Studies on the rare gas content of minerals and the atmosphere

Wiborg, Bjarne Svarstad

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"STUDIES ON THE RARE GAS CONTENT OF MINERALS AND THE ATMOSPHERE".

THESIS

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degree of:-

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by

BJARNE SVARSTAD WIBORG, B.Sc.

The work described in this Thesis was carried out in the Londonderry Laboratory for Radio-Chemistry, University of Durham, between October, 1950, and June, 1953, under the supervision of Professor F.A.Paneth, F.R.S.

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SUMMARY.

The work described in this thesis concerns two problems involving the micro-determination of the rare gases: the estimation of the ages of minerals by the argon-potassium method, and the rare gas content of the atmosphere.

Apparatus has been designed and constructed for the purification and measurement of quantities of argon of the order of 10^{-3} to 10^{-4} cc. N.T.P. to an accuracy of about 0.2%. For the mineral work, further apparatus was constructed for the extraction of the gases and removal of interfering impurities. After this apparatus had been tested, the urgency of the stratosphere analyses made it necessary to postpone further work on the minerals; and it has not yet been possible to take up this aspect of the work again; the argon-potassium method of age determination is, however, critically discussed.

The work on the atmosphere was mainly concerned with samples obtained through collaboration with the U.S. Army Signals Corps who have flown rockets to altitudes of about 100 km. Analyses were made for N_2, A, He and Ne, and the results show that, above about 55 km., there is a significant deviation from the uniform composition which is found up to this height. The results seem to indicate the existence of a state of partial gravitational-diffusional equilibrium in this region, and a theoretical interpretation is developed, based on the work of Lettau and others on the effects of "eddy diffusion", which appears to provide an adequate explanation of the observed facts. The separations observed for helium are somewhat smaller than would have been predicted from the neon and argon separations, a result which is consistent with the occurrence of a steady flow of helium through the atmosphere; the rate of such flow has been deduced, and is found to lie within the range of estimates based on geochemical evidence.

INDEX.

Page.

CHAPTER III(contd).

CHAPTER III(continued) Page.

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CHAPTER I.

CHAPTER I.

Introduction. (1) General.

The work in connection with this thesis involved the investigation of two different problems, the argon content of minerals with a high potassium content, and the composition of the atmosphere.

Of the two problems, that of stratosphere analysis occupied by far most of the time. The question of the argon content of the potassium minerals was taken up initially as a result of the recent discovery of extensive deposits of these minerals in North Yorkshire, with a view to determining their ages by this method. (1). Before much progress had been made, however, results were published from practially identical investigations in Germany (2). As the analysis of the stratosphere samples had to be given a very high priority, the first problem was shelved for the time being; unfortunately, very little opportunity arose later on for tackling it again, and it therefore received a rather incomplete treatment.

With regard to the stratosphere analysis, altogether a dozen samples from heights between 50 and 90 km. were analysed. They were all supplied by the University of Michigan, who collected them with rockets. The results obtained were very interesting and rather unexpected, indicating for the first time a composition of the stratosphere materially different from that of the lower layers. Theoretical reasons for this are rather difficult to find, and the question whether the compositions found are actually representative of the outside air, or whether they are a result of some peculiarity in the sampling technique, remains unsettled.

(2) Historical.

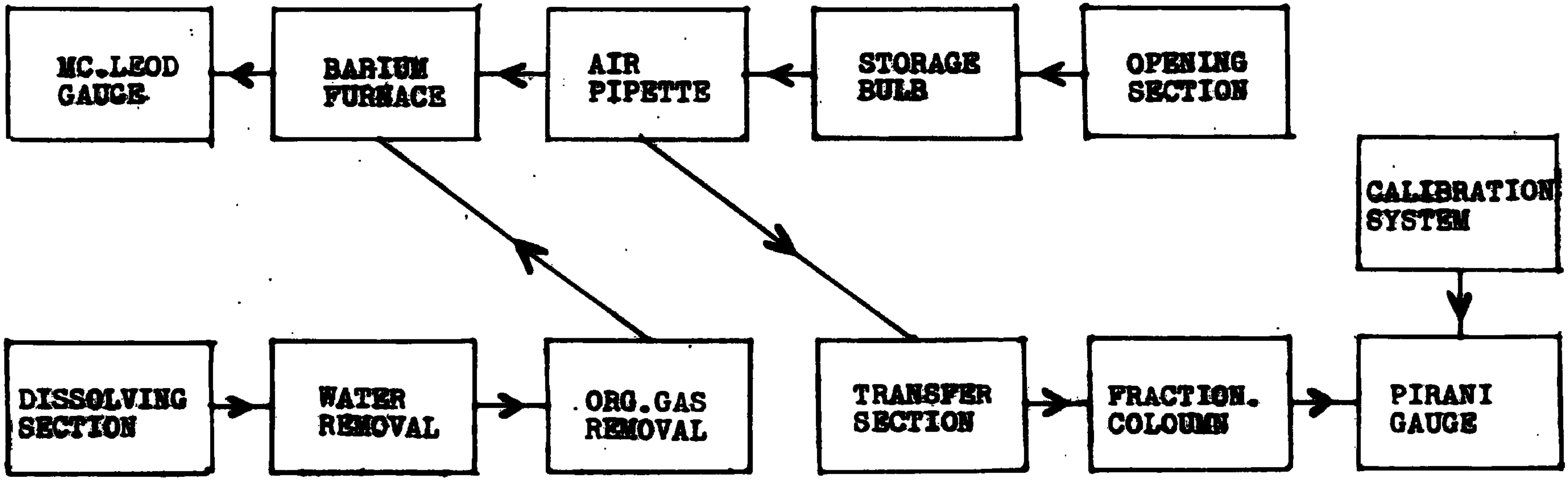
If the two problems themselves are somewhat different, the experimental techniques are very similar, involving the micro-analysis of rare gas quantities of the order of 10^{-7} ccs. Helium and Neon and 10^{-3} ccs. Argon.

The apparatus has been developed over a number of years by several people. (3). For Helium and Neon, the first start was made in 1928, when Paneth (4) and his collaborators managed to construct an apparatus capable of detecting quantities of the order of 10^{-10} ccs. of these gases spectroscopically. They did this by condensing all gases except Helium, Neon and Hydrogen on charcoal at liquid air temperatures. The hydrogen was then removed as water by burning it with oxygen, the excess of which was condensed on charcoal again afterwards. The remaining gases were then measured by using a McLeod gauge, and the proportions of helium and neon were determined by comparing the strengths of their characteristic spectral lines. The accuracy of this method was about 50% when 10^{-7} ccs. helium was involved (4) but was later improved considerably when in 1930 the Pirani gauge was first used for the final measurements (5) (6). The quantities then measured varied between 10^{-8} ccs. with an accuracy of 50% to 10^{-4} ccs. with an accuracy of 1%. The Pirani gauge, being a hot wire manometer, has great advantages over the discharge method of measuring as, during the latter, quantities of hydrogen may be released from the glass walls under vacuum and large amounts of helium and neon may be mopped up by the walls instead. In addition, the mercury and the capillary tube walls very easily become dirty as a result of the discharge, causing the mercury to stick badly.

The helium and neon was first measured separately when, in 1939, (7) Glückauf constructed a fractionating column for these two gases. The accuracy had also been improved by this time, 10^{-6} ccs. of helium being measured with less than 1% error.

The measurements of small quantities of argon has remained basically the same since 1903, when Soddy introduced the calcium furnace (9). By heating a stick of pure calcium metal, he removed all except the rare gases which could then be measured on a McLeod gauge. The furnace was usually made of pyrex glass until quite recently (10) (11), when it was found that stainless steel furnaces after initial cleaning gave equally good results. This made possible the substitution of barium metal for calcium (12), which can give quite a lot of trouble due to impurities. It is at the moment possible to analyse less than 1/10 cc of air with an error of less than 0.5% in the final measurement of argon.

Fig. 1



BLOCK DIAGRAM OF APPARATUS FOR
RARE GAS ANALYSIS

(3) Introduction to the Modern Apparatus (Fig. 1).

A short description of the various sections of the apparatus is given below. A more detailed description and the operating procedure will be found in the experimental sections in the following chapters.

Argon content of minerals.

(a) Dissolving Section where the powdered salts are evacuated and the solvent freed from dissolved gases prior to solution. This section also includes a reservoir of pure hydrogen for flushing the argon out of the solution.

(b) Transfer section which consists of a charcoal U-tube and two cold traps. The gases are here separated from water vapour before the argon is condensed on a charcoal in

(c) Cleaning section. At this stage some electrolytic gas is added as well and the oxygen condensed on the charcoal with the argon. After pumping the hydrogen away, the gases are released and passed over a platinum-iridium spiral at red heat, and the resulting water vapour and carbon dioxide is taken up by KOH pellets. Afterwards the remaining gases are transferred into

(d) The Barium Furnace, a steel furnace containing a stick of pure Ba which on heating combines with all except the rare gases which are then passed into

(e) *McLeod gauge*, where the final argon volume is measured after removal of helium, neon (and hydrogen) by pumping.

Rare gas content of the Stratosphere.

The apparatus for this analysis falls into two parts, one section being used for the analysis of argon, and the other for helium and neon. The first 3 sections however are common.

(a) *The opening Mechanism*, and the section where the sample bottles are attached.

(b) *The Toepler Pump*, and storage bulb to which the sample is transferred immediately the bottle is opened.

(c) *The Air Pipette*, where the initial volume of every portion of the sample is measured prior to analysis. This section also incorporates a Cu-spiral for removal of O_2 and a KOH pellet which removes any water vapour present.

When analysing the sample for the argon content, the sample is passed into the Barium Furnace and then measured on the McLeod gauge as mentioned under (e) above. For the analysis of helium and neon, the gas is passed from the air-pipette on to

(f) *Circulating System*, which includes a Palladium furnace, through which the sample is circulated if the presence of any H_2 is suspected.

(g) The Fractionating Column, consisting of 15 Charcoal units. This operated on the principle that in the He-Ne mixture present about $\frac{1}{4}$ of the Helium and $\frac{3}{4}$ of the Neon is absorbed on the charcoal when this is at the temperature of liquid nitrogen.

(h) Pirani Gauges. When a sufficient number of operations of the fractionating column has ensured the collection of all the Helium, this fraction is compressed into one of the two Pirani gauges and the resultant deflection on a galvanometer is measured. Both the measuring and the compensating gauge are immersed in liquid nitrogen to ensure greater stability, and accuracy, and they are connected in adjacent arms of a Wheatstone Bridge network. The quantities normally measured are of the order of 10^{-7} ccs, but quantities down to 10^{-9} - 10^{-10} ccs. can be detected.

