the extent of impurities in the final sample. This gauge is discussed in detail in Appendix D.

IV. General Procedure

It is impossible to set forth any complete set of rules of operation for the diffusion apparatus which will be universally applicable, for each gas requires its own peculiar technique to a considerable extent. There are, however, certain processes which must be gone through in all cases, and others which are often useful. This section will be concerned with such general methods of procedure.

The first step, in any diffusion experiment, is the evacuation and outgassing of the system. By means of external pumping through V_ℓ with an ordinary Hyvac pump and two stages of mercury diffusion pumps, it is possible to bring the pressure in the system down to about 10^{-4} mm of mercury in a few hours, provided that the pumps in the system are kept running during the evacuation. However, it is invariably found that gas is evolved while the diffusion pumps are operating, long after the system has been so evacuated. The particular gas evolved depends on the gas which was last run through the system, to some extent, but the chief offender is water vapor. It appears that the porous tubes of the diffusion apparatus are rather strongly hygroscopic, so that they take up large amounts of water, when exposed to the air. Inasmuch as each new separation process is ordinarily preceded by preliminary work which requires that the system be opened to the air, one is nearly always confronted with the necessity of removing absorbed water vapor. It has been found that, while the absorbed gases can be removed, eventually, by continued external pumping while the system pumps are running, it is by far quicker to circulate gas in the closed system, at a few mm pressure, for several hours, then to pump this gas out, refill, and repeat the process two or three times. Of course, if the experiment contemplated is on methane, methane should be used in this cleansing process, etc. It is customary to devote 36 or 48 hours to the preliminary "outgassing" of the apparatus.

After this preparation of the system, the gas whose isotopes are to be separated is introduced. In most of the work done on isotopes, enough gas has been admitted to the system to exert a pressure of 9 or 10 mm in V_ℓ. If, as is often the case, the gas admitted to the system contains several tenths of a percent of heavy impurities, it is necessary to perform a preliminary "run" in order to remove this contamination. This preliminary run should occupy only a few hours, inasmuch as the heavy impurities should accumulate quite rapidly in V_s. It is thought that, in most of the work done, so much time hasbeen allowed for this process that the isotope separation has gone a long way towards completion, with the result that an appreciable amount of the heavy isotope has been lost.

When the impurities have been removed, the main separation is begun. During this separation, which has generally been allowed to continue for about 24 hours, care is taken to see that each pump preserves a head of 7 or 8 cm of mercury vapor pressure. It is also necessary to keep the stopcocks cooled in the manner prescribed on p. 24.

While the separation is in progress, a watch can be kept for the appearance of impurities inV_s by visual examinations, with the aid of a pocket spectroscope, of the discharge in the heavy end of the system. In some cases it is possible to form a rough idea as to the extent of impurities in the finished product in this way. However, when any real concern is felt about contamination in the final sample, a fiber gauge analysis is made. There is always enough gas for such analysis left in the mercury diffusion pump used for pumping the heavy sample into the storage bulb. In this way is determined the molecular weight of the non-condensible portion of the heavy sample (As explained in Appendix D, the fiber gauge must always be used in connection with a liquid air trap). The amount of condensible impurity can readily be determined by pressure measurements before and after the application of liquid air to the trap, while the fraction of this condensible impurity which is water vapor can be roughly determined by the behaviour of the McLeod gauge during pressure measurements. In this way it is possible to make a reasonably precide analysis of the impurities in the end-product.

A device has been made use of both in methane and in nitrogen separations whereby the effective enrichment factor of the apparatus is increased by multiple diffusions. The procedure involved has been the obvious one of 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. Obviously, the enrichment factor attainable finally is limited only by the patience of the experimenter and the time available for the work. In practice, an attempt has been made to withdraw through the heavy end of the system about all the gas except that in V_ℓ, at the end of each of these preliminary diffusions.

It is customary to withdraw from the heavy end of the diffusion apparatus, at 24-hour intervals, three or four 300cc samples before the run is completed. Ordinarily the last sample does not differ very much from the first in isotopic composition. The entire separation process, from the outgassing of the system to the removal of the final sample, often occupies a period of a week or ten days, during which time the pumps of the system are never turned off. This length of time is generally just about sufficient to enable one or two of the connecting tubes to become clogged with mercury, which always distills liberally throughout the apparatus. As a result, before another experiment can be performed, it is necessary to open the system and blow this mercury out, by a judicial use of compressed air. This results in the absorption of water vapor, and some air, by the porous members, and requires the rather extensive outgassing already described. This situation can be largely remedied by the enlargement of some of the connecting tubes, and should be taken care of at the first opportunity.

The heavy samples have been stored in 100 and 200cc bulbs, which are filled and sealed off under vacuum. They are provided with the usual thin glass tips which make it possible to seal on stopcocks and use the gas at a later date. In most cases, a 200cc and a 100cc bulb have been filled simultaneously, with the same gas. Many of the 100cc bulbs have received spectroscopic analysis (to be described in the following pages); this has definitely fixed the contents of the corresponding 200cc bulbs.

V. Description of Results

In this section brief consideration will be given to some rather qualitative observations made on the concentration of some of the rarer atmospheric gases and to some unsuccessful work done with water vapor, in an attempt to concentrate the heavy isotope of oxygen. More space will be devoted to a description of the work done on the isotopes of neon, methane, and nitrogen.

Air

While attention was still being directed chiefly to investigating how the diffusion apparatus worked, a rather interesting experiment was carried out. With an apparatus of 24 members, an arrangement was made whereby the air of the laboratory could be circulated through V_ℓ, so that V_ℓ was kept filled to a pressure of 10 to 12 mm with atmospheric air. The pumps were then turned on and the system allowed to run. At the end of one hour the gas in the heavy end of the system, which had of course initially been air, was found to consist principally of carbon dioxide and argon. So much of the latter gas was present, in fact, that the molecular weight of the non-condensible constituent of V_s was 35.6. But the molecular weight of the gas in V_s continued to rise slowly. After 96 hours the gas was analyzed and found to consist of 43.5% carbon dioxide, while the remainder had an average molecular weight of 51.8. Meanwhile, lines had appeared in the visible spectrum which looked very much like the strong green and yellow lines of the krypton discharge. On the assumption that the high molecular weight of the non-condensible part of the gas in V_s was due to the presence of krypton, a simple calculation showed that it constituted 15.5% of this gas. The remaining 41% was argon. Some weight is lent to the validity of this conclusion by the fact that this amount of krypton was about that which would have been collected if all the krypton of all the air which had been circulated through the apparatus had been held in V_s. Krypton is present in the atmosphere normally to the extent of less than one part in a million. This sort of experiment has a practical implication; it is evident that the presence of extremely minute traces of impurities could be detected in a gas by means of an apparatus such as this, if one hadavailable about as much gas as is ordinarily confined in a medium-sized oxygen tank, for example.

Water Vapor

In spite of the hygroscopic nature of the porous members of the diffusion apparatus, attempts were made, with the 24-member system, to produce a concentration of O^{18} by running water vapor in the apparatus. The experimental procedure employed involved the use of a bulb of only 5 liters volume for V_ℓ, but sealed into this end of the system was a liquid air trap in which a few cc of water were maintained at the temperature of melting ice. This served to hold the pressure in V_ℓ steady at 4.5 mm and at the same time provided an effectively infinite volume for V_ℓ, it was hoped. Several separations were made, each of which occupied about 7 hours. The "heavy" water vapor so obtained was introduced into an appropriate tube with external electrodes, in which a discharge was excited by means of a 5-meter oscillator. Photographs of the $\lambda\lambda$2811 Å. and 3064 Å. bands of OH were made on an Adam Hilger quartz spectrograph (E-1). Visual and microphotometer measurements were made on the plates so obtained, but no evidence of bands due to the heavy oxygen isotope was ever obtained. It seems safe to say that, if the heavy bands were present, their intensity could not have been as much as one-twentieth that of the main bands. According to the best evidence[8], O^{18} is normally present to the extent of one part in about five hundred of ordinary oxygen. Therefore the enrichment factor could not have been as large as twenty-five. The calculated separation factor corresponding to the mass ratio 18:20 of the water isotopes turns out to be about 90, for the 24-member apparatus used.

The failure of the work with water vapor probably indicates only that, as might be expected, the isotopes of a gas do not pass through porous tubing according to the simple diffusion law when the gas is absorbed in the tubing. It is yet possible that an appreciable separation might be attained by a much longer run than is necessary with other gases. It will be of interest to investigate this matter further, with the larger apparatus now available.

Neon

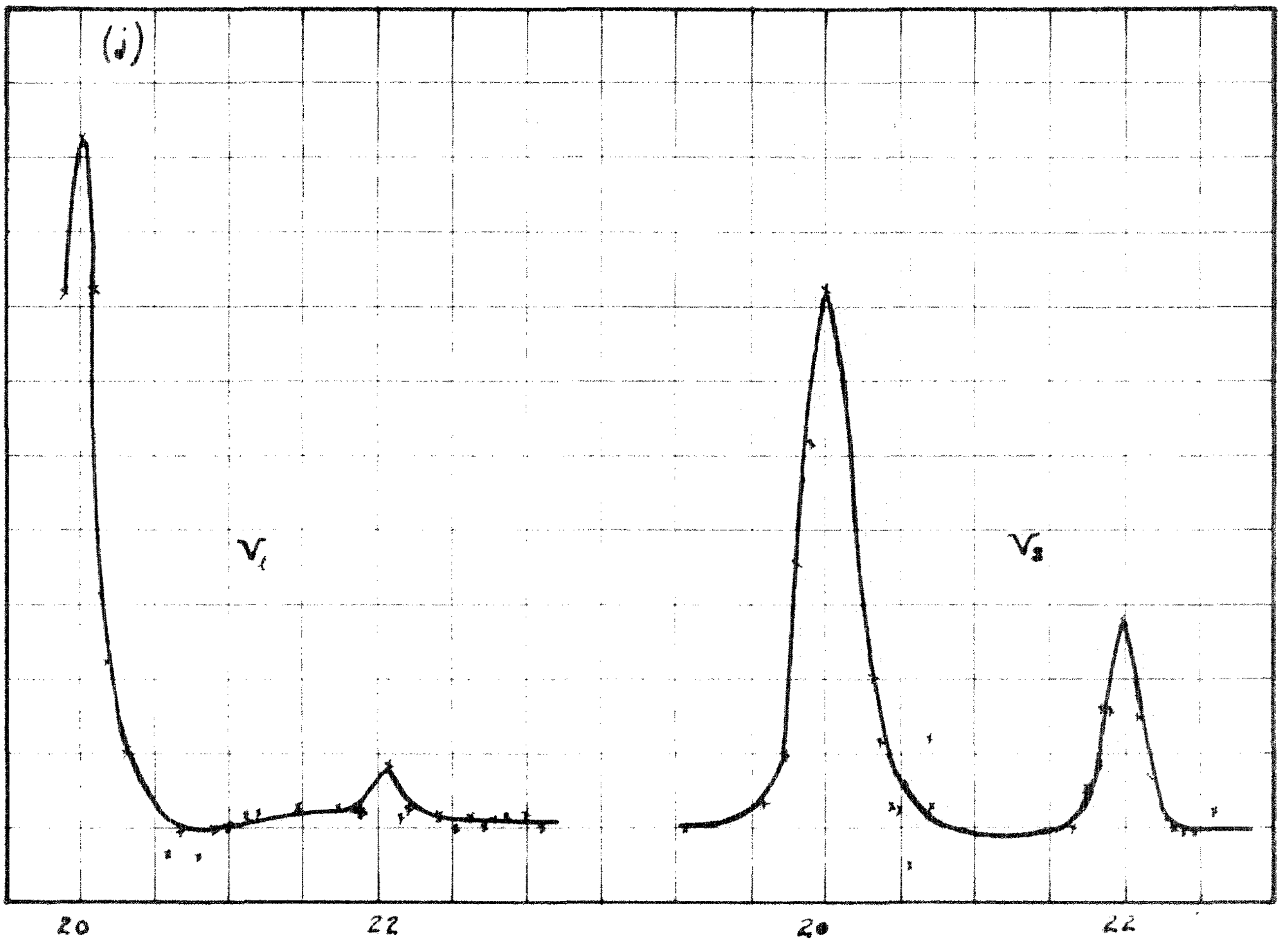
Inasmuch as Hertz has already investigated the application of the diffusion apparatus to the separation of the neon isotopes, and since there has not yet arisen a need for isotopic neon at this laboratory, no attempt has yet been made to separate the isotopes of neon with the 34-member apparatus. However, when tests were being made with carbon dioxide-argon mixtures, in connection with the development of the design of the system, it was thought advisable to perform a separation of the neon isotopes and compare the separation factor so obtained with that obtained with the same apparatus on mixtures of carbon dioxide and argon. The mass ratios are the same in the two cases; hence one should expect the same separation factor. If the factor did indeed turn out to be the same, it was thought safe to conclude that the results obtained with carbon dioxide-argon mixtures were typical of true isotope separations.

The work on neon that is described here was done with the 14-member apparatus which had been found to yield a separation factor of between 8 and 9 for carbon dioxide-argon mixtures (See p. 20). Four separations, at a pressure of 12 mm, were performed on spectroscopically pure neon gas. At the end of each separation, the contents of V_s (which was then 200cc) and part of the contents of V_ℓ (5000cc) were pumped into bulbs which could later be used in the analysis of isotopic compositions. The analysis was carried out on a mass spectrometer[9]. An acknowledgment is due Dr. D. D. Taylor, who built the mass spectrometer, for his valuable aid in performing these analyses.