(i) Calibration System. The quantities of Helium and Neon measured are always calculated by measuring known quantities of the same gases of the same order of magnitude on the Pirani gauge. For this purpose, supplies of spectroscopically pure Helium and Neon are available. First, a volume about 15000 times the amount needed is accurately measured using the McLeod gauge. This volume is then expanded into the bulb and side-tubing and a small known fraction of this is expanded a second time into a bulb of known volume. A small and known fraction of this is finally compressed into the Pirani gauge and the resultant deflection on the galvanometer is measured.

CHAPTER II.

CHAPTER II.

Argon-content of Minerals.

Introduction.

K^{40} is the naturally occuring radio-active isotope of potassium. It decays by by β-ray emission to Ca^{40}, and also by K-capture and γ-ray emission to A^{40}.

If we denote the atomic abundances of K^{40} and A^{40} by N' and N'' respectively in atoms per gram mixed total mass, and call the total disintegration constant of K^{40} λ and the disintegration constant for the formation of A^{40} for λ_N we have

$$dN' = -N'\lambda\, dt \qquad - (1)$$

$$dN'' = N'\lambda_N\, dt \qquad - (2)$$

Let (i) and (p) refer to initial and present moments, and t the time interval, we have then $N'_{(i)}$ is the atomic abundance of N' initially and by integrating we get

$$N'_{(i)} = N'_{(p)}\, e^{\lambda t}$$

and $$N''_{(p)} - N''_{(i)} = N'_{(p)}\,\frac{\lambda_N}{\lambda}\left(e^{\lambda t} - 1\right) \qquad - (3)$$

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$N''_{(p)} - N''_{(i)}$ is usually referred to as the radio-genic argon, and is usually found by subtracting the atmospheric argon determined by mass-spectrometric analysis from the total argon found. $\left\{\lambda_N/\lambda\right\}$ is referred to as the branching ratio. $\lambda_N + \lambda_M = \lambda$, where λ_M is the disintegration constant for the decay by β disintegration of K^{40} to give Ca^{40}.

We therefore have the following expression for t, the time since solidification of the minerals:

$$t = \frac{1}{\lambda} \ln \left[\frac{N''_{(p)} - N''_{(i)}}{N'_{(p)}} \cdot \frac{\lambda}{\lambda_N} + 1 \right] \quad - (4).$$

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At the time, it was thought that the half life and branching ratio of K^{40} was known with an accuracy of at least 10%, (13)→(21), and it would be worth while to use this method of argon and potassium analysis for age determination. The salts in question occur in the Permian Rocks (1) here at a depth of from 3000 feet and downwards. They are sometimes very rich in potassium, an average content of 40-45% KCl was found in a 31 feet layer in the case of one borehole. In general, there are two layers of minerals of commercial value, the Upper Salt with 10-19% KCl and a thickness of 20-28 feet occuring between 3000 and 4000 feet; and the Lower Salt deposits with 25-45% KCl and a thickness of 12-32 feet occuring approximately 200 feet below the first. These deposits consist mainly of

Sylvinite, a mixture of halite ($NaCl$) and sylvite (KCl), in varying proportions; but several other kinds were also found although not in such amounts, carnallite ($KCl \times M_gCl_2 \times 6H_2O$), polyhalite ($K_2SO_4 \times M_gSO_4 \times 2CaSO_4 \times 2H_2O$), and patches of the rare mineral rinneite ($NaCl \times 3KCl \times FeCl_2$).

As all these salts appeared in the Lower Trias and Upper and Middle Permian evaporite beds, there would have been some independent check on their ages as their deposits have been estimated to be from 170-200 million years old on the basis of other geological evidence (22).

It was at the time hoped to carry out a series of analyses of the different types of salts from various depths in each of the 5 boreholes, and also possibly in the borehole sunk by Fyson's at Robins Hoods Bay nearby. This, however, was not carried out. The reasons were firstly that the work in connection with the stratosphere analyses described in Chapter III had to be given absolute priority; coupled with this was the fact that very soon after the work on the potassium minerals had been started, results were published in Germany from almost identical investigations concerning the Stassfurt salt deposits (2). There are reasons, however, why these analyses might be carried out as originally planned, as a result of recent work carried out both in this country and in Germany (23) (24), but this will be dealt with at a later stage.

2. Experimental Procedure.

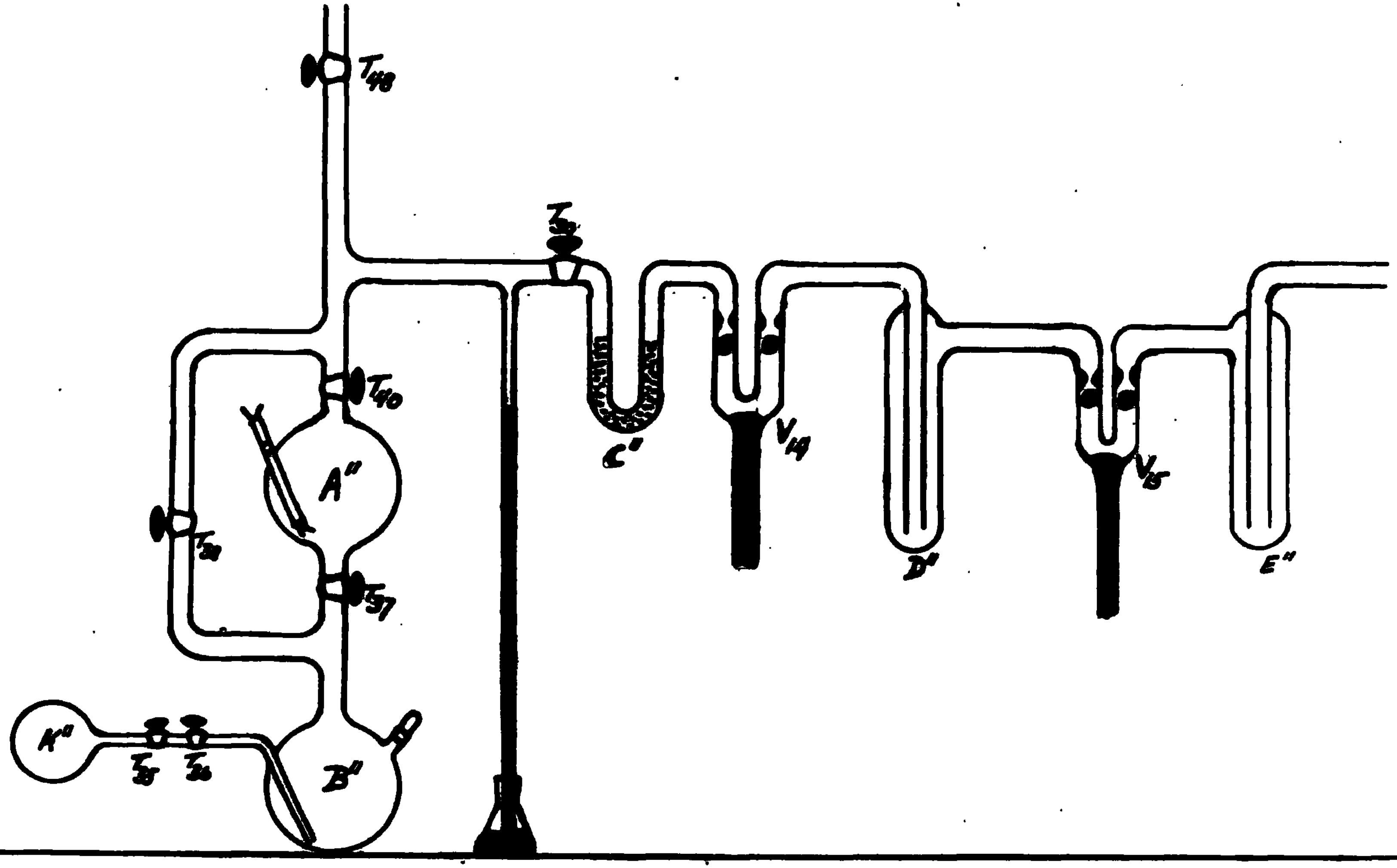
Although no complete analysis was carried out on any sample, the apparatus had been built and tested and the procedure standardised by the time the problem was abandoned. A lot of time was spent on finding a system of dissolving the minerals and flushing the gases out of solution which would prevent too much water vapour from being carried with it at the same time. Another problem to be solved was to find a gas for flushing the solution which would purify easily and itself being easily removed later on. For the initial pumping down of the solvent, electro-lysis could be used, but owing to the liberation of chlorine, this could not be used to remove the gases after dissolving the salt. Oxygen had to be discarded owing to the difficulty in freeing it from argon. Finally hydrogen was used. This was ordinary H_2 from British Oxygen Company which was purified by passing it very slowly through a large U-tube containing charcoal and cooled in liquid nitrogen. This method effectively removed all traces of argon as well as other non-permanent gases; any traces of helium and neon which might have been left would be removed with the hydrogen at a later stage.

The extraction and analysis of the argon content of the minerals, therefore, would have been as follows:-

(i) Dissolving (Fig. 2).

The solution to be introduced into A" consisted of about

Fig. 2



DISSOLVING SECTION AND WATER REMOVAL SECTION

10 grs Na_2SO_4 per litre H_2O which was pumped down to vacuum and any dissolved gases removed by electrolysing six times. A weighed quantity of the salt was introduced into B" and after this too had been completely evacuated it was dissolved by running some of the solution from A" through tap T_{37}. By closing V_{14} and cooling charcoal C" in liquid nitrogen, the gases contained in the mineral were transferred from B" by bubbling hydrogen through K" and then opening T_{38} for a short time. This was repeated six times, and after ten minutes another six times. Finally, after a second interval of ten minutes to allow the solution in B" to warm up again, six more flushings through were carried out.