The results of all measurements agreed in assigning a value of between 6 and 10 to the separation factor. The average of all the data obtained was 7. This figure is probably correct to within about 15%. A sample of the data given by the mass spectrometric measurements is reproduced in curve j. In this figure are plotted the galvanometer deflections of the instrument against an arbitrary (non-linear) mass scale. The two plots shown are for the contents of V_ℓ and V_s at the end of a four-hour run on normal neon. Relative abundances are given directly by the ratios of the heights of the peaks corresponding to Ne^{20} and Ne^{22}.

It was concluded from these measurements that the behaviour of carbon dioxide-argon mixtures was about the same as that of mixtures of neon isotopes. Hence it was thought safe to continue using carbon dioxide and argon in testing the system.

A comparison of the experimental separation factor of 7 or 8 obtained with neon and carbon dioxide-argon mixtures with the theoretically calculated value of 11.5 indicates that the effi-


(j)
V1
V2
20
22
20
22

ciency of these separation processes was lower than the efficiency that has since been obtained, with a larger apparatus, in experiments with carbon dioxide-argon mixtures, as well as in work done on the isotopes of nitrogen and of carbon, in methane gas. The reason for this is not understood, unless it is due to a gradual improvement in technique and methods of handling the gas.

Methane

More work has been done with the diffusion apparatus on methane than on any other gas. Accurate analyses of the enrichment factors obtained have been supplied by Dr. F. A. Jenkins, of the University of California, who has done a considerable amount of band spectroscopic work on some of the heavy samples produced here. His method of analysis has been to compare the intensities of the $\lambda 4737$ Å. head of the $C^{12}C^{12}$ band and the $\lambda 4744$ Å. head of the $C^{12}C^{13}$ band, in the Swann system. Accurate work done previously by Dr. Jenkins[10] on discharges in argon containing small amounts of methane gas have placed the relative intensities of these two band heads at 53:1, which corresponds to something less than 1 atomic percent of C^{13} in normal carbon. In the best specimens of heavy methane produced by the diffusion apparatus, the relative intensities of these two band heads have been 3.3:1, corresponding to an enrichment factor of 16.

Methane for this work has been obtained through the kindness of Drs. Bruce Sage and W. N. Lacey of the Chemistry Department. This gas has been free from ethane and other heavy impurities, with the exception of a few tenths of a percent of nitrogen. The procedure has always been to commence operations by removing the heavy impurities from the methane. This involves a preliminary run of several hours; it also results in the loss of some of the heavy carbon. After the purification of the gas, the apparatus is allowed to run for another twenty-four hours, at the end of which time a heavy sample is removed from V_s. This may be repeated another two or three times before the methane in the system is considered to be "used up." Several bulbs of heavy methane have been produced in this way. Three of them have been analyzed spectroscopically. The first gas produced was found to have a $C^{12}:C^{13}$ ratio of 14.4, corresponding to an enrichment factor of 7.5[11]. The other two samples have been found to have $C^{12}:C^{13}$ ratios of 10.6 and 11.0 ± 1, respectively, corresponding to an enrichment factor of about 10 ± 1. The agreement with theory of these results is discussed in Appendix B.

On one occasion, a considerably larger enrichment factor was obtained by employing the device described in the remarks on "General Procedure." The gas in the heavy end of the system was withdrawn at the end of two diffusion processes, and was reintroduced into the system, together with enough ordinary methane to restore the pressure to 10 or 11 mm in V . A final diffusion resulted in a heavy sample with a $C^{12}:C^{13}$ ratio of 6.7 ± .4, corresponding to an enrichment factor lf 16 ± 1. Each of the separations involved in this entire process required its own preliminary purification, of course.

In Plate III are reproduced photographs of some of the band spectra which have been studied by Jenkins. Fig. 1 shows the Swann bands of C_2. The lower photograph was taken when the discharge tube contained some of the first heavy methane produced

(Enrichment factor only 7.5). The single dot (·) locates the head of the λ4737 Å. $C^{12}C^{12}$ band; the double dot (:) locates the isotope head $C^{12}C^{13}$ at λ4744 Å.; the triple dot (⁝) locates the head of the $C^{13}C^{13}$ band, which is faintly visible in this photograph. In the upper photograph, which was taken when the discharge tube contained a small amount of ordinary methane, the $C^{13}C^{13}$ band, if it appeared, would be only one ten-thousandth as intense as the main band.

Fig. 2 is a print from an intensity plate, taken of the same bands, but with the best sample of heavy methane yet produced in the discharge tube (Enrichment factor 16). By means of the calibrated step-weakener used in taking the exposure pictured here, the relative intensities of the $C^{12}C^{12}$ and the $C^{12}C^{13}$ bands was found to be 3.4 ± .2. The intensity of the $C^{13}C^{13}$ band head, which could be measured, was found to be consistent with these results. The faint lines marked with double dots in the left of the picture are heads of $C^{13}N^{14}$ bands, which entered as contamination.

With heavy methane of enrichment factor 10, 21-foot grating photographs of the (0,0), (0,1), and (0,2) bands of CN, of λλ3883, 4216, and 4606 Å., respectively, have been made, in which enough isotope lines could be measured to make possible an accurate determination of the mass of C^{13}. Fig. 3 is an enlargement of two photographs of the (0,1) band, the upper exposure taken with ordinary methane (plus a small quantity of nitrogen, of course) in the discharge tube, the lower exposure taken with the enriched gas. From measurements on plates such as this, preliminary calculations by Jenkins have assigned the value 13.0088 ± .0005 to the mass of $C^{13\ 12}$, taking the mass of C^{12} to have the value in-

Plate III

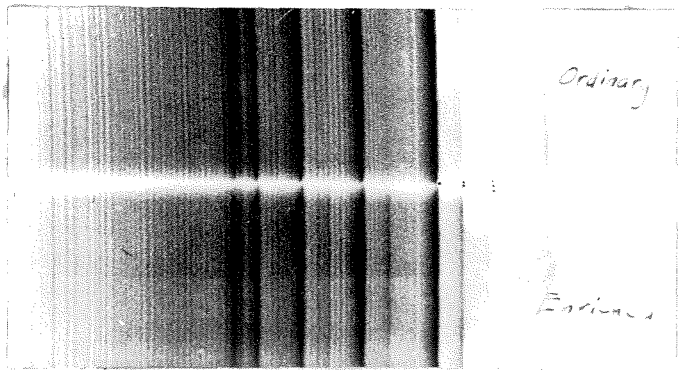


Fig. 1

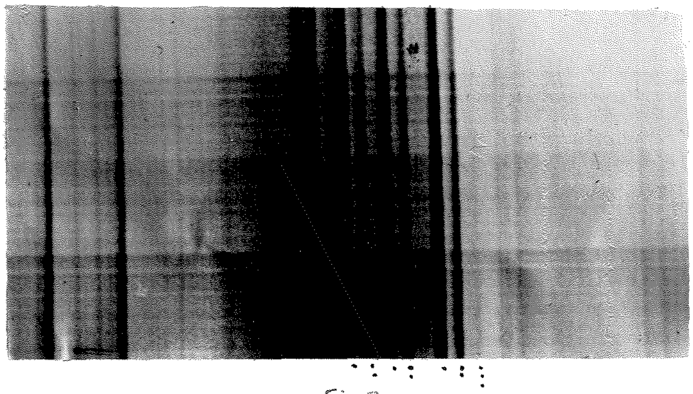


Fig. 2

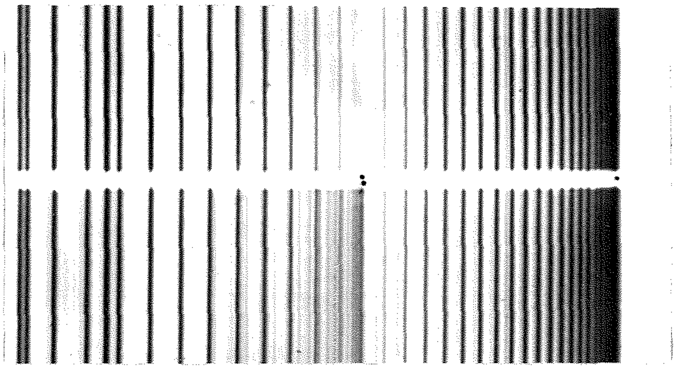


Fig. 3

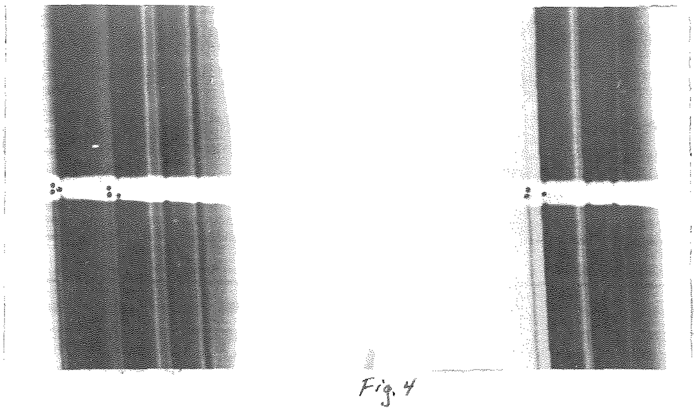


Fig. 4

dicated by the results of nuclear disintegrative processes.

For the near future, further calculations in connection with the mass of C^{13} are required. It is also thought that, with some of the heaviest gas, it might be possible to get sufficient intensity of the $C^{13}C^{13}$ Swann band at λ4751 Å. to make it possible to measure the spin of C^{13} by the method of alternating intensities. Of course, other molecules containing carbon should be studied.

Besides the spectroscopic work, attempts have been made here to study the nuclear disintegrative properties of heavy carbon, but these attempts have, so far, met with but indifferent success. The difficulty has been in getting the carbon deposited on a solid target which can be bombarded in the high-voltage experimental tube of the radiation laboratory. In order to deposit the carbon, an arrangement was devised whereby a small piece of nickel, of the proper dimensions for a target, could be brought to incandescence (by means of an induction furnace) in an atmosphere of about 1 cm pressure of heavy methane. By the introduction of a small amount of oxygen, it has sometimes been possible to deposit some of the carbon from the methane on the target, but the number of failures has far exceeded the number of successful operations, and this work has been abandoned for the time being at least. With the two or three targets which did acquire carbon in this way, some data have been secured by Fowler and Delsasso[13] of the radiation laboratory here which indicate that certain long-range proton tracks observed in a cloud chamber when carbon is bombarded by 900,000 volt deuterons are due to the reaction

$$C_6^{13} + H_1^2 \rightarrow C_6^{14} + H_1^1 + Q$$

Nitrogen

In connection with the spectroscopic work on CN described in the foregoing, it has been thought worth while to attempt to produce nitrogen gas in which N^{15} is sufficiently abundant to make possible measurements on the bands due to $C^{12}N^{15}$. In particular, it is desirable to obtain an accurate spectroscopic value for the mass of N^{15}. Accordingly, nitrogen gas has been run through the system. The method employed has been the same as that used in producing methane with an enrichment factor of 16, except that, in the case of nitrogen, three preliminary diffusions were performed before the final separation. Also, it was unnecessary to purify the gas in these preliminary diffusions. A single purification, just before the final separation, was thought adequate in this case.

Several bulbs have been filled with the heavy products of this run. One of these bulbs was sent to Dr. Jenkins, who examined the gas therein for traces of N^{15}. In Fig. 4, Plate III, are shown photographs of the (1,0) and (2,0) ($\lambda\lambda$3159 Å. and 2977 Å respectively) bands of N_2. The upper photograph was taken when the discharge tube contained ordinary nitrogen, the lower one when some of the heavy gas had been introduced. In normal nitrogen, the relative intensities of the $N^{14}N^{14}$ and $N^{14}N^{15}$ bands have been measured to be 175:1.[14] Jenkins' measurements on the lower photograph gave a value of 16.5:1 for these relative intensities, corresponding to an enrichment factof of 11 for the entire process[15]. Photographs have since been taken of the CN bands, using some of this gas. A sufficient intensity of the bands due to heavy nitrogen is present to make possible an accurate determination of the mass of N^{15}. This work is to be completed in the near future.

Appendix B should be consulted for the development of the equations governing the separation of nitrogen. It is there shown that the agreement of the results of this experiment with the theory is quite good.

VI. Plans for Future Work

In the immediate future, work is to be done on the isotopes of oxygen. Oxygen gas is to be used in the diffusion apparatus, and it is expected that a heavy sample containing about 10% O^{18}, instead of the usual 0.2%, can be produced.

The next problem now contemplated is a somewhat more ambitious project, but one which should be certain to yield interpretable results. Starting with pure heavy hydrogen (H_2^2), a series of diffusions is to be made. The heavy product of about thirty such diffusions is to be collected and reintroduced into the system, together with enough normal heavy hydrogen to supply the proper pressure. The final heavy product should include nearly all the H^3 that was initially in the one gram of heavy hydrogen which will have been led through the system by that time--concentrated in a volume of 300cc at a pressure of 6mm. If, as has been estimated[16], H^3 exists in H^2 to the extent of one part in 200,000, the final product should contain about two or three percent of this "heavy heavy hydrogen." Probably 0.1% can be detected spectroscopically.