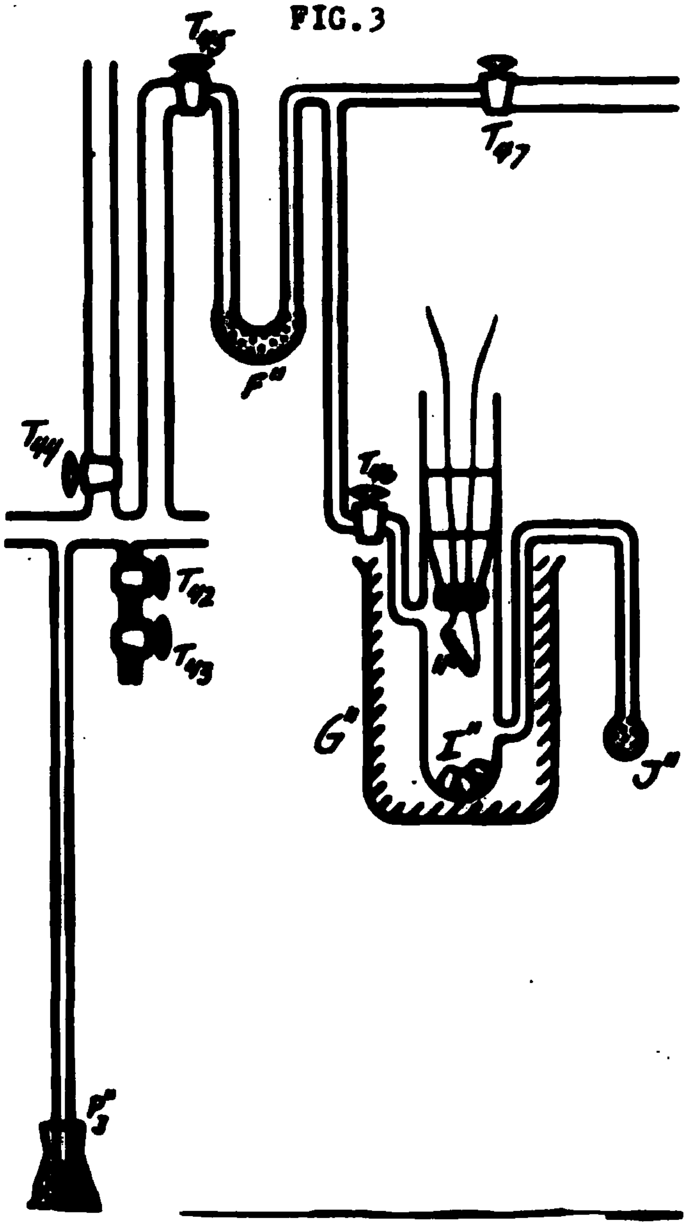
(ii) Removal of Water Vapour (Fig.2).

All the gases in the mineral thus being condensed on C", T_{39} was closed while V_{14} and V_{15} were only just closed, T_{45} open and D", E" and F" all cooled in liquid nitrogen. Charcoal C" was then slowly allowed to heat up and the gases to bubble past V_{14} and V_{15}. The water vapour was mostly taken up by D", the rest being removed in E'' and the condensible gases absorbed by the charcoal in F''.

When C" had warmed up to room temperature, T_{45} was closed, V_{14} and V_{15} opened completely and E" allowed to warm up, thus transferring all the water vapour to D". When this was completed, T_{45} was again opened and the water vapour slowly redistilled into E". This was done to remove any traces of

Fig 3

FIG. 3



SECTION FOR REMOVAL OF ORGANIC VAPOURS

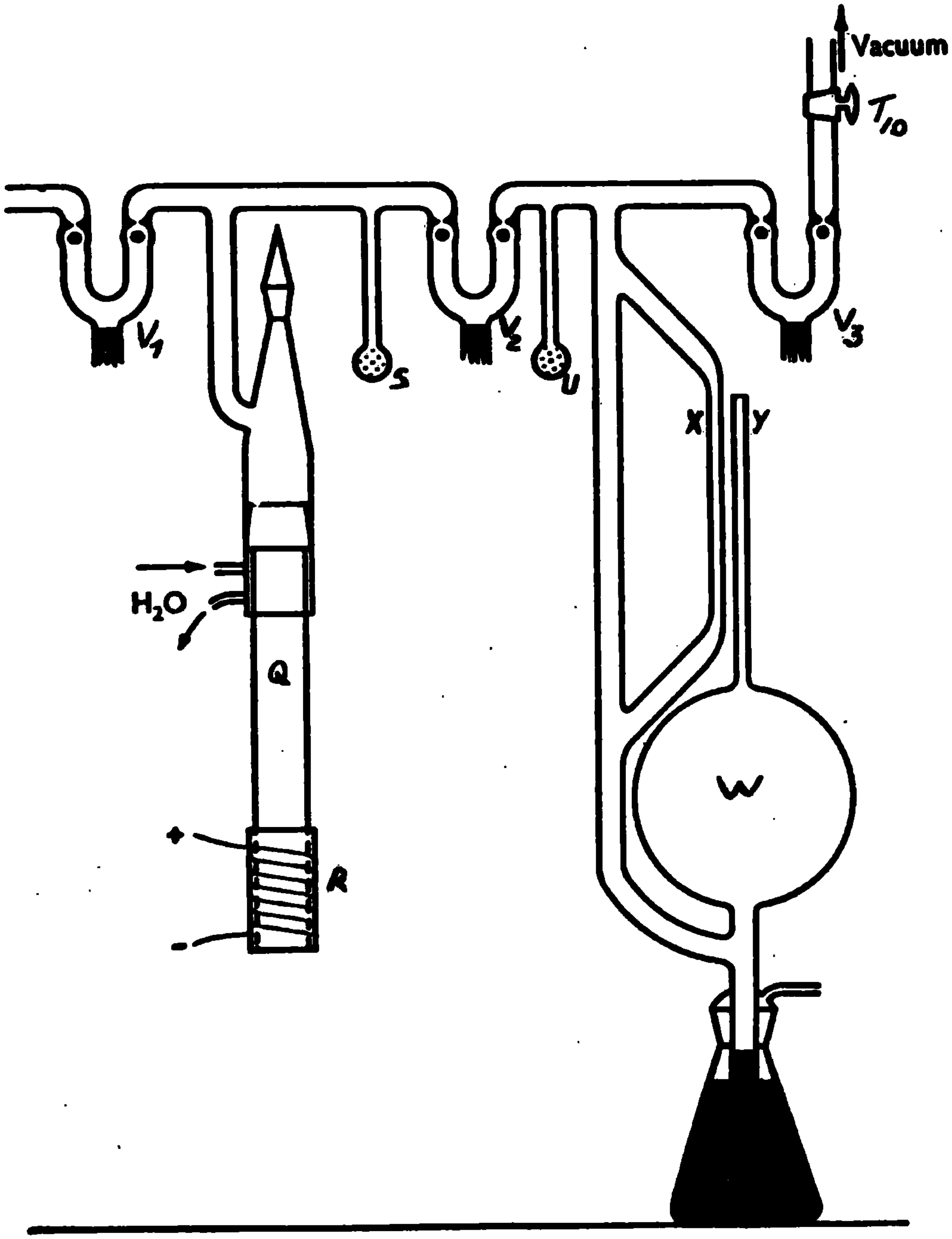
trapped argon from the ice and condensing it on F". One redistillation is sufficient for the purpose after which the ventils 14 and 15 were shut and the H_2, He and Ne pumped away from F" through T_{44}.

(iii) Removal of Organic Gases (Fig.3) There are always some methane and ethane in gases from salts and minerals (25), and these ought to be removed before the remainder of gases are treated in the Barium furnace as they otherwise cause the formation of barium carbide which may stop the action of the furnace owing to its high melting point.

This removal was done by burning the gases with oxygen in a small glass chamber G" containing a Pt-Ir spiral H" and some KOH pellets I". By adding a small amount of electrolytic gas and pumping away the hydrogen, sufficient pure oxygen for the purpose was obtained. The spiral H" was electrically heated to a very bright red heat and the KOH pellets absorbed any CO_2 and H_2O being formed in the process.

The burning was carried out by passing the gas mixture from F" to J" 4-5 times while the spiral was hot, and then allowing the gases to cool down for 10 minutes before transferring them to the Barium furnace. The whole of the burning off chamber was immersed in cold water during the treatment to prevent the glass cracking.

Fig. 4



Barium furnace and McLeod gauge.

(iv) Barium Furnace (Fig.4).

When the organic gases had been removed, V_1 was lowered. By cooling charcoal S in liquid N_2, the whole of the sample was transferred in a matter of 45-60 mins. Then, with both V_1 and V_2 shut the current was switched on in R, the heating element, and when this was red-hot, causing the Ba inside Q to evaporate, the sample on S was released and given 25-30 minutes treatment at 900 - 920°C. The heating element R was then at a very bright red-orange temperature, and would burn out every so often. It consisted of an iron core with 4 layers of asbestos paper on which was wound .025" nichrome wire in 2 layers with 4 layers of asbestos paper between, followed by 10-12 layers of asbestos on top; the cause of a burn-out was the two layers of nichrome wire coming in contact with each other due to the asbestos paper reacting with it, and producing a hot point which subsequently fused the nichrome wire as well. As asbestos fuses round 950°C, it was assumed that the temperature of the furnace as a rule was 20-30°C lower than this. The total resistance of the furnace winding was 8-10Ω and the current used was 5 - 5.5 amps.

The furnace itself consists simply of a hollow steel rod with an accurately turned cone on top to fit a standard B-19 glass socket and a water-jacket to keep the joint cool. Black picein wax was used as a joining material. Another cone and socket was situated on top of the glass envelope so that the furnace could be recharged without dismantling it altogether. This black-wax join between the actual furnace and the glass envelope is liable to fracture when the cooling water is put on unless both the metal cone and the glass socket are thoroughly warmed when first put together, and they must of course be well ground into each other originally to ensure a perfect fit. The furnace itself should preferably be drilled from stainless steel. Ordinary mild steel was tried out at one stage, but it tends to give a lot of trouble. The initial degassing takes longer, and the furnace walls flake rather badly on the outside after each heating with the result that after a while it develops leaks and has to be discarded perhaps within a matter of months. With stainless steel, however, although the initial drilling and machining is much more difficult, the furnace once it has been thoroughly degassed will give continuous service for years.

Initial degassing of a steel furnace even in the case of stainless steel takes quite a long time and even when the furnace is continuously pumped while heating it with a glass-blowing torch to a bright red heat, it takes several days before it will give a good vacuum. It was found to be quite an advantage towards the end to introduce 1-2 cms. pressure of H_2, leaving it overnight after a moderate heating the night before. The hydrogen presumably displaces the other gases absorbed in the walls and is itself very much easier to pump away.

Once the furnace is sufficiently degassed to give a good vacuum while hot, the Ba is introduced. The Ba used was supplied in sticks from the G.E.C.Research Laboratories. It requires only a few hours pumping and heating, in order to give a good vacuum. After a couple of hours pumping and heating at a dull red heat, the current can be increased until normal operating temperature is reached when very soon a black and silver mirror will start forming on the glass envelope above the furnace, indicating that it is ready for use. The Ba of course forms solid compounds with all except the rare gases. But if at all possible, one should try and prevent H_2O or any organic gases or CO_2 from entering the furnace. With water the Ba forms oxides and hydroxides, the latter dissociating again quite freely at normal working temperature, giving endless trouble later on with H_2 being evolved. If quantities of water vapour do by mistake get treated in the Ba-furnace, the best thing to do seems to be to dismantle the furnace, scrape out the deposits (careful drilling being the best) and recharge it, as this takes very much less time than trying to remove the H_2 gas, which seems to be evolved continuously from the $Ba(OH)_2$ formed in the first place. With CO_2, CO and organic compounds , the reason for keeping them out of the Ba furnace at all cost is the fact that one of their products will be Barium carbide which forms a skin on the pure Barium. As the carbide has a very high $m._{pt}$ ($\sim 1700^{\circ}C$), this effectively stops the action of the rest of the Barium completely with the result,as in the case of water,that one has to remove the furnace for scraping or drilling and recharge it. With these precautions and an initial charge of 1-2 grams (1" stick) the furnace is quite capable of well over a years continued service without recharging.

After 25-30 minutes treatment in the Ba-furnace, the current is switched off and the content allowed to cool. At the same time, the McLeod gauge has been pumped down to a sticking vacuum and t_{10} closed again. Charcoal U is then cooled in liquid Nitrogen and when the Ba-furnace is cool, v_2 is opened and the gases allowed to condense on U. This process is easily followed by measuring the pressure in the McLeod gauge when it is found that all the argon is condensed inside 20-25 minutes. The argon is, however, frequently accompanied by varying amounts of H_2, especially with a new Ba-furnace. In those cases, it was found that not only was the decrease in pressure much slower, but after 30-40 minutes pressure started increasing again which was taken to indicate a steady evolution of H_2 from the furnace combined with the saturation of the charcoal U with this gas.

This surplus gas being mostly H_2 therefore with small amounts of He and Ne as well, it is easily removed by pumping. For this purpose, the traps on the pumps must be scrupulously clean, both having been cleaned out by heating with near-boiling water immediately beforehand and cooled in liquid N_2 during the pumping. The level of this liquid N_2 must not be allowed to fall during pumping, and it is therefore preferable to have the dewar-flasks only half-filled when the pumping starts and to fill them up gradually as pumping proceeds. Unless these precautions are taken there is a danger of condensible gases, in particular water-vapour condensing back from the cold traps on to the charcoal, when the level of the liquid N_2 in the dewar flasks fall, giving an apparent excess of argon.

The removal of H_2 is completed in about 5 minutes and v_3 is closed. The liquid N_2 is removed from around U and the argon released. 10 minutes is allowed for this, and the volume of the gas is determined by means of the McLeod gauge W. The gas is then taken back in the Barium furnace for a second treatment of about 10 minutes. This process is repeated until the volumes after two consecutive treatments agree to within 2-3 parts in 1000. Normally this is so with just the first two treatments, but a third treatment is sometimes necessary if there has been a lot of H_2 evolved or the pumps have not been cleaned out carefully enough.

The charcoals S and U must also be cleaned out periodically by flaming the glass three or four times in a soft gas-flame while pumping. It is however sufficient to do this after every 3 or 4 analyses.

(v) The McLeod Gauge. (Fig. 4).

The McLeod gauge has a bulb of approximately 275 ccs. and the parallel closed and open limbs are both taken from the same piece of tubing, with an internal diameter of 3mm. The closed limb has a flat top and the McLeod gauge was usually read by bringing the shoulder of the meniscus in the open limb level with the top of the closed limb, and then reading the level of the shoulder on the meniscus in the closed limb.

The volume of the closed limb was calibrated by weighing with mercury and measuring the length of the thread each time. By plotting the mass of the mercury M versus the length of the thread 1, the relationship

$M = 1.054\,(1) - 0.058$ was obtained, and hence the radius of the tubing $r = 0.153$ cms. From

$$V_m = \frac{\pi}{3} a^2 \left[\frac{3}{2} \frac{(r^2 + a^2)}{a} - a \right],$$ where

V_m = meniscus volume

a = meniscus height

the mass of the meniscus was found $m = 0.0263$ gms.

$$(M - 2m) = 1.054(1) - 0.111$$

This was fitted into the general equation:

$$V_{NTP} = \frac{(M - 2m)}{\Delta Hg} \cdot \frac{1}{76} \cdot \frac{273}{293} \cdot f$$

where

ΔHg = specific weight of mercury

f = dead-space factor = 1.238

giving the equation

$$V_{NTP} = 1.179\ 1^2 - 0.123\ 1 \text{ cu.mm}$$

when 1 is read at 20°C.

The deadspace factor was determined directly by expanding a measured quantity of gas from the McLeod gauge into the previously evacuated sidetubing and remeasuring the volume.

The question of error due to non-linearity of the tube walls was settled by fitting the observed values of M to a curve of the form

$\underline{M - 2m = A + Bl + Cl^2}$ by the method of least squares.

This gave $\underline{M - 2m = 0.110 + 1.053\,l - 0.001\,l^2}$.

from which it will be seen that this error at reading of l = 1 cm only amounts to 0.1% and the second order term was therefore left out.

Finally, a table was constructed by calculating V_{NTP} for values of l between 0.5 and 3 cms. in intervals of 0.02 cm. and interpolating between these values so that the table can be read with the same accuracy as the cathetometer, namely 0.002 cm.

The range of volumes which can be determined by this method is from 0.2 → 10.2 cu.mm. But as smaller volumes had sometimes to be determined, a graph was constructed covering the range of 0.2 - 0.5 cms. for l corresponding to a range in volumes of 0.02 → 0.2 cu.mm. At readings around 0.2 cms. the experimental error involved is as large as 10% sinking to 1% at 0.5 cms. and 0.5% at 1 cm.

3. Discussion.

As was mentioned in the introduction, no full analysis was carried out on the potassium minerals for several reasons although the apparatus was built and the procedure standardised.

There are, however, some justifications for taking the whole question up again in connection with recent publications.

Firstly, the branching ratio of K^{40} was until recently thought to be fairly well established at 12K-captures for every 88 β-ray transformations, with about 10% accuracy (26). Mousouf (27) however, when analysing some very old rock salt whose age was well defined by other methods, found the value of the branching to be around 0.06, a value consistent with that found by a few earlier workers (28)(29)(30). This then brings in the possibility of an error of 50% in the accepted value for the branching ratios. If Mousouf's figures are proved to be correct, the ages found by the potassium-argon method would be increased by a factor of two. This would indicate an apparent excess of argon in samples from deposits in geological formations whose ages are already well established. The Strassfurt salts f.inst. from the lower oligocene period, $20 \cdot 10^6$ years old, analysed by Smits and Gentner and the North Yorkshire salts appearing in the permian rocks thought to be about $100 \cdot 10^6$ years old. A series of experiments covering several deposits from the very young to the very old would therefore be very useful as a guide to the actual value of the branching ratio, although the final proof will have to be sought elsewhere by more accurate methods using counting techniques.

This question of excessive amounts of rare gases in rocks and salts has turned up in connection with helium as well as argon. Wardle (24) has found helium in coloured rocksalts far in excess of what was expected from the uranium, thorium and radium contents, and he discussed the possibility of occlusion of small amounts of brine in the crystals at the time of the deposit. Both helium and argon are sufficiently soluble in brine to make this theory seem at least plausible, the solubility of argon in saturated brine is about 0.14 ccs. NTP/litre under atmospheric conditions and 0.2-0.4 ccs NTP/litre in sea water in equilibrium with air. That is, 0.07 ccs. of brine per gm. of KCl would account for the amount of atmospheric argon found in the Strassfurt salts by Smits and Gentner and seems a not unreasonable quantity. If, this, however, is the origin of the atmospheric argon found with the radio-genic in these salts, there ought to be an appreciable amount of argon in other rocksalts which contain no potassium, and experiments ought to be carried out in this connection, perhaps firstly on the same kind of coloured rock salts in which Wardle found excess helium.

One final problem which ought to be investigated further is that of diffusion of argon in salts. Gentner, Prag and Smits (23) obtained results which indicated a relationship between the A content and the size of the crystals, the larger the crystals the more argon they contained. They interpretated this as a volume diffusion process and even determined the diffusion constant. It might, however, be possible for these deposits to remain in a liquid state for a considerable period owing to the enormous pressure they would have been subjected to, and the crystals might well be of more recent origin. One possibility then is that the difference in argon content is the result of the larger crystals trapping comparatively more brine than the smaller ones, but this question cannot be decided either before considerably more experimental evidence is available.

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CHAPTER III.

CHAPTER III.

Rare gas content of the Stratosphere.

1. Introduction.

As a result of a world wide investigation by Gluckauf and Paneth (31), it was concluded that the composition of the atmosphere remains constant over the whole surface of the earth with respect to the rare gases helium, neon, and argon. Very small variations in the amounts of non-permanent gases do occur from place to place as a result of local conditions, such as the presence of large industrial centres, oceans, jungles, and so on, but these variations are usually ignored and the composition of the atmosphere at ground level is generally regarded as constant, the values for the different gases in Table 1 being quoted from Gluckauf's figures (32), where the oxygen results are those found by Benedict (33), the argon by Moissan (34) and the CO_2 by Krogh (35).

TABLE 1.

Gas.	% in air (by vol.)	Density (air = 1.000)	Mol.wt. (0 = 16).
Nitrogen	78.084 ± 0.004	0.967	28.016
Oxygen	20.946 ± 0.002	1.105	32.000
Argon	0.934 ± 0.001	1.375	39.444
Carbon Dioxide	0.033 ± 0.001	1.529	44.01
Neon	$1.818 \times 10^{-3} \pm 0.04 \times 10^{-3}$	0.695	20.183
Helium	$5.24 \times 10^{-4} \pm 0.004 \times 10^{-4}$	0.138	4.003
Methane	2×10^{-4}		16.042
Krypton	$1.14 \times 10^{-4} \pm 0.001 \times 10^{-4}$	2.868	83.7
Hydrogen	5×10^{-5}	0.0695	2.016
Xenon	$8.7 \times 10^{-6} \pm 0.1 \times 10^{-6}$	4.525	131.3
Ozone (1)	$0 - 7 \times 10^{-6}$	1.624	48.000
Radon (2)	6×10^{-18}		

(1) Variable: increases with height and varies with the season as well

(2) Variable: decreases with height.

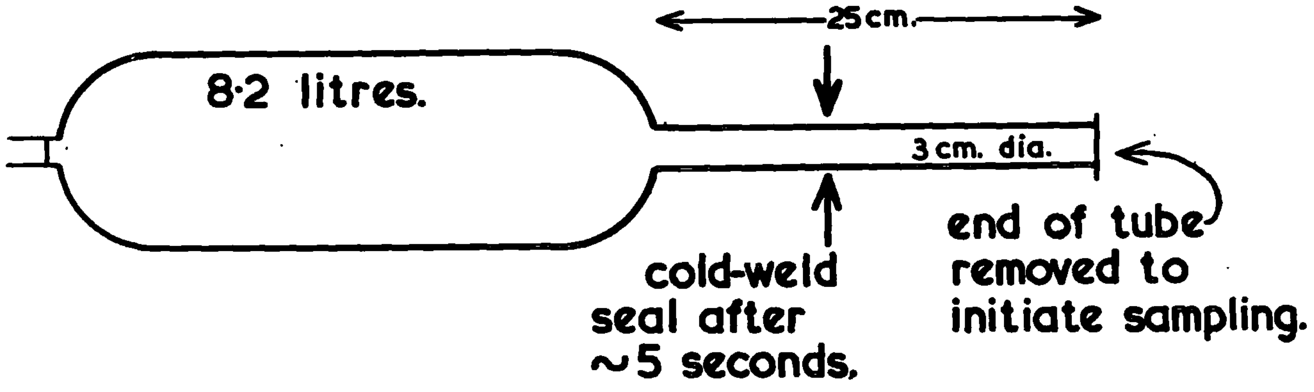
-o-o-o-o-o-

Other gases like sulpher dioxide and carbon monoxide occur only in certain places and cannot be said to be universal constituents of the atmosphere (36).