Work of an incidental nature will be done on neon. Argon will be worked with at some time. It will be of interest because it is the light isotope which is the rarer in this case, and because the mass ratio, 36:40, is such as to result in a very high separation factor. The isotopes of sulphyr will be studied, if it proves possible to run hydrogen sulphide gas in a system containing so much hot mercury. Chlorine is subject to the same uncertainty.

VII. Suggestions for Improvement of the Apparatus and Technique

More separation members will be required in order to produce the isotopic specimens which one would like to have for many experiments. Probably the present apparatus can be enlarged to about fifty members without any change in design, but already some difficulty is being experienced with the pressure gradient between V_ℓ and V_s. Although no precise measurements have been made, it is known that, when the pressure in V_ℓ is 10 mm, that in V_s is only 6 or 7 mm. When the pressure in V_ℓ is diminished, the relative pressure gradient becomes worse. The large gradient in this diffusion apparatus is undoubtedly due to the high speed at which the gas is circulated, which of course cannot be diminished, even if this were desirable, without changing the porous tubes and increasing the equilibrium time of the system. This difficulty can be eliminated, of course, by the use of larger tubing throughout (including the porous tubing), without cutting down the speed of separation. Something might be gained simply by shortening and enlarging some of the leads, without changing the porous members.

As is pointed out elsewhere in this thesis, another requirement of the apparatus is that some of the leads be sufficiently enlarged that they will not clog up with mercury in the course of a week's operation of the system. Of course, if any means could be devised to prevent the circulation of so much mercury vapor, this would be very desirable.

A study should be made of times of equilibrium, and their dependence on the masses of the gaseous isotopes, their relative abundances, etc. It is believed that much time is being wasted by allowing the apparatus to continue running after equilibrium has been reached.

It is also important to ascertain the effect on the equilibrium time of increasing V_s. It seems fairly certain that considerably larger quantities of gas could be gathered than have been so far, without any appreciable influence on the time of separation.

Finally, the effect of pressures should be studied more carefully than it has been. This work must be done on the isotopes of several gases, if possible. It may be permissible to work at considerably higher pressures than have been so far used, for many gases. By using a different style of porous tubing (See discussion on viscosity effects, in Appendix A) it may be possible to take full advantage of the possible speed of the pumps; it is even conceivable that a system might be devised to work at several cm pressure, making use of mechanical pumps of some sort for circulation.

This problem was suggested by Prof. Wm. R. Smythe, whose steady interest and invaluable suggestions have been of the greatest assistance in the work which has been done. The author would also like to make a blanket acknowledgement to the entire staffs

of the Physics and Chemistry Departments, for at one time or another the advice of most of the members thereof has been solicited. Certainly the facilities provided for this work and the cooperation afforded by everyone concerned have been all that could be hoped for.

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APPENDIX A

Theory and Operation of the Diffusion Apparatus

1. Hertz' Simple Theory

In his first paper[3] on the diffusion apparatus, Hertz gave a simple derivation of the equations governing its operation. This derivation is here reproduced in essentially the form in which Hertz gave it. Considerable extension of and correction to this simple development is given in following paragraphs.

In his derivation, Hertz made the following explicit assumptions:

1. The diffusion of the gas through the walls of the tubing is not affected by its motion along the length of the tubing. (This involves the assumption that both types of molecules travel at the same speeds along the diffusion tubes)
2. Diffusion along the tube is negligible.
3. The amount of gas which diffuses through ℓ_2 (See Fig.2) bears to the amount which diffuses through ℓ_1 the ratio of the lengths of the tubes, $\ell_2 : \ell_1$.

In addition, his derivation is applicable only when the following conditions are met:

4. The pressure is zero on the outside of the porous tubes.
5. The gas consists of a mixture of two isotopes only.
6. The total pressure is the same at corresponding points of all separation members.
7. The pressure is sufficiently low that viscosity effects are negligible.

The notation to be used throughout this appendix is as follows:

m_ℓ--molecular weight of light isotope

m_h--molecular weight of heavy isotope

ρ-- $\sqrt{\frac{m_\ell}{m_h}}$

ℓ_1--length of porous tube AE (See Fig.2)

ℓ_2--length of porous tube ED

S_i--"stream" of light isotope, i. e., number of light molecules per second passing the point i.

C_i--"concentration" of heavy isotope, i. e., ratio of number of heavy molecules to number of light molecules passing point i in any time interval.

q --"separation factor," i. e., ratio of the C's at corresponding points in adjacent separation members.

Other symbols will be introduced as needed.

All derivations given apply only to the steady state, after equilibrium has been reached.

In accordance with assumption 1, we may attack the problem by first dealing with the stationary diffusion of a mixture of isotopes through the porous walls of a vessel in which the gas is confined. Condition 4 enables us to assume the diffusion to be entirely one-way, i. e., inside-out. Under such circumstances the usual formulas apply:

$$N_h = (N_h)_0 e^{-\alpha_h t} ; \quad N_\ell = (N_\ell)_0 e^{-\alpha_\ell t}$$

where

$$\frac{\alpha_h}{\alpha_\ell} = \sqrt{\frac{m_\ell}{m_h}} = \rho$$

Therefore

$$\frac{N_h}{N_\ell} = \left(\frac{N_h}{N_\ell}\right)_0 e^{-\alpha_h t} e^{\alpha_\ell t}$$

$$= \left(\frac{N_h}{N_\ell}\right)_0 e^{-(\rho-1)\alpha_\ell t}$$

But

$$e^{-\alpha_\ell t} = \frac{N_\ell}{(N_\ell)_0}$$

Therefore

$$\left(\frac{N_h}{N_\ell}\right) = \left(\frac{N_h}{N_\ell}\right)_0 \left[\frac{N_\ell}{(N_\ell)_0}\right]^{\rho-1}$$

This result may be transferred over into the "stream flow" language, (by condition 1), giving

$$\frac{c}{c_0} = \left(\frac{s}{s_0}\right)^{\mu-1}$$

or

$$\left.\frac{c_2}{c_1} = \left(\frac{s_2}{s_1}\right)^{\mu-1}\right\} \qquad \text{Eq. A1}$$

This relation finds specific application in the equations

$$\frac{C_E}{C_A} = \left(\frac{S_E}{S_A}\right)^{\mu-1} \qquad \text{Eq. A2}$$

$$\frac{C_D}{C_A} = \left(\frac{S_D}{S_A}\right)^{\mu-1} \qquad \text{Eq. A3}$$

We shall need also the equation

$$C_A S_A = C_B S_B + C_E S_E \qquad \text{Eq. A4}$$

which merely expresses the fact that the total number of heavy molecules flowing into tube ℓ_1 in any time interval equals the number flowing out, and

$$S_D(1+C_D) = S_B(1+C_B) \qquad \text{Eq. A5}$$

which expresses a similar "conservation" law for all the molecules (based on the validity of postulate 6). In writing down this equation, use has been made of the fact that S_B and C_B equal $S_{D'}$ and $C_{D'}$, when a steady state exists.

A final "conservation" law required is, simply

$$S_A = S_B + S_E$$

Or, if we write

$$f = \frac{S_B}{S_A} \qquad \text{Eq. A6}$$

then

$$\frac{S_E}{S_A} = (1-f) \qquad \text{Eq. A7}$$

Now

$$g = \frac{C_D}{C_{D'}} = \frac{C_D}{C_B} = \frac{C_D}{C_A}\,\frac{C_A}{C_B}$$

Equations A4, A2, and A7 give

$$C_A S_A \left[1-(1-f)^{\mu}\right] = C_B S_B$$

whence reference to Eq. A6 shows

$$\frac{C_A}{C_B} = \frac{f}{1-(1-f)^{\mu}} \qquad \text{Eq. A7.1}$$

Equations A3, A5, and A6 give

$$\frac{C_D}{C_A} = \left(f\,\frac{1+C_B}{1+C_D}\right)^{\mu-1} \qquad \text{Eq. A7.2}$$

Therefore

$$g = \left[\frac{f^{\mu}}{1-(1-f)^{\mu}}\right]\left(\frac{1+C_B}{1+C_D}\right)^{\mu-1} \qquad \text{Eq. A8}$$

$$= g_0 \left(\frac{1+C_B}{1+C_D}\right)^{\mu-1} \qquad \text{Eq. A8'}$$

where $$q_0 = \frac{f^n}{1-(1-f)^n}$$ Eq. A9

Ordinarily, it will be seen, it is sufficiently accurate to set $q = q_0$. It is generally only when one is dealing with a mixture of gases of widely different weights that the other factor departs appreciably from unity.

f has yet to be evaluated. For this purpose we may invoke a final conservation equation. This equation requires the use of the relation stated in postulate 3:

$$\frac{s_C}{s_B} = \frac{l_2}{l_1}$$ Eq. A10

This also assumes that the variation in C from member to member is a small quantity. Such an assumption is strictly true in all cases which occur, and will not be explicitly stated again. Making no stronger assumptions, we may write

$$s_B + \frac{l_2}{l_1} s_B + s_B = s_A$$ Eq. A11

The first two terms pertain to the light gas passing through the pump and thence into A; the third term recognizes the fact that, for equilibrium, the number of light molecules going from one separation member to the next in one connecting tube must exactly equal the number of light molecules going back in the other connecting tube.

Equations A11 and A6 enable f to be determined as

$$f = \frac{1}{2 + \frac{l_2}{l_1}}$$ Eq. A12

Equations A9 and A12 constitute the important results of this section. By means of them one can calculate closely the separation factor of a diffusion apparatus under many circumstances.

Speed of Separation: Evidently it is impossible to make any direct calculation as to the rapidity with which equilibrium is reached, but Hertz has taken as an indication of this equilibrium time the net increase in the number of heavy molecules in going from D' to D, i. e., he considers an indication of the speed to be provided by the factor

$$s_D c_D - s_B c_B = \left(\frac{s_D}{s_B}\frac{c_D}{c_A} - \frac{c_B}{c_A}\right) s_A c_A \frac{s_B}{s_A}$$

$$= \left(f^{\mu-1} - \frac{1-(1-f)^\mu}{f}\right) f \cdot s_A c_A$$

$$= \left[f^\mu - 1 + (1-f)^\mu\right] s_A c_A \qquad \text{Eq. A13}$$

to the degree of approximation involved in setting $s_D = s_B$ *and* $q = q_0$. Hertz sets

$$G = \left[f^\mu - 1 + (1-f)^\mu\right] \qquad \text{Eq. A14}$$

and considers this to be an indication of the relative speed of the apparatus. To a sufficiently close approximation for must purposes Equations A9 and A14 may be written

$$q_0 = \frac{1}{\mu} f^{\mu-1} \qquad \text{Eq. A9'}$$

$$G = f^\mu - \mu f \qquad \text{Eq. A14'}$$

Since $\mu < 1$, q decreases with increasing f, while G and f increase together. In Hertz' first paper[3] are reproduced curves showing this dependence of G and q_0 on f.

2. A Critical Examination of the Simple Theory

Of the explicit assumptions involved in the foregoing development, there seems to be no reason to doubt the validity of the first, as long as the pressure is so low that the effect of viscosity in slowing down the flow of the gas along the tubes is negligible. It seems safe to assume that this type of viscosity effect cannot be large enough to be troublesome, for such large tubes and for pressures of only a few cm of mercury. The second assumption has been investigated by the use of separation members of large and small bore porous tubes, with the results described in the text of this thesis. The third would seem to be ordinarily beyond serious criticism, although one might expect effects at the two ends of each porous tube to impair slightly the accuracy of the values of f calculated on the purely geometrical considerations of this section. Also, it will be seen necessary to modify this assumption somewhat when there is present a third gas in the system.

Assumptions 4, 5, 6, and 7 require experimental conditions which cannot always be met. The failure of each of these conditions leads to a correction to the simple theory. These corrections will be considered in order in the following paragraphs.

I. Correction to Simple Theory Due to Backward Diffusion Through the Porous Tubes:

The calculation will be carried out for the case commonly interested in--for which C, the concentration of the heavy isotope, is small. We must add to our terminology the following:

p_1 --total pressure in the channel of the porous tube

p_2 --total pressure outside porous tube (previously assumed negligible)

n_1'--number of light molecules per unit volume at some point inside the tube

n_2'--number of light molecules per unit volume in region out side the tube

$\overline{C}_1$ --average C inside the tube being dealt with

$\overline{C}_2$ --average C outside the tube being dealt with

p_2/p_1 will be considered small enough for its higher powers to be neglected.