Apart from analysis of air samples from all over the world, Gluckauf also analysed samples from the troposphere and the lower stratosphere, and found the content of helium and neon to be very nearly constant (37) (31). He nowehere found any composition where the helium content exceed that of ground level air by more than 8%, and the variations were of a quite random character. His results have been used by other people (38), to prove a state of partial separation of the atmosphere between heights of 14 and 28 kms. in conjunction with the figures obtained by Regener (39)(40) for the oxygen content of the lower stratosphere. Regener found a gradual decrease in the percentage of oxygen with height from 14 up to about 25 kms. but these figures are not quite reliable owing to the ease with which oxygen is adsorbed by most materials used in the sampling apparatus and during analysis. Hence the conclusion has to be drawn that the composition of the atmosphere remains constant up to these heights as well.

After the war, it became possible to obtain samples of air from much greater heights than previously by the use of rockets, and several samples were analysed from 40-60 kms. height by Chackett and Wilson and at the University of Michigan (12) (41) (42) (47), but no difference in composition from ground level air was found. The present work concerns the analysis of a number of samples obtained by rockets from heights between 50 and 90 kms. the majority of which do show a substantial difference in the composition with regard to helium, neon and argon from that of ground level air.

Fig 5



Impedance of inlet tube ~0·1 second / litre under molecular flow conditions; effectively less at higher pressures.

2. Experimental Procedure.

(a) Sampling.

The samples of stratosphere air which have been analysed were all obtained by means of rockets, either German V-2, or Aerobee rockets, developed by the United States Air Force. All flights took place at White Sands Proving Ground in New Mexico, and were arranged by the Engineering Research Laboratories, University of Michigan, under contract with the United States Signal Corps.

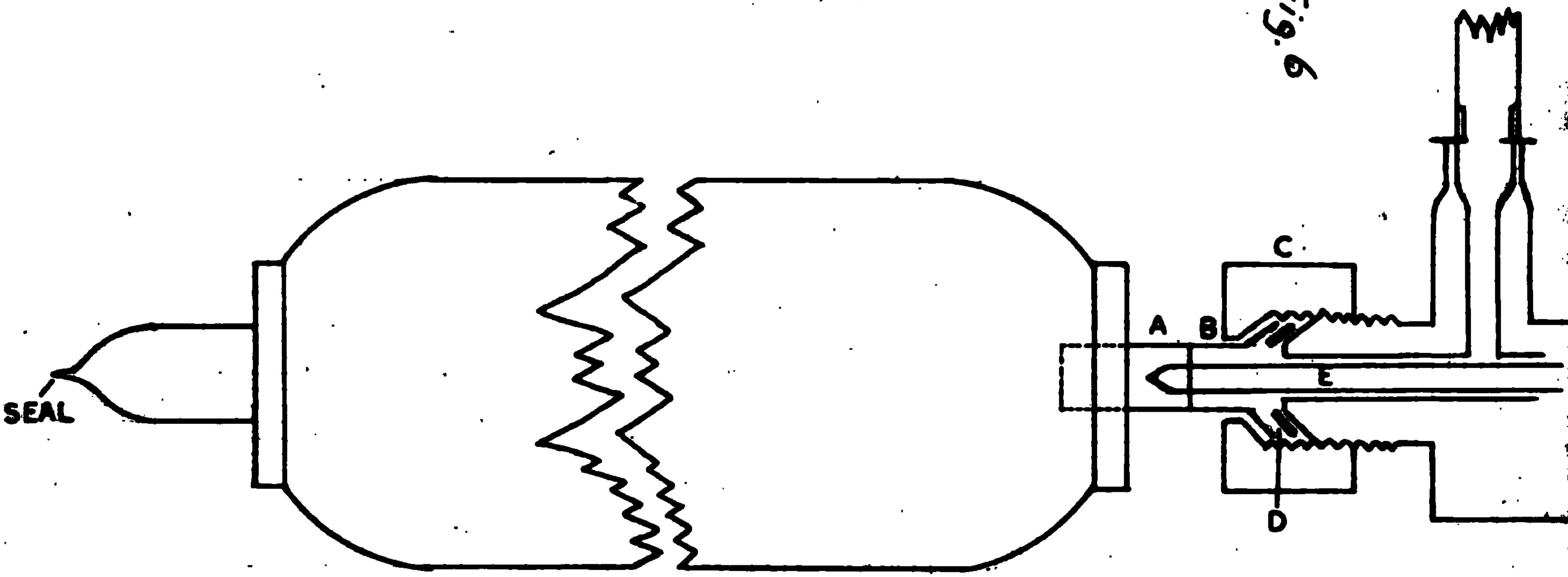
Three evacuated steel bottles were usually located immediately behind the hollow nose cone of the rocket, although in one instance seven bottles were used (46). The bottles (Fig.5) were soldered to thin copper tubes, one inch in diameter, the sealed-off ends projecting into the cone. The latter was ejected automatically before sampling. At a predetermined instant, a steel knife was arranged to cut through one tube and a few seconds later this was squeezed shut at a lower point by a pyrotechnically operated vice. The second and third bottles were opened and shut at successively later times. When sampling was completed, the bottles were ejected and the section lowered to the ground by means of parachutes.

Before installing the bottles in the rockets, control experiments were carried out to ensure their vacuum tightness. The original welds were first tested, then the whole bottle was washed, dried and evacuated. It was pumped for 24-48 hours at a maximum of 150°C and sealed off. It was then checked for leaks by means of a pirani gauge incorporated in the bottle before use. The data from this leak check are not always available, but in the case of 19D and 25D they were 2×10^{-5} mm/Hg/hr and 5×10^{-7} mm/Hg/hr respectively (48). In the case of the last rocket, the preflight pressure in the seven bottles was determined and were 4×10^{-5} mm Hg in the case of C11B and C5, 2×10^{-5} mm Hg for C4, C7B and C6B1, 1×10^{-5} for C1 and too small to be measured in the case of C3 (49). Thus, in the case of C1, it amounted to only 1% of the total pressure found in the bottle after sampling. As is pointed out later on, however, the rates of leakage observed with previous bottles which are frequently of the order of 2×10^{-5} mm Hg/hr, makes it impossible to rely too much on the results obtained for C1 and C3.

In all, 14 samples were available for analysis from 4 rocket flights, covering the atmosphere from 50.4 km to 105.8 km. Of these, two samples were wasted through leakage into the bottle after sampling, one sample showed slight leakage, but not sufficient to completely invalidate the analysis, and one sample has not been analysed yet for reasons given later on.

Apart from 19D and 25D, which were transferred into glass vials at the University of Michigan, all samples were shipped to us in the original steel bottles. This overcomes the objection present with earlier experiments of running the risk of losing part of the Helium in particular by adbsorption in the glass (12). On the other hand, it prevents any reliable oxygen figures from being

Fig. 6



STEEL BOTTLE AND JOINT

obtained as O_2 readily combines with the copper tubing attached to the bottles, even at room temperature. This is amply borne out by the measured O_2 contents shown in the table at the end of this section, and also by the O_2 contents of the 4 sample bottles described later on.

(b) Analysis.

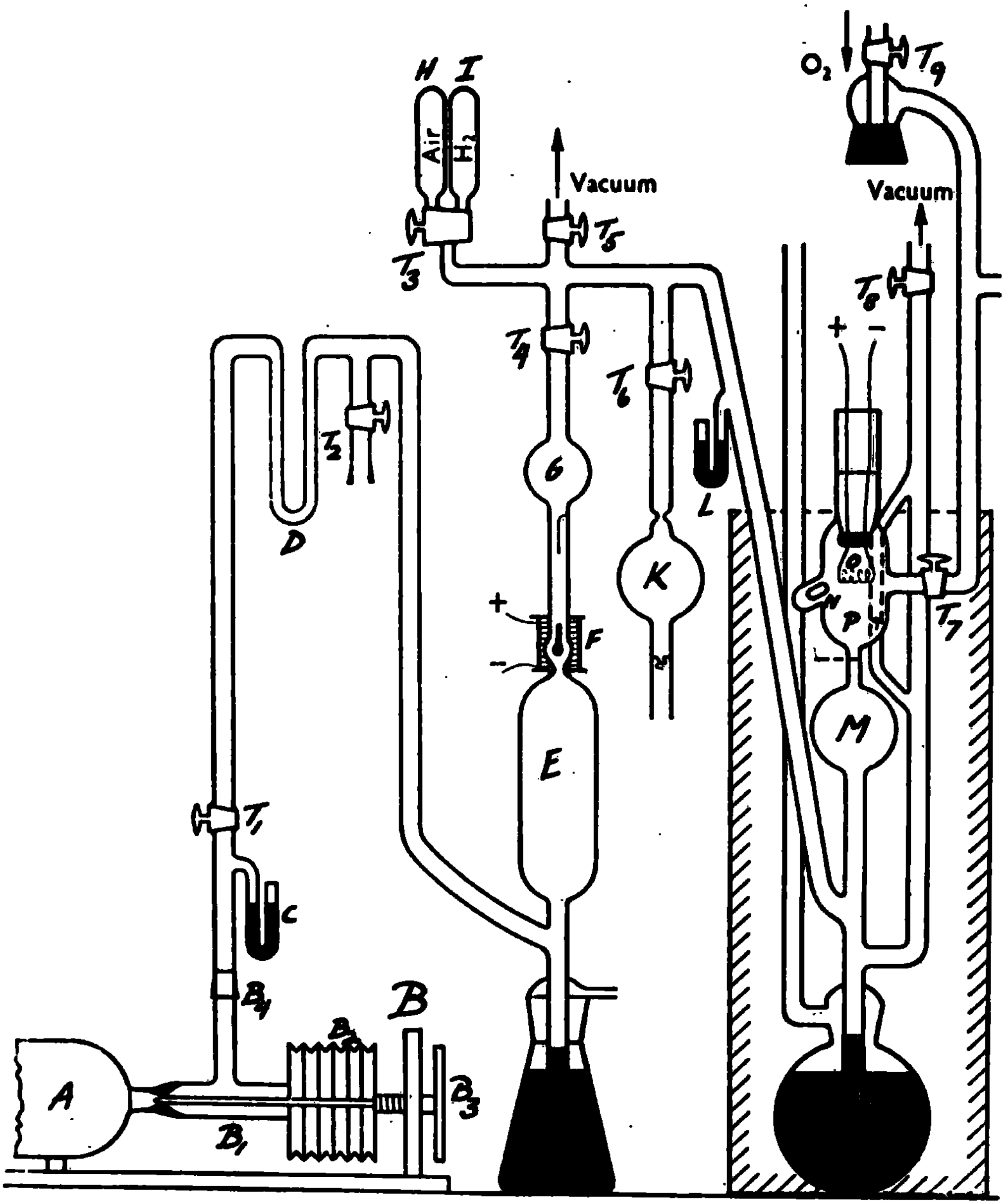
The steel bottles were then shipped to Durham where the samples were extracted, measured and then analysed for helium, neon, argon and oxygen on the apparatus described below.