For the investigation required, it will be convenient for us to fix our attention on a small quantity of the gas and follow its history as it progresses through the tube. This quantity is steadily being diminished by diffusion through the porous wall of the tube; it is being partially augmented by diffusion in the opposite direction. We need an expression for the net rates at which heavy and light molecules are lost from such a small quantity of gas as it proceeds along its path. Suppose, at some instant, our chosen group of molecules is confined within a length element dl of the tube, which has a cross-section A. The rate of loss of light molecules by diffusion from region 1 (inside the tube) to region 2 (outside the tube) will be

$$\left(\frac{dn_1}{dt}\right)_{12} = \frac{K}{\sqrt{m_1}}\, n_1'\, dl = \frac{K}{\sqrt{m_1}}\, \frac{n_1}{A}$$

where n_1 represents the total number of light molecules in the selected group. This loss will be partially compensated for by the diffusion from 2 to 1 of amount

$$\left(\frac{dn_1}{dt}\right)_{21} = \frac{K}{\sqrt{m_1}}\, n_2'\, dl$$

Hence the net rate of loss of light gas from our chosen group of molecules is

$$\left(\frac{dn_1}{dt}\right)_{\substack{net\\12}} = \frac{K}{A\sqrt{m_1}}\left[n_1 - n_2'\frac{n_1}{n_1'}\right] = \frac{K}{A\sqrt{m_1}}\left(1 - \frac{p_2}{p_1}\right)n_1$$

to the order of approximation involved in the assumption that the light gas constitutes the major portion of the isotopic mixture. Similarly, for the heavy gas

$$\left(\frac{d(c_1 n_1)}{dt}\right)_{\substack{net\\12}} = \frac{K}{A\sqrt{m_2}}\left[c_1 n_1 - c_2 n_2'\frac{n_1}{n_1'}\right] = \frac{K}{A\sqrt{m_2}}\left(1 - \frac{c_2}{c_1}\frac{p_2}{p_1}\right)c_1 n_1$$

To a sufficient approximation, we may write, therefore

$$n_1 = N_0\, e^{-\frac{K}{A\sqrt{m_1}}\left(1 - \frac{p_2}{p_1}\right)t} \; ; \; c_1 n_1 = (c_0 N_0)\, e^{-\frac{K}{A\sqrt{m_2}}\left(1 - \frac{\overline{c_2}}{\overline{c_1}}\frac{p_2}{p_1}\right)t}$$

where $\frac{\overline{c_2}}{\overline{c_1}}$ has been substituted for the variable $\frac{c_2}{c_1}$ in the exponent. Combination of these two equations in the usual way gives the result

$$\frac{c_1}{c_0} = \left(\frac{n_1}{N_0}\right)^{\mu' - 1}$$

where

$$\mu' \equiv \mu\, \frac{1 - \frac{\overline{c_2}}{\overline{c_1}}\frac{p_2}{p_1}}{1 - p_2/p_1} \qquad \text{Eq. A15}$$

$\frac{\overline{c_2}}{\overline{c_1}}$ must now be evaluated. This may be done by noting the obvious equality

$$\bar{c}_2 = \frac{\left(\frac{d(c_1 n_1)}{dt}\right)_{net\ 12}}{\left(\frac{dn_1}{dt}\right)_{net\ 12}} = \sqrt{\frac{m_1}{m_2}}\ \frac{1 - \frac{\bar{c}_2}{c_1}\frac{p_2}{p_1}}{1 - \frac{p_2}{p_1}} \cdot \bar{c}_1$$

or

$$\frac{\bar{c}_2}{\bar{c}_1} = \frac{\nu}{1-(1-\nu)\frac{p_2}{p_1}} = \nu\left[1+(1-\nu)\frac{p_2}{p_1}\right]$$

Substitution in Eq. A15 gives, neglecting squares and higher powers of p_2/p_1

$$\nu' = \nu\left[1+\frac{p_2}{p_1}(1-\nu)\right] \qquad \text{Eq. A16}$$

The magnitued of this effect may best be appreciated by reference to an actual example. For the diffusion apparatus of 34 members, described in the text of this thesis, when used to separate the isotopes of methane gas, calculations show

p_2/p_1	Q
0	44
1/10	30
1/5	18

The surprisingly large effect of poor pumping explains the trouble that was taken to develop adequate pumps for the diffusion apparatus. Even with the final apparatus, it seems likely that this effect is not always entirely negligible. However, manometers permanently sealed into the high vacuum side of some of the separation members have indicated that, when the system is run at pressures up to 10 or 11 mm of mercury, p_2/p_1 can scarcely be greater than 1/20.

II. Correction to Simple Theory Due to the Presence of a Third Gas:

In this section the development of Part 1 will be modified so as to permit the calculation of the separation factor of two gaseous isotopes when a third gas is present in the system. Let us denote by γ the concentration factor of the third gas relative to the lighter of the two isotopes, and by η the square root of the ratio of the molecular weights of the lighter isotope and this impurity.

The development through Equation A4 is applicable without modification. Equation A5 must be modified to take account of the presence of the third gas. Also, a simplification used in writing Equation A5, there permissible owing to the smallness of the deviation of μ from unity, is no longer possible, since η may differ appreciably from 1. The general differential equation

$$-\frac{dn}{dt} = \frac{K}{\sqrt{m}}\, n$$

suffices to show that $\frac{1}{\sqrt{m}}$ is a measure of the ease with which each gas diffuses through the porous members. Therefore it seems reasonable to assert that the total amount of gas passing point D' in any time interval should not be equal to the amount passing D, even though there is no pressure drop in the apparatus. Rather, the flow through D' should exceed that through D, since the average molecular weight of the gas at D' is less than that at D. The factor by which the total amount of gas circulated by the diffusion pump of one separation member exceeds that circulated by the diffusion pump of the next separation member on its left (See Fig.2B) should be, approximately

$$\frac{1+\mu c_{D'}+\eta\gamma_{D'}}{1+c_{D'}+\gamma_{D'}} \div \frac{1+\mu c_D+\eta\gamma_D}{1+c_D+\gamma_D}$$

The analogue of Equation A5 is, therefore

$$\frac{s_B(1+c_B+\gamma_B)}{s_D(1+c_D+\gamma_D)} = \frac{(1+c_D+\gamma_D)}{(1+c_B+\gamma_B)}\,\frac{(1+\mu c_B+\eta\gamma_B)}{(1+\mu c_D+\eta\gamma_D)} \qquad \text{Eq. A17}$$

or, approximately,

$$s_B\left[1+(2-\mu)c_B+(2-\eta)\gamma_B\right] = s_D\left[1+(2-\mu)c_D+(2-\eta)\gamma_D\right] \qquad \text{Eq. A18}$$

Equation A18 was obtained from A17 only by assuming $c_B, \gamma_B, c_D, + \gamma_D$ so small that their squares may be neglected. This is always true for the C's, but not invariably so for the γ's. This limitation on the theory must be borne in mind in applying it.

If Equation A18 is substituted for Equation A5, the subsequent development gives, for Equation A8

$$g = g_0 \left[\frac{1+(2-\mu)c_B+(2-\eta)\gamma_B}{1+(2-\mu)c_D+(2-\eta)\gamma_D} \right]^{\mu-1} \qquad \text{Eq. A19}$$

In order to derive an expression for f, Hertz' postulate 3 must be modified in accordance with the foregoing considerations as to rates of diffusion. The same kind of argument shows that Equation A10 must now be replaced by

$$\frac{s_C(1+c_C+\gamma_C)}{s_B(1+c_B+\gamma_B)} = \frac{l_2}{l_1} \times F$$

where F is a factor which takes account of the greater ease with which the gas inside l_1 diffuses, owing to its smaller average molecular weight. A little consideration shows that

$$F = \frac{\overline{S}_2 + (\overline{Sc})_2\mu + (\overline{S\gamma})_2\eta}{\overline{S}_2 + (\overline{Sc})_2 + (\overline{S\gamma})_2} \div \frac{\overline{S}_1 + (\overline{Sc})_1\mu + (\overline{S\gamma})_1\eta}{\overline{S}_1 + (\overline{Sc})_1 + (\overline{S\gamma})_1}$$

where $\overline{S}_2$ is the average value of S throughout the tube l_2, etc. These average values are evidently given by the expressions

$$s_B = \kappa\overline{S}_1 \quad ; \quad s_C = \kappa'\overline{S}_2$$

$$c_B s_B = \mu\kappa(\overline{Sc})_1 \quad ; \quad c_C s_C = \mu\kappa'(\overline{Sc})_2$$

$$\gamma_B s_B = \eta\kappa(\overline{S\gamma})_1 \quad ; \quad \gamma_C s_C = \eta\kappa'(\overline{S\gamma})_2$$

Combining these expressions, we have

$$\frac{s_C(1+c_C+\gamma_C)}{s_B(1+c_B+\gamma_B)} = \frac{l_2}{l_1} \times \frac{(1+c_C+\gamma_C)}{\left(1+\frac{c_C}{\mu}+\frac{\gamma_C}{\eta}\right)} \times \frac{\left(1+\frac{c_B}{\mu}+\frac{\gamma_B}{\eta}\right)}{(1+c_B+\gamma_B)}$$

or

$$\frac{l_2}{l_1} = \frac{s_C}{s_B} \, \frac{1+\frac{c_C}{\mu}+\frac{\gamma_C}{\eta}}{1+\frac{c_B}{\mu}+\frac{\gamma_B}{\eta}} \qquad \text{Eq. A20}$$

Now the correct expression to which Equation A11 is an approximation is

$$s_A(1+c_A+\gamma_A) = s_B(1+c_B+\gamma_B) + s_C(1+c_C+\gamma_C) + s_D(1+c_D+\gamma_D) \qquad \text{Eq. A21}$$

Substitution of Equations A18, A20 and A6 in Equation A21 gives

$$\frac{1}{f} = \frac{1+c_B+\gamma_B}{1+c_A+\gamma_A} + \frac{1+c_D+\gamma_D}{1+c_A+\gamma_A}\,\frac{1+(2-\mu)c_B+(2-\eta)\gamma_B}{1+(2-\mu)c_D+(2-\eta)\gamma_D} + \frac{l_2}{l_1}\,\frac{1+c_C+\gamma_C}{1+c_A+\gamma_A}\,\frac{1+\frac{c_B}{\mu}+\frac{\gamma_B}{\eta}}{1+\frac{c_C}{\mu}+\frac{\gamma_C}{\eta}}$$

Now

$$\mu = 1-\epsilon$$

where ϵ is a small positive quantity. Therefore

$$2-\mu = 1+\epsilon \approx \frac{1}{\mu}$$

Similarly $$2-\eta \sim \frac{1}{\eta}$$

A further simplification may be introduced by noting that Equation A7.1 is, very nearly

$$\left.\begin{aligned} c_A &= \frac{c_B}{\mu} \\ \gamma_A &= \frac{\gamma_B}{\eta} \end{aligned}\right\} \qquad \text{Eq. A7.1'}$$

Similarly

This gives
$$\frac{1}{f} = \frac{1+c_B+\gamma_B}{1+\frac{c_B}{\mu}+\frac{\gamma_B}{\eta}} + \frac{1+c_D+\gamma_D}{1+\frac{c_D}{\mu}+\frac{\gamma_D}{\eta}} + \frac{l_2}{l_1}\,\frac{1+c_C+\gamma_C}{1+\frac{c_C}{\mu}+\frac{\gamma_C}{\eta}}$$

Writing $1-\mu=\epsilon$ and $1-\eta=\delta$:
$$\frac{1}{f} = (1-\epsilon c_B-\delta\gamma_B)+(1-\epsilon c_D-\delta\gamma_D)+\frac{l_2}{l_1}(1-\epsilon c_C-\delta\gamma_C)$$
$$= \left(2+\frac{l_2}{l_1}\right)-\epsilon\left(c_B+c_D+\frac{l_2}{l_1}c_C\right)-\delta\left(\gamma_B+\gamma_D+\frac{l_2}{l_1}\gamma_C\right)$$

In the actual diffusion apparatus, $\frac{l_2}{l_1}$ is about 10, so that it is enough to write $$\frac{1}{f} = \frac{1}{f_0} - \left(\epsilon\frac{l_2}{l_1}c_C+\delta\frac{l_2}{l_1}\gamma_C\right)$$
where $1/f_0$ is defined as $$2+\frac{l_2}{l_1}$$

Now, since nearly all the gas which enters tube l_2 diffuses through its wall, c_C must differ inappreciably (for the present purposes) from c_E, and γ_C from γ_E. But, from Equation A1
$$c_E = c_A\left(\frac{S_C}{S_A}\right)^{\mu-1} = c_A(1-f)^{\mu-1}$$

Or, from Equation A7.1,
$$c_E = \frac{c_B}{\mu}(1-f)^{\mu-1} \sim c_C$$
$$\gamma_E = \frac{\gamma_B}{\eta}(1-f)^{\eta-1} \sim \gamma_C$$

and we have, approximately
$$\frac{1}{f} = \frac{1}{f_0} - \left[\frac{l_2}{l_1}\epsilon\frac{c_B}{\mu}(1-f)^{\mu-1}+\frac{l_2}{l_1}\delta\frac{\gamma_B}{\eta}(1-f)^{\eta-1}\right]$$
$$\sim \frac{1}{f_0} - \frac{l_2}{l_1}(c_B\epsilon+\gamma_B\delta)$$

For the apparatus used, $$\frac{l_2}{l_1} \sim \frac{1}{f_0}$$

Therefore $$\frac{1}{f} \sim \frac{1}{f_0}(1-\epsilon c_B-\delta\gamma_B) \qquad \text{Eq. A22}$$

Now, in accordance with Equations A9', A19, and A22, we have
$$g = \frac{1}{\mu}f_0^{\mu-1}(1-c_B\epsilon-\gamma_B\delta)^{\epsilon}\left(\frac{1+\frac{c_D}{\mu}+\frac{\gamma_D}{\eta}}{1+\frac{c_B}{\mu}+\frac{\gamma_B}{\eta}}\right)^{\epsilon}$$

Writing $$c_D = g\,c_B\,;\ \gamma_D = g'\gamma_B\,;\ g' = \frac{\gamma_D}{\gamma_{D'}}$$
$$g = \frac{1}{\mu}\left(\frac{1}{f_0}\right)^{1-\mu}(1-c_B\epsilon-\gamma_B\delta)^{\epsilon}\left[1+(g-1)\frac{c_B}{\mu}+(g'-1)\frac{\gamma_B}{\eta}\right]^{\epsilon}$$
$$= \frac{1}{\mu}\left(\frac{1}{f_0}\right)^{1-\mu}\left[1-c_B\left(\epsilon-\frac{g-1}{\mu}\right)-\gamma_B\left(\delta-\frac{g'-1}{\eta}\right)\right]^{\epsilon}$$

or
$$q = \frac{1}{\mu}\left(\frac{1}{f'}\right)^{1-\mu}$$

where
$$\frac{1}{f'} = \frac{1}{f_0}\left[1 + c_B(q-1) + \gamma_B(q'-1)\right] \qquad \text{Eq. A23}$$

Now $c_B(q-1)$ is negligibly small, for actual separations, while $\gamma_B(q'-1)$ will be $\lesssim$ 1/10 for all except the last two or three separation members, at any rate. Hence it appears, from Equation A23, that the effect on q of impurities is almost entirely negligible, and for most purposes can be ignored. This result in itself justifies the looseness of the method used in its derivation, inasmuch as only the order of magnitude of the correction term here concerns us. Nevertheless, the conclusion here drawn is subject to the approximations made in deriving Equation A23, and may not apply if the impurity is more than two or three times as heavy as the gas being worked with. Neither does Equation A23 apply when the amount of impurity present is greater than 15 or 20%.