(i) The Opening Mechanism. (Figs. 6 and 7.)

The steel bottle containing the stratosphere sample is joined at A to the opening mechanism B; this consists of a steel plunger E (Fig.6), which is attached to the end of a brass bellows B_2 (Fig.7). By rotating the disc B_3, the plunger is moved forward by means of a screw and pierces the copper diaphragm at the mouth of A. The opening mechanisim is attached to the rest of the apparatus through a glass-metal seal which is joined by a standard cone and socket at B_4. C is a manometer giving a rough guide to the pressure during the initial pumping down of the opening mechanism. After the bottle is opened, however, the pressure is too small to give any indication on C, but the change in pressure will be shown by the use of a Tesla coil.

The method of attaching A to B was mostly by soldering a short piece of copper tubing B to the tubing at the end of A,

Fig. 7



Opening mechanism, storage bulb, and air pipette.

(Fig.7), the other end of the tubing (Fig.6) having a flange which fitted a flange on the opening mechanism and was joined on to this (with a rubber washer D to make it vacuum tight) by means of a nut (c). This system worked satisfactorily in the beginning, but after a while it became increasingly difficult to get a vacuum-tight seal. This was probably in part due to slight alterations in the shape of the cone and socket type of flanges, bringing them slightly out of line; but it was mostly due to difficulties with the rubber washers. These were at first stamped out from ordinary Dunlop's cycle tyre patches and used as they were, without any grease which tended to make them suck in. After the first lot of material had to be discarded through aging, however, great difficulty was found in acquiring new material which would give a vacuum tight seal. Neither PVC, polythene, neoprene, or ordinary rubber would give a gas-free seal although some rubber washers gave a reasonable vacuum after a considerable time of pumping and degassing. As against 3 - 4 days with the first type of materials, a matter of weeks had to be spent on getting the seal vacuum-tight towards the end,and finally the whole method of opening was altered. The bellows-type of mechanism was discarded altogether, and the bottle was joined to the apparatus in a vertical position through a standard cone and socket. The opening was done simply by lowering a steel plunger which was normally held in position by a small steel bar which could be removed by means of a magnet. This system seems to work admirably, it pumps down to a good, lasting vacuum on a couple of days.

(ii) The Toepler Pump and Storage Bulb (Fig. 7).

After opening the bottle, the contents were transferred by means of the Toepler pump E to the storage space at G confined between tap T_4 and the ventil F on top of the Toepler pump. This requires about 100 strokes. By raising the mercury to a certain level in G, the volume of which had been determined accurately to be 24.516 ccs. and measuring the pressure on a travelling microscope (cathetometer) the volume of the sample could be found. During transfer the U-tube D was cooled in liquid N_2 to remove any CO_2 and H_2O there might be in the sample.

(iii) Contamination Monitoring by Active Carbon Dioxide (Fig.7).

Active CO_2 is released in the sampling compartment five seconds before the sampling starts in order to check any possible contamination by air swept up with the rocket. In practise, therefore, after all the sample has been collected in G, tap T_1 is closed, and a certain amount of inactive CO_2 is introduced through T_2. This is allowed to mix with any active CO_2 by removing the liquid N_2 around D, and is then withdrawn in 2 lots by condensing it back into the sample tube by cooling it in liquid nitrogen for 20 minutes. When the sample had been withdrawn, the tube was detached and analysed for any ^{14}C activity on a specially designed Geiger counter. The results of this investigation are quoted later on.

(iv) The Air Pipette (Fig. 7).

When a sample is needed for analysis, the whole section between T_3, T_4, T_5, T_6, T_8, and V is first pumped down to a "sticking" vacuum. T_5, T_7 and T_8 are then closed and the mercury raised a couple of centimetres above the cut-off below M. T_4 is then opened, and enough gas admitted to the line to give 0.5-1 cm. pressure on the manometer L. After shutting T_4 again, the mercury is lowered and the sample admitted into the air pipette M and P. The mercury is raised again until the top of the meniscus just touches the etch mark at P. The whole system is immersed in a waterbath whose temperature is thermostatically controlled, and 5 - 10 minutes is allowed to let the sample reach equilibrium.

The volume of the air pipette is known with an accuracy of more than 1/1000. The calibration was at first done by gas-expansion. Some dry N_2 was confined in the air pipette and the pressure measured by reading the mercury levels in the two parallel tubes. The mercury was then lowered and the gas expanded into the sidetubing which was previously evacuated, and the pressure was read on the manometer attached to the side-tubing. Finally, the gas was expanded into a bulb of known volume (about 48 ccs) and the final pressure was measured on the manometer.

We then have :

$$\underline{p_1 \cdot v_1 = p_2 \cdot (v_1 + v_2)}$$

$$\underline{p_2 \cdot (v_1 + v_2) = (v_1 + v_2 + v_3) \cdot p_3}$$

where v_1 = Volume of air pipette,

v_2 = volume of the sidetubing and v_3 is the known volume of the expansion bulb.

Eliminating v_2, we find:

$$\underline{\underline{v_1 = \left[\frac{v_3}{\frac{p_1}{p_2} \cdot \frac{p_2}{p_3} - \frac{p_1}{p_2}}\right]}} \qquad \text{or if } \left(\frac{P_1}{P_2}\right) = x$$

$$\left(\frac{P_2}{P_3}\right) = y$$

$$\underline{\underline{v_1 = \left(\frac{v_3}{x(y-1)}\right)}} \quad \text{ccs.}$$

The results obtained by this method, however, were very poor. At first, the values found varied from 5.5. to 12 ccs. for the air pipette. The air pipette was then fitted with thermostated water tank and the temperature of the whole room was also thermostatically controlled. This reduced the spread in the results considerably, but the mean volume obtained after several dozen determinations was still far from satisfactory, 8.5 ± 0.25 ccs The manometer was then remade; the new one having a wider bore to reduce the effect of sticking mercury, and several more determinations were made. These gave values for the volume of the air pipette with a much smaller spread, but as the error was still nearly 1% the above method was abandoned altogether. Instead, the air pipette was cut off, and its volume determined by filling it with an accurately measured quantity of water. This is a rather more tedious procedure. The volume of the KOH pellet at N was determined by weighing and substracted from the total volume. This method has been used repeatedly over the last 30 months, and gave very consistent results around 8.838 ccs. whereas the gas-expansion method gave volumes varying between 6 and 12 ccs.

(v) Estimation and Removal of Oxygen (Fig.7)

After reading the pressure p_1, the mercury is lowered a couple of centimetres and the Cu-spiral O is heated slowly until it reaches a very dull red heat. It takes out all the O_2 in the air sample in the course of 10 - 15 minutes. The current is then switched off, and 10 minutes is allowed for the temperature to reach equilibrium when the Hg is raised and the pressure read, p_2. The process is repeated after a further 5 minutes heating and pressure p_3 read. p_3 should never be less than p_2, but it is sometimes a little higher (a matter of 2 - 3%), which is probably due to the Cu-spiral being too hot, causing some of the oxides forming to dissociate again at a rate appreciably higher than that at which they are formed. In such cases, p_2 was taken as the pressure representing the N_2 + A content of the sample.

The Cu-spiral had to be cleaned at intervals, It was found that after it had been used a few times, the action became rather slow and it was difficult to remove the last traces of O_2 from the samples. The Cu surface was regenerated by heating it in the presence of H_2, from the reservoir I, at a fairly bright red heat. Whereas 3-3.5 amps. was necessary for the removal of O_2, as much as 6.5 - 7 amps. was needed to set the reaction between the copper oxide and H_2 going, or rather to get the spiral to a red heat. Once this was obtained, the current had to be reduced at once. To prevent the spiral from burning out, it had to be carefully watched all the time and the current reduced as the pressure in the air pipette went down, the final current being 1.5 - 2 amps. less than the initial one. After 10 - 15 minutes, treatment, the mercury was lowered and the surplus hydrogen pumped away. The pumping was continued for a while with the spiral at a dull red heat to remove any traces of H_2 absorbed in the metal, and after about 5 minutes the current switched off and pumping continued for a further 10 - 15 minutes, until a good "sticking" vacuum was obtained. The H_2 used was ordinary H_2, as supplied on cylinders without further purification.

Any water formed will be taken up by the KOH pellet N lying in a side arm of the air-pippette.

Owing to the presence of the KOH pellett, and the fact that mercury vapour had a tendency to condense on the sidewalls, and in particular on the Cu-spiral from which it would flash on to the walls and sidetubing together with other impurities, the air-pipette had to be removed for cleaning every 3-4 months to prevent the mercury sticking. This usually happens very suddenly, when one may get a depression of the mercury in the tube leading into the air-pipette of the order of .05 cm. or 5 - 10% of the expected total reading. For this reason, as well as one of accuracy, the setting of the cathetometer x-wires on the mercury levels in the two tubes was always checked while the apparatus was evacuated immediately prior to starting an analysis.

(vi) Estimation of Argon Content (Fig. 4).