The result obtained in this analysis has been borne out by experiment. Among the samples of heavy methane produced by the diffusion apparatus have been specimens in which the amount of air present varied from a few percent to about 50%. There has been observed no difference in separation factor that could be attributed to this cause.

III. Correction to Simple Theory Due to a Pressure Gradient Along the Diffusion Apparatus:

In actual operation, there is likely to be an appreciable pressure difference between the two ends of the system. If ρ is the factor by which the total pressure at a point in the nth separation member from V_ℓ exceeds that at the corresponding point in the (n-1)st member, then Equation A5 must be modified to read

$$S_D(1+C_D) = \rho S_B(1+C_B)$$

This alteration next appears in Equation A7.2, giving

$$\frac{C_D}{C_A} = \left[1 + \frac{(1+C_B)\rho}{(1+C_D)}\right]^{\mu-1}$$

while Equation A8' becomes

$$g = g_0 \left(\frac{1+C_B}{1+C_D}\right)^{\mu-1} \rho^{\mu-1}$$

In practice, when the pressure in V_ℓ is around 10 or 11 mm, $\rho^{34} \sim \frac{1}{2}$. Hence, for work with a 34-member apparatus on methane, this term increases the separation of the entire apparatus by a factor

$$2^{.03} = 1.02$$

which is seen to be negligible. The influence of the pressure gradient on f can similarly be shown to be too small to cause concern.

IV. Correction to Simple Theory Due to Viscosity Effects:

The derivation of the simple diffusion equation

$$N = N_0 e^{-\alpha t}$$

is based upon the assumption that the probability for a gas molecule to escape through the semi-porous wall of its particular container is proportional only to the number of collisions it makes with the wall. This number will, in turn, be proportional to the mean velocity of the molecule in question. The picture tacitly implied is that of a wall whose surface is spotted with holes. These holes are of such a nature that, if a molecule impinges upon one of them, it escapes from its container, i. e., the holes are assumed to be without depth. Actually, however, from the microscopic point of view, the holes in the clay tubing used must be more nearly like capillary tubes. At low pressures, this will not be significant, but if the pressure is high enough that the molecular mean free path is smaller than the dimensions of these capillaries, it will be necessary to use a viscous flow equation, rather than a diffusion equation, to predict the relative rates of flow of different isotopes.

Considerations of a rather qualitative nature will be sufficient to show that the effect of viscosity must be in such a direction as to decrease the separation factor of the diffusion apparatus. We start by calculating the relative rates of flow through the porous wall (thought of as a number of capillary tubes in parallel) of the pure light gas and the pure heavy gas. Poiseuille's formula shows that, if the porous container were filled to a given pressure with the light isotope, the number of molecules passing through its walls in unit time (if the flow were purely viscous) would exceed the number of heavy isotope molecules which would pass through the wall in unit time (for the same pressure conditions) in the ratio

$$\frac{S'_L}{S'_H} = \frac{\eta_H}{\eta_L}$$

where the primes differentiate these "pure gas streams" from the actual gas streams treated earlier in this appendix, η_H and η_L are the coefficients of viscosity of the two pure isotopes, and evidently have the ratio

$$\frac{\eta_H}{\eta_L} = \frac{\rho_H \bar{v}_H \lambda_H}{\rho_L \bar{v}_L \lambda_L}$$

where ρ = density = mn'; $\bar{v}$ = mean thermal velocity, and λ, the mean free path, is proportional to $\frac{1}{n'\sigma^2}$. σ, the molecular diameter, must be the same for both isotopes. Hence we have

$$\frac{\eta_H}{\eta_L} = \frac{m_H n'_H}{m_L n'_L}\,\mu\,\frac{n'_L}{n'_H} = \frac{1}{\mu}$$

Thus the ratio of the pure gas streams is

$$\frac{S'_L}{S'_H} = \frac{1}{\mu}$$

Now this is exactly the relative rate of actual flow in the pure diffusion process. Hence, in order to determine whether or not viscosity diminishes the separation factor of the diffusion apparatus, it is necessary only to examine whether or not the relative rate of viscous flow in the mixture of isotopes is less than the relative rate of flow of the pure constituents. This can readily be seen to be the case. For, if the two gases are mixed and allowed to flow through the capillary tube by which we are now replacing the clay wall of the separation member, it is clear that the light gas will be held back, by molecular collisions with molecules of the heavy gas, while the heavy gas, in turn, will flow through the capillary tube more rapidly than it would if it were not being helped by the light gas. Hence, the difference between the rates of transport of heavy and light molecules must be less for the mixture of gases than for the pure constituents separately, and the effect of viscosity must always be to lower the separation factor of the apparatus.

3. Comments on the Importance of the Corrections

Once the effects discussed in the foregoing pages are known to exist, the logical thing to do is to attempt to operate the diffusion apparatus in such a way as to minimize their importance. The error due to backward diffusion has, it is felt, been practically eliminated, for pressures up to 10 or 11 mm, by the design and operation of the pumps, as described in the text of this thesis.

The deleterious influence of viscosity can always be avoided by operating at low enough pressures, of course; what constitutes a "low enough pressure," however, will certainly depend on the gas being worked with. For methane, the separation factor has been found to be as large for runs at 10 or 11 mm pressure (See text of thesis) as for runs at 7 or 8 mm pressure. For mixtures of carbon dioxide and argon gases, there seems to be good reason to believe that viscosity effects set in rather suddenly at pressures of 9 or 10 mm. It should be possible to find a correlation of some sort between the maximum safe pressure for the diffusion apparatus and the pressure at which the gas begins to obey laws of viscosity. Certainly this should also depend on the particular clay tubes used. It seems likely that an apparatus could be constructed which would operate satisfactorily for considerably higher pressures than the present apparatus, by using tubes of thin walls and fewer openings.

The harmful influence of impurities has been found to be small, as far as the separation factor of the apparatus is concerned, as long as the percentage of impurity does not become too high anywhere in the system. However, only a small amount of heavy impurity in the gas admitted to the system suffices to displace almost entirely from the heavy end of the system the gas whose heavy component the experiment seeks to concentrate. For this reason, it is necessary to keep the gas being worked with as free from contamination as possible. This requires thorough preliminary out-gassing of the apparatus, and the use of pure gas to start with. Naturally, the system must be free from leaks. The first and the third condition can generally be met, but one is often unable to obtain or produce as pure a starting material as he would like. As a result, it is often necessary to make use of the diffusion apparatus itself to purify the gas. As discussed elsewhere, this results in a loss of some of the isotopic constituent the experiment seeks to concentrate.

APPENDIX B

Calculation of Enrichment Factors

In Appendix A attention has been given to the accurate computation of the "separation factor" of the diffusion apparatus. For a single member, it has been seen that this factor is, subject to the restrictions and approximations discussed

$$g = \frac{f^n}{1-(1-f)^n}$$

The separation factor for the entire apparatus of m members in series will be, therefore

$$Q = g^m = \left[\frac{f^n}{1-(1-f)^n}\right]^m$$

However, one is ordinarily interested, not in Q, the ratio of the heavy gas concentrations at the two ends of the apparatus, but in the factor by which the concentration of the heavy isotope at the "heavy" end of the system exceeds that of the gas introduced originally into the system. This "enrichment factor," which we may call E, will evidently be less than the separation factor Q, since the diffusion process achieves separation both by increasing the concentration of the heavy gas at one end of the system and by decreasing it at the other end. In order to make E as near to Q as possible, this diminution of heavy gas concentration at the "light" end of the system must be minimized by making V_ℓ, the volume at that end, as large as practicable compared with that of the rest of the system. Inasmuch as this volume can never be made infinite by comparison with the rest of the apparatus, it is desirable to evolve equations expressing E in terms of Q and the other constants of the system.

The notation to be used is as follows:

m---number of separation members

v---volume of each separation member

V_ℓ--volume of "light" reservoir

V_s--volume of "heavy" reservoir

P---total pressure in V_ℓ

ρ --ratio of total pressure in nth separation member from V_ℓ to that in the (n-1)st separation member

x_n--pressure of heavy isotope (at equilibrium) in the nth separation member from V_ℓ

x_0--pressure of heavy isotope in V_ℓ

x_{m+1}--pressure of heavy isotope in V_s

p_0--pressure of heavy isotope in V_ℓ at start of diffusion

This notation will have to be enlarged somewhat in the course of the development.

It has been assumed in the above definition of ρ that the pressure drop is logarithmically uniform from V_ℓ to V_s, so that the total pressure in the nth separation member from V_ℓ is $\rho^n P$. In particular, the total pressure in V_s is $\rho^{m+1} P$. Of course, $\rho < 1$.

The entire development may be based on an equation expressing the fact that the total amount of heavy gas in the system after equilibrium is reached is the same as that in the system at the beginning of the diffusion process:

$$v \sum_{n=1}^{m} x_n + x_0 V_\ell + x_{m+1} V_s = v p_0 \sum_{1}^{m} \rho^n + p_0 V_\ell + p_0 \rho^{m+1} V_s$$

$$= p_0 \left\{ V_\ell + \rho^{m+1} V_s + v \frac{(1-\rho^m)}{1-\rho} \right\}$$

Let us write $$V_t \equiv \left\{ V_\ell + \rho^{m+1} V_s + v \frac{(1-\rho^m)}{1-\rho} \right\} \qquad \text{Eq. B1}$$

Then we have $$v \sum_{n=1}^{m} x_n + x_0 V_\ell + x_{m+1} V_s = p_0 V_t \qquad \text{Eq. B2}$$

It will be found convenient to define the "effective volume" of the separation members as

$$V_e \equiv \frac{v \sum_{n=1}^{m} x_n}{x_{m+1}} \qquad \text{Eq. B3}$$

Then Equation B2 becomes $$x_0 V_\ell + x_{m+1} (V_e + V_s) = p_0 V_t \qquad \text{Eq. B4}$$

Now, from the definition of q,

$$\frac{x_n}{P\rho^n - x_n} = q^n \frac{x_0}{P - x_0}$$

or

$$x_n = \frac{P\rho^n g^n}{(g^n-1)x_0 + P}\,x_0 \qquad \text{Eq. B5}$$

Substitution in Equation B4 yields

$$x_0 V_\ell + (V_e + V_s)\frac{P\rho^{m+1} g^{m+1}}{(g^{m+1}-1)x_0 + P}\,x_0 = \rho_0 V_t$$

or

$$x_0^2\left[V_\ell(g^{m+1}-1)\right] + x_0\left[P\rho^{m+1}g^{m+1}(V_e+V_s) + PV_\ell - \rho_0 V_t(g^{m+1}-1)\right] - P\rho_0 V_t = 0 \qquad \text{Eq. B6}$$

Define $\frac{(V_s+V_e)\rho^{m+1}}{V_\ell} \equiv r$ and $\frac{V_t}{V_\ell} \equiv t$

Then

$$x_0^2\left[g^{m+1}-1\right] + x_0\left[Prg^{m+1} + P - \rho_0 t(g^{m+1}-1)\right] + \left[-P\rho_0 t\right] = 0$$

or

$$\frac{x_0}{P} = \frac{-b+\sqrt{b^2-4ac}}{2a}$$

where

$$a \equiv g^{m+1}-1$$

$$b \equiv rg^{m+1} + 1 - \frac{\rho_0}{P}t(g^{m+1}-1)$$

$$c \equiv -\frac{\rho_0}{P}t \qquad \text{Eq. B7}$$

To complete the solution for x_0 it is necessary to evaluate V_e, which has itself been defined in terms of the unknown quantities x_n in Equation B3. It is necessary to consider V_e in conjunction with Equation B7; they may be solved by a method of successive approximations.