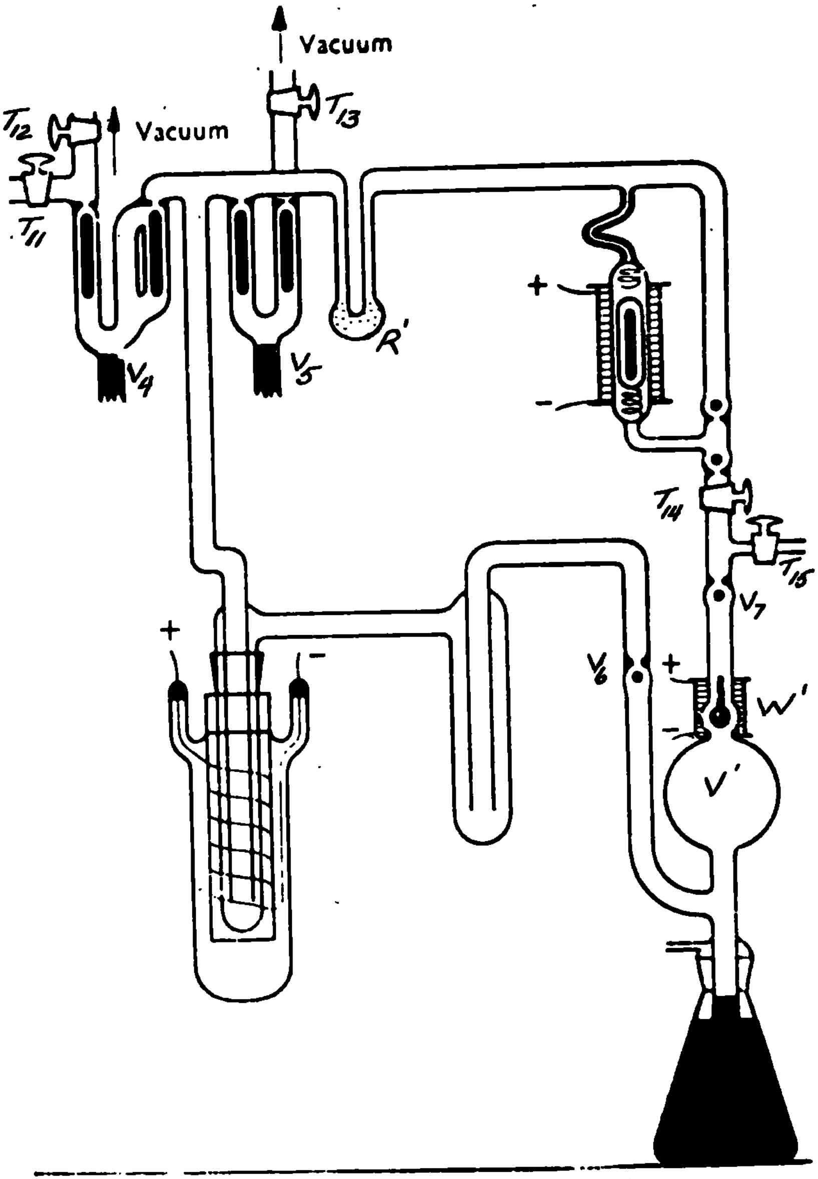
When the amount of oxygen has been found, it remains to determine the argon content or the helium and neon content. In the case of an argon determination, the sample is transferred to the Barium furnace by cooling the charcoal for 45 minutes. After closing T_7 and V_1 again, it is treated in the same way as described in the first part of this thesis for the analysis of potassium salts, in Chapter II, section (IV) and (V), and the final volume is read on the McLeod gauge described in the same place

(vii) Transfer, Fractionation and Measurement of Helium and Neon.

The present helium apparatus described below and built specifically for this work, is capable of measuring amounts of helium and neon of the order of 10^{-8} ccs with an accuracy of 1% to 2%.

As was mentioned in the introduction to this thesis,

Fig. 8



Palladium furnace and circulating system.

the method of estimating the helium and neon is based upon the earlier work by Glückauf and others who have published a full description of the theory behind it (3) → (8), and the conditions governing the separation of helium and neon (36) (37) (50).

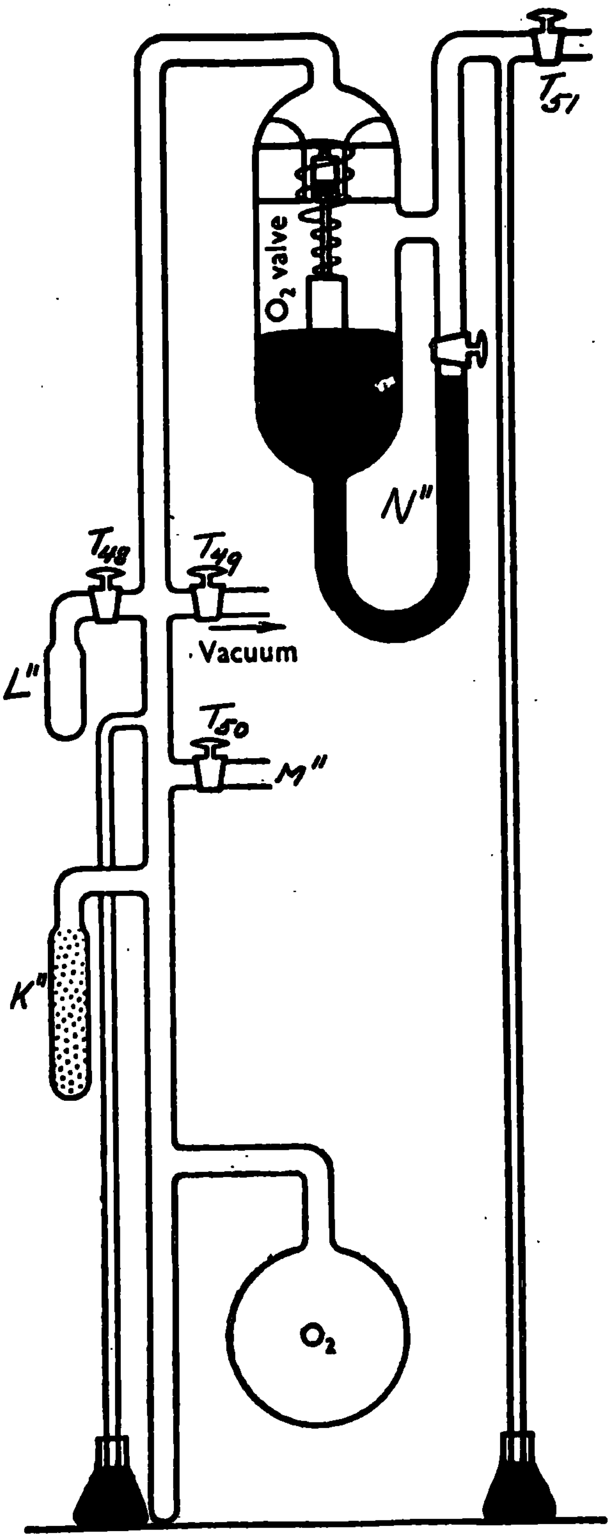
For this reason, only an outline of the principle involved will be given here together with the present operating procedure.

When a mixture of helium and neon is brought into contact with charcoal at the temperature of liquid nitrogen, they are absorbed to a different degree (51). In fact, under certain conditions only about 25% of the helium is absorbed by the charcoal and 75% of it remains in the gas phase whereas 75% of the neon is absorbed leaving 25% of it in the gas phase, at the temperature of liquid nitrogen. The two other factors governing this process apart from the quality of the charcoal is the amount of it and the volume of the gas phase.. By repeating this absorption process a number of times on successive charcoals, one can separate the two gases completely. The present apparatus utilises 15 such charcoal units, compared to 12 on Gluckaufs, which makes it possible to get a better separation of the two gases.

(viii) Transfer (Fig.8)

The gases remaining in the combustion chamber P are then transferred to the first charcoal CH_1, as follows. T_7 is opened, and T_{11} closed, the mercury in V_4 lowered, at the same time the

Fig 9



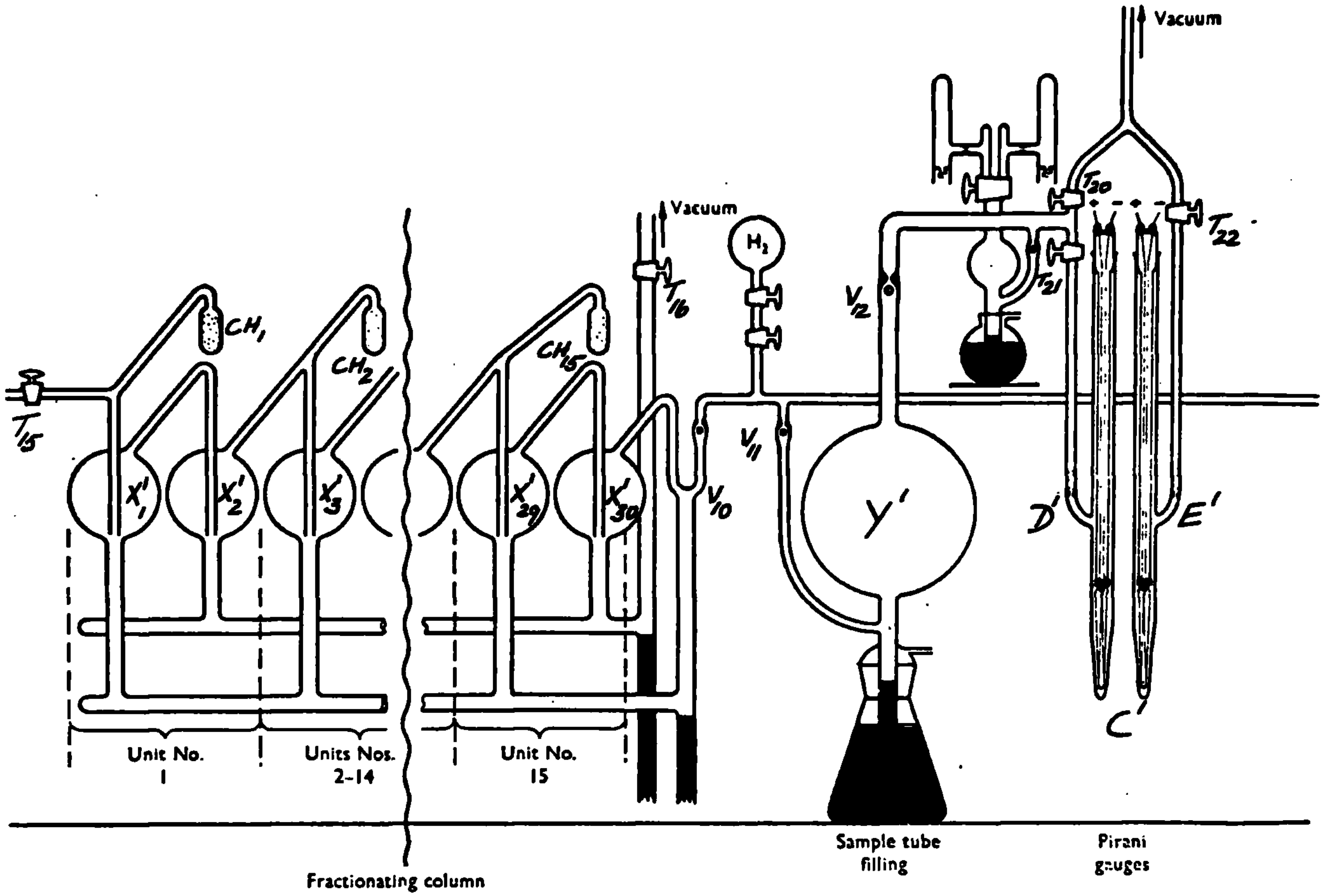
Oxygen reservoir.

mercury in the Toepler pump V^1 is just above the cut off, the mercury in the front and the back of the column is raised; with T_{14} closed, and T_{15} open and the charcoals on the fractionating column immersed in liquid nitrogen. By opening T_9 a few millimetres of O_2 to act as a carrier gas is admitted, and on opening T_{11} the mixture of air sample and pure oxygen is admitted into the circulating system. By operating the Toepler pump 8 times, about 99% of the mixture is transferred to the first charcoal. This process was repeated five times which had been found to give 100% transfer of the gases.