From Equations B3 and B5

$$V_e = v\frac{\left[\frac{g^{m+1}-1}{s}+1\right]}{\rho^{m+1}g^{m+1}}\sum_{n=1}^{m}\frac{\rho^n g^n}{\frac{g^{n-1}}{s}+1} \qquad \text{Eq. B8}$$

where $s \equiv \frac{P}{x_0}$

We may guess at x_0 and solve from Equation B8 for V_e. The result may then be set in Equation B7, and a second approximation to x_0 obtained, etc. Generally only two or three such approximations need be made before sufficient accuracy is attained.

It is now of interest to investigate means of evaluating the summation in Equation B8. Such evaluation may be considerably simplified if the pressure drop in the system is assumed negligible. Although this is not a very good assumption for the present apparatus, the consideration of this case is instructive.

In this case $\rho \equiv 1$, and the summation may be replaced by

$$S_m \equiv \sum_{n=1}^{m} u(n)$$

where

$$u(n) \equiv s\cdot\frac{e^{\alpha n}}{e^{\alpha n}+\beta}$$

$$\alpha \equiv \ln g;\ \beta \equiv s-1 \qquad \text{Eq. B9}$$

The form of this expression suggests defining

$$u(x) \equiv s \cdot \frac{e^{\alpha x}}{e^{\alpha x}+\beta} \qquad \text{Eq. B10}$$

This is a monotonically increasing function of x. The value of the summation sought differs only slightly from $\int_{x=0}^{m} u(x)dx$. To determine the amount of error involved in such an approximation, one has to observe the inequality

$$\int_0^m u(x)dx < S_m < \int_1^{m+1} u(x)dx \qquad \text{Eq. B11}$$

which is due to the monotonic character of u(x). Thus there is afforded an easy means of determining the limits within which the desired sum must lie. The integration is very easily performed

$$\int u(x)dx = \frac{s}{\log_e g} \log_e \left[g^x + (s-1)\right] \qquad \text{Eq. B12}$$

$$\left.\begin{aligned} \therefore \int_0^m u(x)dx &= \frac{s}{\log_e g} \log_e \left[\frac{g^m+(s-1)}{s}\right] \\ \int_1^{m+1} u(x)dx &= \frac{s}{\log_e g} \log_e \left[\frac{g^{m+1}+(s-1)}{g+(s-1)}\right] \end{aligned}\right\} \qquad \text{Eq. B13}$$

Hence, for this case of no pressure gradient, we have

$$V_e = \frac{v\left[1+\frac{s-1}{g^{m+1}}\right]}{2\log g} \log\left[\frac{g^{m+1}+(s-1)}{g+(s-1)} \cdot \frac{g^m+(s-1)}{s}\right] \qquad \text{Eq. B14}$$

$$\text{Probable fractional error} = \frac{1}{2}\,\frac{\log\left[\frac{g^{m+1}+(s-1)}{g+(s-1)} - \frac{s}{g^m+(s-1)}\right]}{\log\left[\frac{g^m+(s-1)}{s}\right]} \qquad \text{Eq. B15}$$

Equations B7 and B14 may be handled together to yield a solution for x_0, the pressure, at equilibrium, of the heavy gas in V_ℓ. x_{m+1} may then be calculated easily by means of Equation B5, and the problem is solved.

When $\rho \neq 1$ the problem is more difficult, due to the fact that the u(x) one obtains in this case cannot easily be integrated. It is therefore probably easiest to perform the summation of Equation B8 graphically. This graphical method will be employed in connection with the following examples, which illustrate the whole method.

Example 1: Carbon Dioxide-Argon Mixtures

On pages 22 and 23 were recorded the results of three runs on mixtures of various concentrations of carbon dioxide and argon gases. It was there stated that the data given could be used to evaluate some of the constants of the apparatus. The constants that are not known with certainty are ρ and v. ρ is somewhat doubtful on account of the inadequacy of the mercury manometer used for measuring p_s; v, the volume of a separation member, cannot be directly determined by the geometry of the system, inasmuch as the boiler of the mercury pump contains an unknown average pressure of gas. Pressure measurements made before and after turning on the diffusion pumps have indicated that v is around 60 or 70 cc, but this figure must be considered only very approximate. Similarly, ρ^{25} is known to be not far from 2/3. Remembering that there are only 24 complete separation members (plus a fraction) in a system of 25 pumps, we may summarize by the table:

m--24

ρ^{25}-2/3

$\therefore$ ρ--0.98

V_ℓ-5000cc

V_s-300cc

v--60cc

V_t-6160cc

t--1.23

Of the three runs listed on pages 22 and 23, II and III are the most valuable for the purpose at hand, inasmuch as these two runs were allowed to go practically to completion before the first gas was removed for analysis. The significant data for these two runs may be written in the more useful form:

<u>Run</u> <u>II</u>: $\frac{\rho_0}{p} = \frac{1}{11.0}$

$g^{24} = 75$; $c_0 = \frac{1}{48}$; $c_{m+1} = 1.57$

$\therefore \frac{x_0}{p} = \frac{1}{49}$

<u>Run</u> <u>III</u>: $\frac{\rho_0}{p} = \frac{1}{51}$

$g^{24} = 74$; $c_0 = \frac{1}{350}$; $c_{m+1} = 0.21$

$\therefore \frac{x_0}{p} = \frac{1}{350}$

Let us see how nearly x_o/P can be calculated, making use of the constants set forth.

For Run II: $q^{24} = 75$; $q = 1.18$; $q^{25} = 88.5$

We commence by obtaining the first approximation for V_e, by means of Eq. B8, assuming the likely value of 1/50 for x_o/P, i. e., we try $S = 50$. Substituting in these values, Equation B8 becomes

$$(V_e)_1 = 140\text{cc} \sum_{n=1}^{24} \frac{1.16^n}{49+1.18^n}$$

Figure B1 represents this summation. Its area is 3.68. This gives

$$V_e = 515\text{cc}$$

Now Equation B7 may be solved for the second approximation to x_o/P. Substitution in the obvious way gives

$$r = 0.088$$

$$a = 87.6$$

$$b = -0.99$$

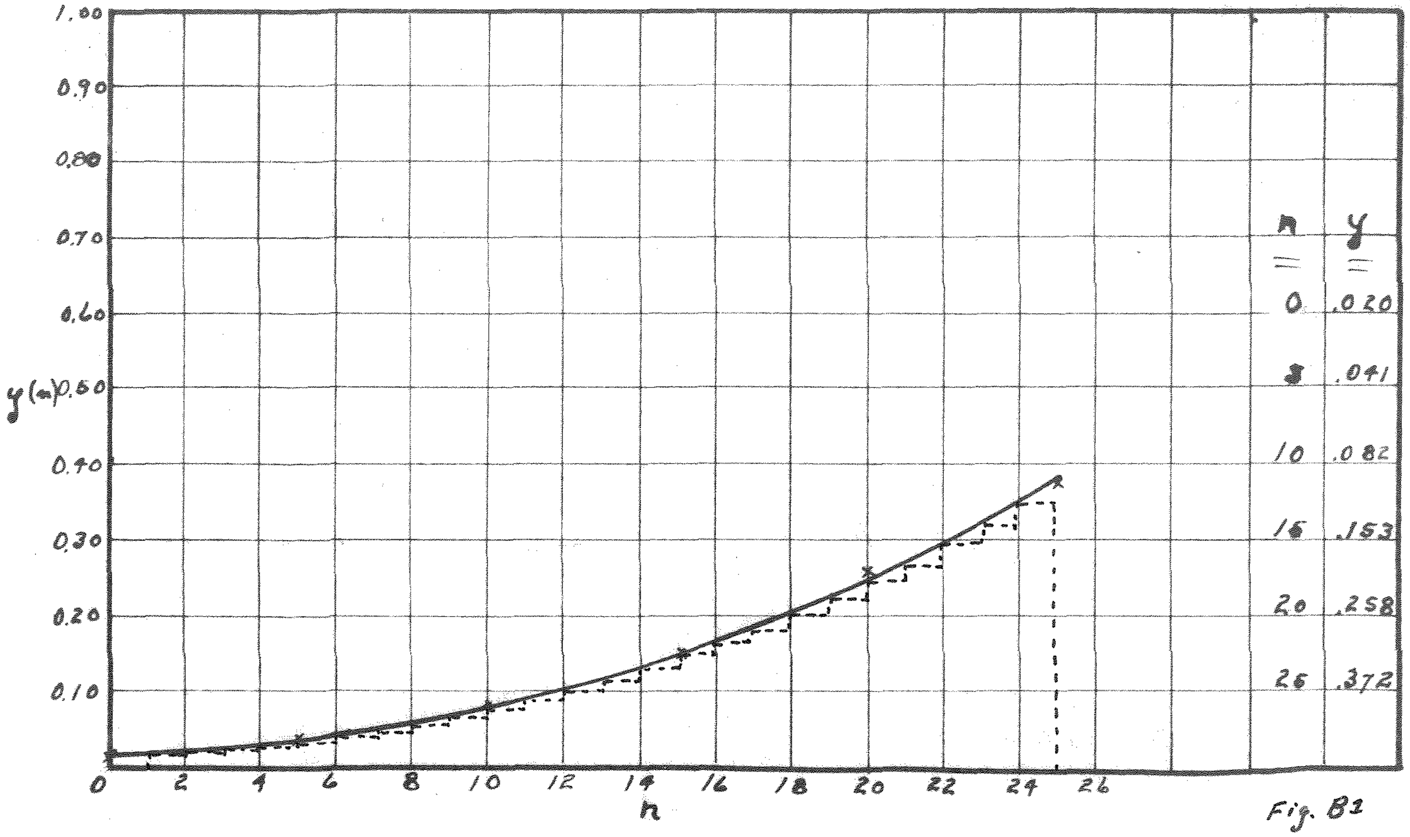
$$c = -0.112$$

whence

$$(x_o/P)_2 = 1/23.8$$

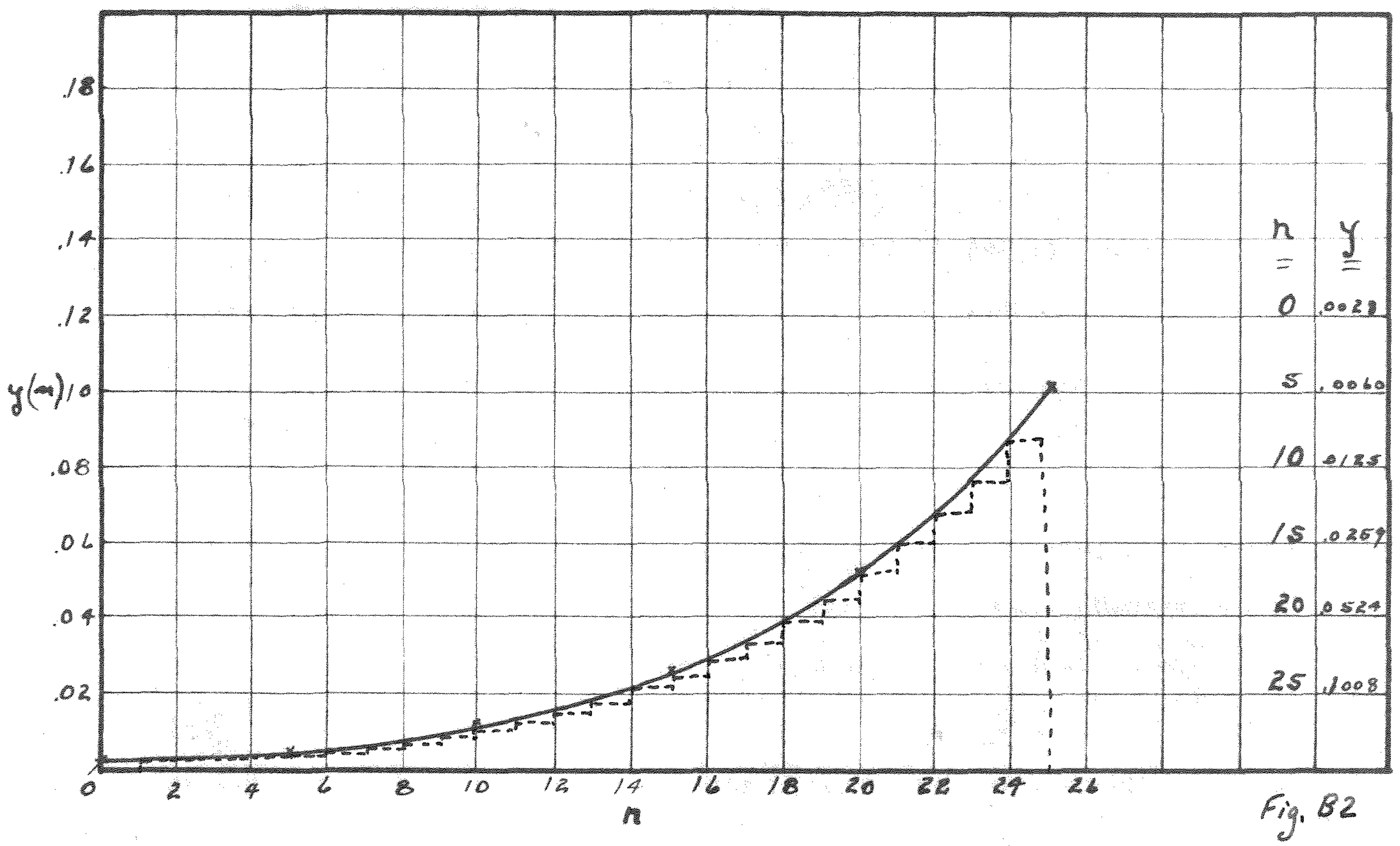
It can be verified that the value of (x_o/P) approached by further approximations will lie between $(x_o/P)_1$ and $(x_o/P)_2$, but it will be closer to the latter. A somewhat larger value of v is indicated. Repetition of the above calculation enables the following table to be made out, connecting the second approximate value of (x_o/P) with the value of v assumed. In each case the first approximate value is taken to be 1/50:

v	$(x_o/P)_2$
60cc	1/23.8
75	1/37.4
90	1/43.0
100	1/46.5
110	1/51.0



n	y
0	.020
5	.041
10	.082
15	.153
20	.258
25	.372

Fig. B1



n	y
0	.0023
5	.0060
10	.0125
15	.0259
20	.0524
25	.1008

Fig. B2

From this table it appears that a value of 105cc for v will fit the results of this run quite well. This is larger than it was thought v should be, but not alarmingly so. If this value of v makes it possible to fit the results of Run III also, it will be considered satisfactory.

<u>For Run III</u>:

A similar procedure must be carried out. Using

$$v = 105\text{cc};\ t = 1.375$$

we get, taking S = 350:

$$(V_e)_1 = 744\text{cc} \sum_{n=1}^{24} \frac{1.16^n}{349+1.18^n}$$

The summation is represented by Fig. B2. Its area is 0.66. Therefore

$$(V_e)_1 = 515\text{cc}$$

This gives

$$r = 0.1088$$

$$a = 87.5$$

$$b = 8.26$$

$$c = -0.0270$$

whence

$$(x_o/P)_2 = 1/320$$

Although the agreement is not perfect, it is sufficiently close, for the experimental error in measuring Q is of this order of magnitude.

From these data, it is believed reasonably safe to set v approximately equal to 110cc, in the calculation of enrichment factors to be expected in the application of the diffusion apparatus to the separation of isotopes. However, one must always be aware of a certain danger involved in assuming the results obtained for v with carbon dioxide-argon mixtures to be indicative of v for other gases. If water vapor were run in the system, for example, one might expect to have to use a much larger value for v, owing to the strong tendency of water to be absorbed in the porous tubing. Such an effect, to a smaller extent, might be exhibited by carbon dioxide, making 110cc too large for some other gases. It is believed that this effect is usually negligibly small, but no very definite information on the matter has yet been gathered. This would be an interesting, and rather simple, line of investigation. Further, due to the pressure gradient in the system, one would expect v to depend, to some extent, on the pressure of the run.

On account of these uncertainties, the calculation of enrichment factors must be regarded as only approximate, but the degree of approximation should be sufficient for most purposes.

Example 2: Work Done on Methane with 34-Member Apparatus

Assuming a 100% efficiency, the theory predicts, for the 34-member apparatus described in the text, a separation factor of 44 for the isotopes $C^{13}H^1_4$ - $C^{12}H^1_4$ of methane. A calculation is to be made below of the enrichment factor to be expected of a run on normal methane gas. The data believed best to fit the conditions of the runs actually performed are:

m--34
ρ^{35}-1/2
ρ--0.980
V_ℓ -22,000cc
V_s-300cc
v--110cc
V_t-24,850cc
t--1.13

For normal methane, the best spectroscopic measurements[10] show that the relative abundance of C^{13} is 1:103. It will be accurate enough for the present purposes, therefore, to set $p_o/P = 1/100$.

We use also: $q^{34} = 44$; $q = 1.118$; $q^{35} = 49.1$. As a first approximation, let us try $(x_o/P)_1 = 1/201$. Then

$$(V_e)_1 = 1115cc \sum_{n=1}^{34} \frac{(1.095)^n}{200+(1.118)^n}$$

The usual method of summation gives the result

$$(V_e)_1 = 1230cc$$

Equations B7 again give

$$r = 0.0348$$

$$a = 48.1$$

$$b = 2.17$$

$$c = -0.0113$$

whence $(x_0/P)_2 = 1/214$

It is clear that the true value of S cannot be far from 200. Hence, for runs made on normal methane, the enrichment factor should be just half the separation factor.

However, in every experiment it was found necessary to make a preliminary run in order to remove the air and other heavy impurities from the gas. Ordinarily this purging took the form of a partial evacuation through the heavy end of the system a few hours after the circulation had been started. The order of magnitude of the net enrichment factor to be expected from such a process may be obtained if we assign to p_0/P after the preliminary cleansing the value of 1/150. The results of the run then performed on this gas may be calculated in the usual way. The calculation yields a value of 300 for S, as compared with the value of 100 for P/p_0 in normal methane. Hence, one would expect the enrichment factor attained in this combination of processes to be of the order of 1/3 the theoretical separation factor. The enrichment factors actually attained, as has been set forth in the text, were around 10--i. e., about 1/4 the theoretical separation factor. The discrepancy between 1/3 and 1/4 is probably not significant.

Example 3: Work Done on Nitrogen with 34-Member Apparatus

Assuming a 100% efficiency, the theory predicts, for the 34-member apparatus, a separation factor of 10.0 for the isotopes $N^{15}N^{14}$ - $N^{14}N^{14}$ of nitrogen gas. A calculation is to be made of the enrichment factor to be expected of a run with normal nitrogen. The data believed best to fit the conditions of the experiment are

m--34

ρ^{35}-1/2

∴ ρ--0.980

V_ℓ -22,000cc

V_s-400cc

v--110cc

V_t-24,950cc

t--1.13

For normal nitrogen, the best spectroscopic measurements[14] show that the relative abundance of N^{15} is 1:350. This will be the value required for p_o/P.

We use also: $q^{34} = 10.0$; $q = 1.069$; $q^{35} = 10.69$. As a first approximation, let us try $(x_o/P)_1 = 1/500$. The usual methods give a value of 1/450 for $(x_o/P)_2$, while further approximations do not change this by more than 1 or 2%.

Thus we conclude, for the case of nitrogen separations, the enrichment factor for a simple process should be 350/450ths the separation factor. That is, the enrichment factor should be 7.8.

In the first work done with nitrogen, described on p. 37, the procedure was to introduce into the system the heavy gas from three simple runs, plus enough ordinary nitrogen to produce the pressure required. In this way it was hoped that the enrichment factor obtained would be greater than the above calculated factor by about the ratio of the amount of heavy nitrogen so introduced to the amount which would have been introduced into the system if nothing but ordinary nitrogen had been used. A semi-quantitative calculation is here possible.

In the preliminary collections of heavy gas, an attempt was made in each case to draw out of the heavy end of the system the gas contained within all the apparatus except V_ℓ. Of course, it is likely that an appreciable amount of mixing took place while the withdrawal of gas was taking place, so that the calculations here made may be considerably too optimistic. In the best circumstances, however, such a process would withdraw from the system approximately 10/45ths of the N^{15} originally introduced (from the foregoing results). Since this was done three times, and the gas added to ordinary nitrogen in filling the system for the final separation, the value of p_o/P to be used in calculating the resulting enrichment factor should be, approximately

$$(1/350)\cdot 1.67 = 1/210$$

The usual calculation, based upon this value of p_o/P, assigns to (x_o/P) the value 1/275. This would correspond to a heavy sample in which the $N^{15}:N^{14}$ ratio was 3.6/100. The relative abundance actually attained, as measured spectroscopically, has been previously given as 3.3/100. Unfortunately, the agreement must be regarded as partly accidental, since two other processes took place in the experiment which must have affected the enrichment factor. In the first place, a discharge was run continually in V_s when the preliminary heavy samples were being collected. Due to poor design, the discharge tube became coated with mercury early in the first diffusion process, so that the amount of current which passed in the discharge was probably too small to be effective in breaking up the molecules of the gas at that end of the system, but this effect is not definitely known to be negligible. If the tube had operated as originally hoped, the separation factor, for these preliminary runs, would have been doubled (See Appendix C). In the second place, after the system was filled with gas for the final separation, a preliminary $6\frac{1}{2}$ hour run was employed to remove the impurities. There can be little doubt that this resulted in a diminished enrichment factor. If we assume equilibrium was reached in the $6\frac{1}{2}$ hour period, which may not be far wrong, the final value of x_o/P should have been 1/360. This would correspond to a heavy sample in which the $N^{15}:N^{14}$ ratio was 2.8/100. The actual results seem consistent with the conclusion that the discharge tube did little, if any, good, but that the efficiency of the diffusion process was 100%.

APPENDIX C

Use of a Discharge Tube

In his work on heavy hydrogen[5], Hertz ran discharge tubes continually in the diffusion apparatus, in order to break up the H^2H^1 molecules into H^2 and H^1 atoms, and make it possible in this way for H^2H^2 molecules to be formed on recombination. Inasmuch as this is a device which should be useful whenever the gas being worked with is of the form X_2--i. e., H_2, N_2, O_2, etc.--it has been thought worth while to work out the equations which should govern the behaviour of the diffusion apparatus when the gas at the heavy end of the system is maintained in equilibrium with the products of a disintegrative discharge.

We shall denote by a and b the two isotopes of the gas being worked with. a will refer to the lighter isotope, which will also be assumed the more abundant. In order of their abundance, ordinary gas will contain molecules of types aa, ab, and bb. We shall denote by n_{aa}, n_{ab}, and n_{bb} the corresponding molecular densities. n_a and n_b will represent the densities of the two types of atoms. Evidently, at any point in the apparatus,

$$\left.\begin{aligned} n_a &= 2n_{aa} + n_{ab} \\ n_b &= 2n_{bb} + n_{ab} \end{aligned}\right\} \qquad \text{Eq. C1}$$

We shall assume that the values of n_{aa}, n_{ab}, and n_{bb} in V_s are the values which would be found if n_a atoms of type a were mixed with n_b atoms of type b and combination into diatomic molecules allowed to proceed at random. It is clear that an efficient discharge in V_s would produce this condition. In such a case, it is evident that

$$n_{aa} : n_{ab} : n_{bb} = n_a^2 : 2n_a n_b : n_b^2 \qquad \text{Eq. C2}$$

Equations C1 and C2 may be combined to give

$$\left.\begin{aligned} n_{aa} &= \frac{\frac{1}{2} n_a^2}{n_a + n_b} \\ n_{ab} &= \frac{n_a n_b}{n_a + n_b} \\ n_{bb} &= \frac{\frac{1}{2} n_b^2}{n_a + n_b} \end{aligned}\right\} \qquad \text{Eq. C3}$$

These relations will be true only at the heavy end of the system, where the discharge tube is located. Equation C1, however, must apply everywhere.

As usual, the subscripts l and s will refer to the light and heavy ends of the system, respectively. Now, however, instead of one separation factor, two are needed. We shall use

$$g_1 \equiv g_{bb}^{aa}$$

$$g_2 \equiv g_{ab}^{aa}$$

where g_{ab}^{aa} is the separation factor for the entire system, calculated on the assumption that there are present molecules of types aa and ab only, etc. Evidently $g_1 > g_2$.

Also, it will be convenient to write R for the value of n_a/n_b for the gas originally admitted to the system, while $\frac{\rho}{2}$ will be used to represent the total molecular density.

Two simplifications will be made: first, that the volume of the separation members is negligible; second, that there is no pressure gradient in the system. For the most part, these assumptions will not materially affect the result. When they do, the extension of the theory can be made in an obvious fashion.

From the definitions given, the equalities exist:

$$\frac{n_{bb}^s}{n_{aa}^s} = g_1 \frac{n_{bb}^\ell}{n_{aa}^\ell} \qquad \text{Eq. C4}$$

$$\frac{n_{ab}^s}{n_{aa}^s} = g_2 \frac{n_{ab}^\ell}{n_{aa}^\ell} \qquad \text{Eq. C5}$$

$$V_\ell n_a^\ell + V_s n_a^s = R\left(V_\ell n_b^\ell + V_s n_b^s\right) \qquad \text{Eq. C6}$$

$$n_a^\ell + n_b^\ell = \rho \qquad \text{Eq. C7}$$

$$n_a^s + n_b^s = \rho \qquad \text{Eq. C8}$$

$$n_a^\ell = 2n_{aa}^\ell + n_{ab}^\ell \qquad \text{Eq. C9}$$

$$n_b^\ell = 2n_{bb}^\ell + n_{ab}^\ell \qquad \text{Eq. C10}$$

Substitution of Equations C9 and C10 in C7 and C8 gives

$$2(n_{aa}^\ell + n_{ab}^\ell + n_{bb}^\ell) = \rho \qquad \text{Eq. C11}$$

$$n_a^s + n_b^s = \rho \qquad \text{Eq. C12}$$

Substitution of Equations C9 and C10 in C6 gives

$$V_\ell\,(2n_{aa}^\ell + n_{ab}^\ell) + V_s n_a^s = R\left[V_\ell(2n_{bb}^\ell + n_{ab}^\ell) + V_s n_b^s\right] \qquad \text{Eq. C13}$$

Equations C2 in C4 and C5 give

$$\left(\frac{n_b^s}{n_a^s}\right)^2 = g_1 \frac{n_{bb}^\ell}{n_{aa}^\ell} \qquad \text{Eq. C14}$$

$$2\frac{n_b^s}{n_a^s} = g_2 \frac{n_{ab}^\ell}{n_{aa}^\ell} \qquad \text{Eq. C15}$$

Now solve Equations C14 and C15 for n_{ab}^1 and n_{bb}^1 in terms of n_{aa}^1 and substitute in Equation C11. This gives

$$2n_{aa}^\ell\left[1 + \frac{2}{g_2}\frac{n_b^s}{n_a^s} + \frac{1}{g_1}\left(\frac{n_b^s}{n_a^s}\right)^2\right] = \rho \qquad \text{Eq. C16}$$

Substituting similarly in Equation C13:

$$V_\ell\left(2 + \frac{2}{g_2}\frac{n_b^s}{n_a^s}\right) + \frac{V_s n_a^s}{n_{aa}^\ell} = R\left\{V_\ell\left[\frac{2}{g_1}\left(\frac{n_b^s}{n_a^s}\right)^2 + \frac{2}{g_2}\frac{n_b^s}{n_a^s}\right] + \frac{V_s n_b^s}{n_{aa}^\ell}\right\}$$

or, from Equation C16

$$V_\ell\left[1 + \frac{1}{g_2}\frac{n_b^s}{n_a^s}\right] - RV_\ell\frac{n_b^s}{n_a^s}\left[\frac{1}{g_2} + \frac{1}{g_1}\frac{n_b^s}{n_a^s}\right] = \frac{RV_s n_b^s - V_s n_a^s}{\rho}\left[1 + \frac{2}{g_2}\frac{n_b^s}{n_a^s} + \frac{1}{g_1}\left(\frac{n_b^s}{n_a^s}\right)^2\right] \qquad \text{Eq. C17}$$

From Equations C12 and C17 we must get n_a^s and n_b^s. Let

$$\frac{n_b^s}{n_a^s} \equiv z$$

Then Equation C12 becomes

$$n_a^s = \rho - n_a^s z = \frac{\rho}{1+z}$$

and Equation C17 may be written

$$\left[\frac{R(1+r)}{g_1}\right]z^3 + \left[\frac{R-r}{g_1} + \frac{R+2rR-1}{g_2}\right]z^2 + \left[\frac{R-2r-1}{g_2} + (rR-1)\right]z - (1+r) = 0 \qquad \text{Eq. C18}$$

where r has been written for the ratio V_s/V_ℓ.

Now, for N_2, $R = 350$; for O_2, $R = 500$, etc., whereas $r \lesssim 1/10$.

Hence it is accurate enough to write

$$\frac{1}{g_1}z^3 + \left[\frac{1}{g_1} + \frac{1+2r}{g_2}\right]z^2 + \left[\frac{1}{g_2} + \left(r - \frac{1}{R}\right)\right]z - \frac{1+r}{R} = 0 \qquad \text{Eq. C19}$$

In the problems which have thus far arisen, $z \ll 1$, so that Equation C19 becomes

$$z = \frac{\dfrac{1+r}{R}}{\dfrac{1}{g_2} + \left(r - \dfrac{1}{R}\right)}$$

The most favorable case is that for which $r \ll 1/q_2$. In this case

$$z \rightarrow \frac{q_2}{R}$$

Now, from Equation C2, in the heavy end of the system

$$n_{aa}^{s} : n_{ab}^{s} : n_{bb}^{s} = 1 : 2z : z^2$$

Or

$$\frac{n_{ab}^{s}}{n_{aa}^{s}} = 2z = \frac{2q_2}{R}$$

If the discharge were not running, the value of $\frac{n_{ab}^{s}}{n_{aa}^{s}}$ would be only one-half as large as this. Hence, in the most favorable circumstances, the use of a discharge can double the separation factor of the apparatus.

APPENDIX D

Fiber Gauge.

In Fig. D1 the fiber gauge[17] used in connection with the diffusion apparatus is drawn roughly to scale. Its essential part is a flat quartz fiber, of 6 or 8 cm length, which can be set in vibration, by an appropriate magnetically operated hammer, in an atmosphere of several microns of the gas whose molecular weight it is desired to measure. The fiber is illuminated and observed by means of a low-power microscope. The length of time, t, required for the amplitude of vibration to drop from one predetermined mark to another on the fixed scale of the eyepiece is found to give a direct measurement of the molecular weight, M, if the pressure, p, is known:

Consider a section of the fiber (Fig. D2), of dimensions $\Delta x \times W \times d$, moving towards the right with velocity V. If V is small compared with the thermal velocity of the molecules, then we may consider all the impacts on the front face of the slab to be due to the molecules moving towards the left, in the region to the right of the slab. The time rate of transfer of momentum to these molecules by the slab is, therefore

$$\frac{1}{3} n (c+V)^2 m W \Delta x$$

where c is the average thermal velocity, n is the molecular density, and m is the mass of a molecule.

Due to impacts from behind, there is an opposite force

$$\frac{1}{3} n (c-V)^2 m W \Delta x$$

Hence the net force tending to decelerate the slab is

$$\frac{1}{3} n m W \Delta x \cdot 4 c V$$

On the entire fiber, work is being done at the rate

$$P = \frac{4}{3} c n m W \int_0^l [V(x)]^2 dx$$

Over a time interval sufficiently large for several vibrations

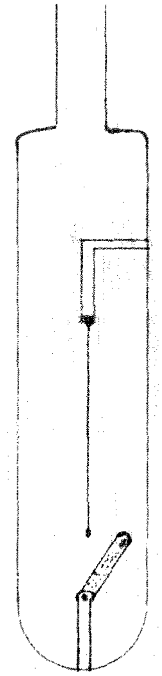


Fig. D1

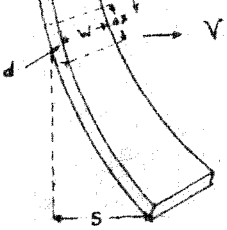


Fig. D2

$$p_{av} = \frac{4}{3} c n m W f(s)$$

where $\int_0^l [V(x)]^2 dx$ has been set equal to a function of s, the amplitude of the vibrations of the end of the fiber, alone.

Now the energy of the vibrating fiber is a function of s only--E(s). Hence

$$-\frac{dE(s)}{dt} = \frac{4}{3} c n m W f(s)$$

$$-\frac{E'(s)}{f(s)} ds = \frac{4}{3} c n m W \, dt$$

or

$$\Phi(s_2) - \Phi(s_1) = \frac{4}{3} c n m W t$$

where Φ is some function of the amplitude, and t is the time required for the amplitude to decrease from s_1 to s_2.

Hence, if t is always measured between the same values of s_1 and s_2 (i. e., the same two marks on the scale of the eyepiece), then

$$\frac{1}{t} \propto c n m$$

But

$$p = \frac{1}{3} m n c^2$$

Therefore

$$\frac{1}{t} \propto \frac{p}{c}$$

Also

$$\frac{1}{2} m c^2 = \frac{3}{2} k T$$

Therefore

$$c \propto \left(\frac{T}{M}\right)^{\frac{1}{2}}$$

and

$$\frac{1}{t} \propto \frac{p\sqrt{M}}{\sqrt{T}}$$

or

$$\frac{1}{t} = \left(K \frac{p}{\sqrt{T}}\right) M^{\frac{1}{2}}$$

If the atmosphere consists of a mixture of gases, the equation may evidently be written

$$\frac{1}{t} = \left(\frac{Kp}{\sqrt{T}}\right) \sum_i x_i M_i^{\frac{1}{2}}$$

where p is the total pressure, and px_i is the partial pressure of the ith component.

The foregoing development has neglected the possibility of other damping forces acting on the fiber besides those due to impacts with the gas molecules. Actually, there is a small, but appreciable, effect of "viscosity" in the quartz itself which would bring the amplitude of vibration from s_1 to s_2 in a time t_0, in vacuum. The resulting equation can be written

$$\frac{1}{t} = \frac{1}{t_0} + \left(\frac{Kp}{\sqrt{T}}\right) \sum_i x_i M_i^{\frac{1}{2}}$$

This linear relation between 1/t and $pM^{\frac{1}{2}}$ is found to hold quite accurately, for gases of as widely different molecular weights as hydrogen and argon, for pressures up to many microns. Although it is likely that this simple theory is not strictly correct, the inaccuracies cannot be detected with the arrangement used with the diffusion apparatus, since the errors in the molecular weight determinations are limited by the accuracy with which the McLeod Gauge can be read in measuring p.

Of course, the gauge must be connected to the rest of the system through a liquid air trap, as mercury vapor must be excluded from the instrument.

In Fig. D3 are plotted the results of a calibration of this gauge. The points for hydrogen cannot be distinguished from those for air. In practice, it is customary to recalibrate the gauge occasionally by taking two or three measurements on air. This is necessitated only by the fact that the supports on which the apparatus is mounted are not sufficiently rigid to prevent some relative slipping of the gauge and microscope.

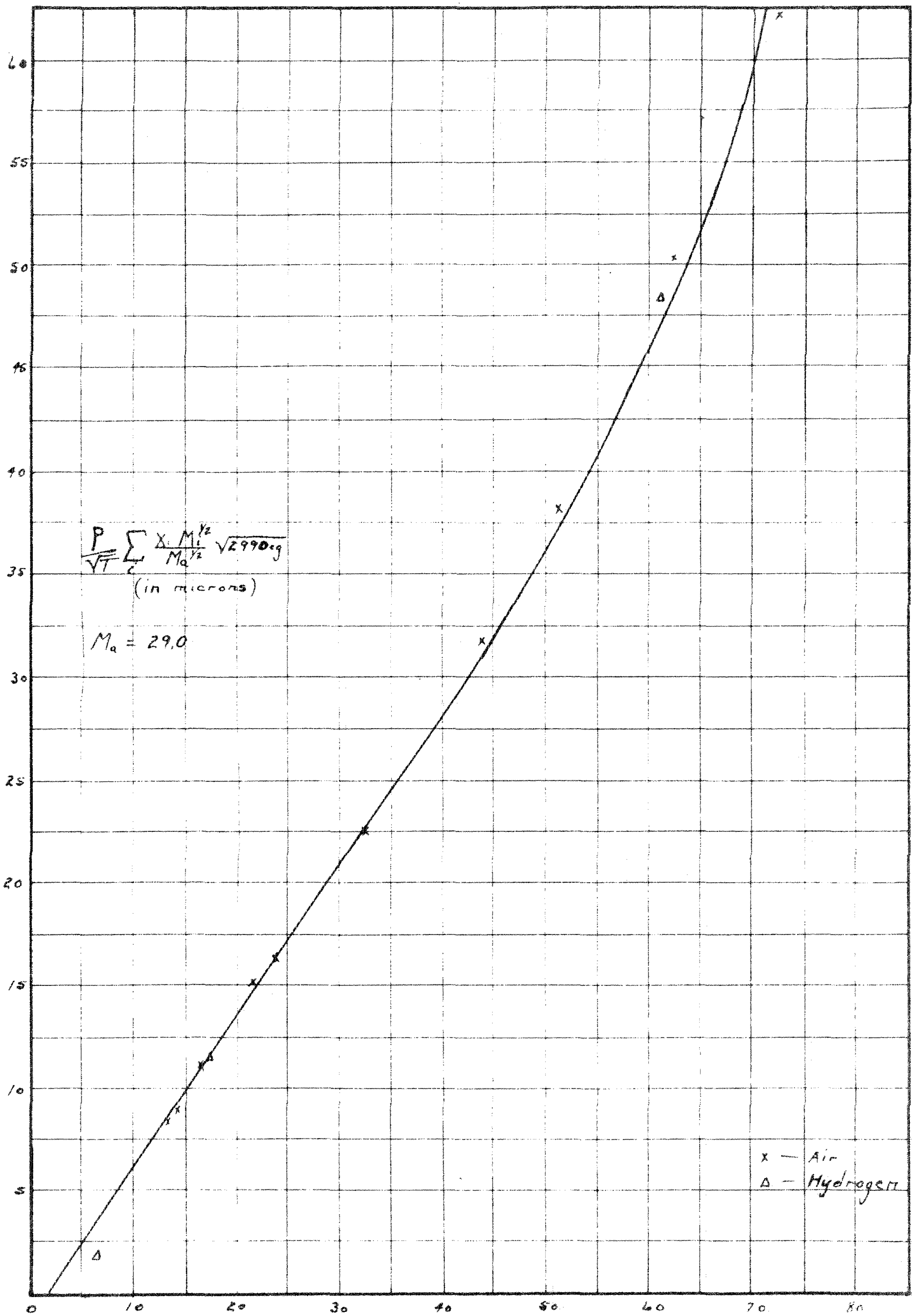

60
55
50
45
40
35
30
25
20
15
10
5
0
10
20
30
40
50
60
70
80
$\frac{P}{\sqrt{T}} \sum_i \frac{X_i M_i^{1/2}}{M_a^{1/2}} \sqrt{2990cg}$
(in microns)
$M_a = 29.0$
x — Air
Δ — Hydrogen
$1/t \times 10^3$ (Sec^{-1})

Fig. D3