The oxygen used as a carrier gas was supplied from the oxygen reservoir, Fig.9. It was purified from ordinary cylinder oxygen as follows.

First, the whole reservoir was evacuated and the charcoal in K" baked out for about one hour at 200°C. The oxygen cylinder was then connected up at M" by rubber tubing, and a T piece digging into a mercury flask was included in the connection. After this was well flushed, out and the O_2 bubbling continuously past the mercury, T_{50} was slowly opened admitting the gas into the reservoir. When atmospheric pressure had been obtained T_{50} was closed, and the major part of the oxygen condensed on L" by means of liquid nitrogen. T_{48} was then closed and most of the remainder was condensed on K" leaving only a few mms. of pressure in the system. T_{49} was then opened and this remaining gas, which contains most of the helium and neon, was pumped away for 5 minutes.

Fig. 10



Fractionating column and Pirani gauges.

When T_{49} was closed again K" was first allowed to warm up and then L" releasing all the adsorbed and condensed gas into the reservoir again. The whole process was then repeated six times, and afterwards some of the oxygen, about ten times the amount normally used, was passed through the fractionating column to make sure than no trace of helium and neon was present. Once the oxygen is purified, in this way, it will remain helium and neon-free for months in the reservoir.

(ix) <u>The Fractionating Column (Fig.10)</u>, was automatically operated, and up to 27 operations could be carried out without further attention. This was done by having the vacuum and air inlet to the mercury reservoirs drawn out to fine jets, the opening and closing of which was done by steel slugs with rubber gaskets on the bottom. The raising and lowering of the slugs was done by solenoids controlled in pairs by means of two relays, cam-operated by a synchronous motor. The cams were connected up in such a way that when at the front of the column f.inst. the air inlet was open and the vacuum lead closed, the opposite would be the case at the back of the column. One complete operation consists of lowering the mercury in the front of the column to just below the bulb, that is in bulbs X_1^1 , X_3^1, X_5^1 ... X_{29}^1, and raising it again followed by the same procedure for the back of the column, bulbs X_2^1, X_4^1, X_6^1 ...X_{30}^1.

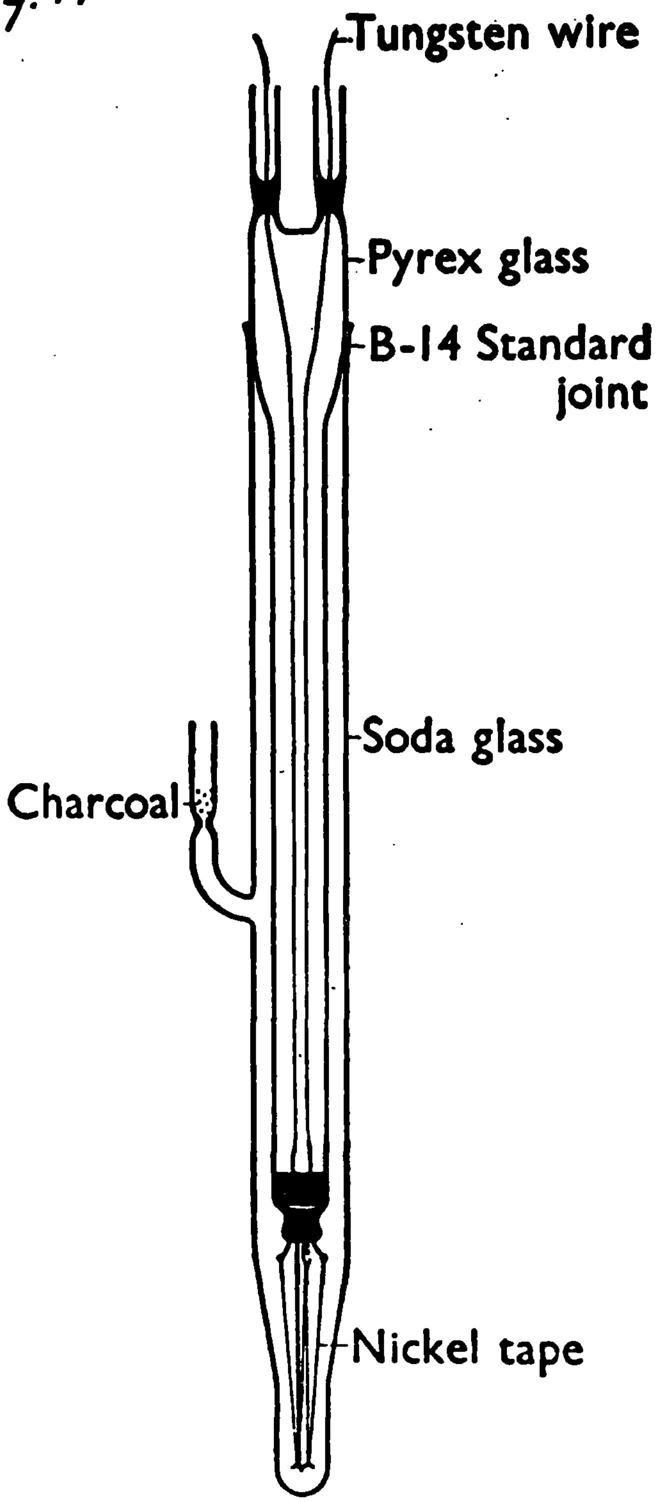
The column was first set for 15 operations and at the end of these the mercury in the compression bulb X' was raised to close Ventil V_{12} and the tap T_{21} to the measuring Pirani gauge was opened in order to see if any deflection of the galvanometer resulted. As the first amounts of helium only begin to come through after operation 16, this check after 15 operations was done to see if the column had been properly evacuated before the experiment was started. No deflection was in fact ever found at this stage.

After this, the column was reset to perform operations 16 to 36, and the deflection caused by the gas coming through during those 21 operations was measured. This number of operations had been found experimentally to give the same deflection as 100% of the helium, although it in fact contained 99.3% helium and 0.1% neon. A further 25 operations were sufficient to get all the neon through the column, but only if the liquid nitrogen is removed from the charcoals at successive stages during the operations 16 -36. The first charcoal is always dipping into the liquid nitrogen to prevent the oxygen and nitrogen in the gas mixture from desorbing, but the 2, 3 and 4th charcoal are allowed to warm up after operation 25 as the last amounts of helium have passed this stage by then. After operation 29, the next four charcoals are allowed to warm up, after the 33rd operation the liquid nitrogen is removed from charcoals CH_9 - CH_{12} and CH_{13} - CH_{15} is warmed up after the 36th operation.

(x) Measuring the Helium and Neon (Figs. 10 and 11.)

The helium and neon were measured on a Pirani gauge D^1. This is balanced in a Wheatstone Bridge network by a compensating gauge of identical design E^1. The filaments are about 30 cms.

Fig. 11



Pirani gauge.

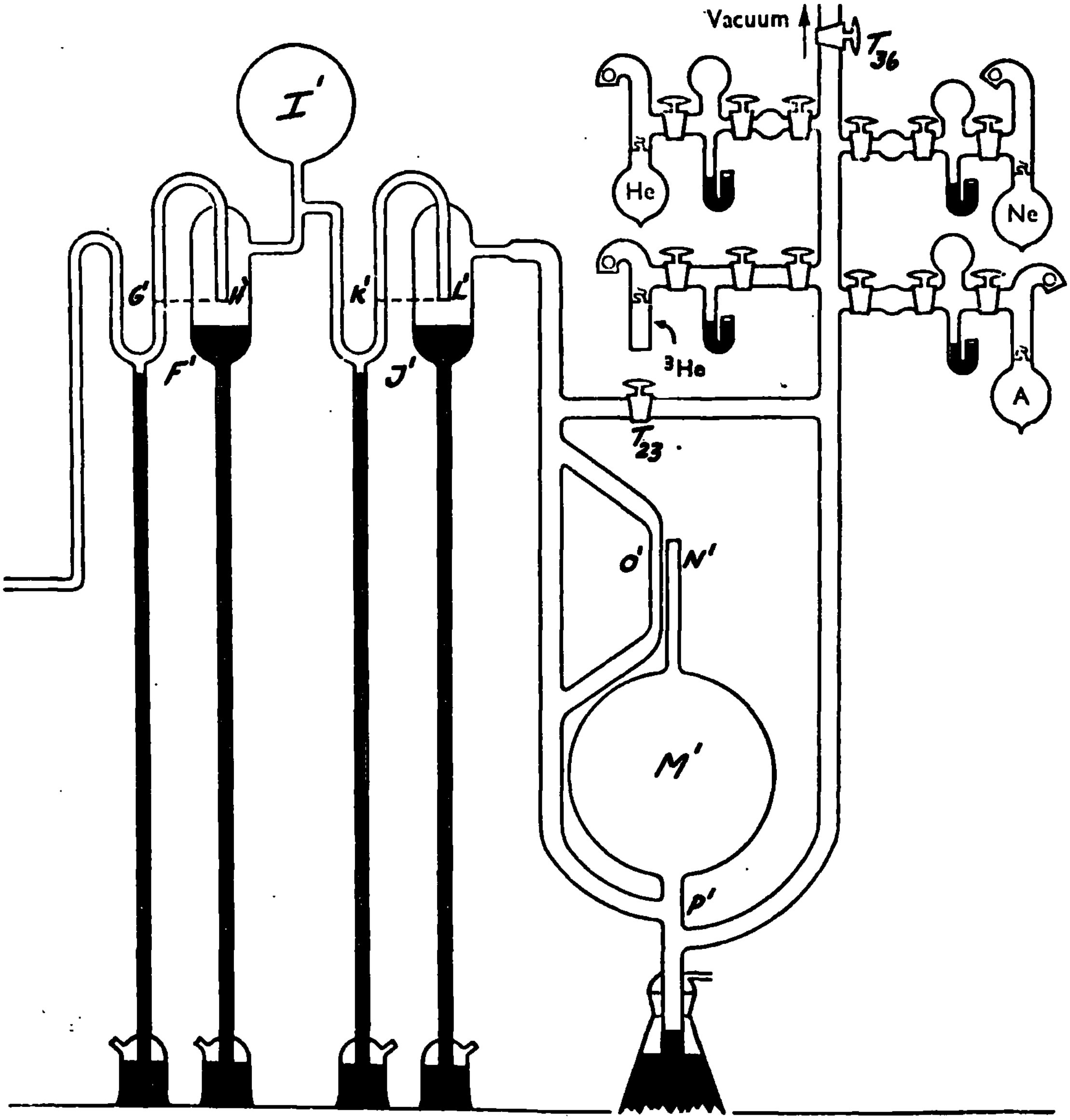
long, and they are made of very fine nickel tape which is in the shape of a W. A small amount of charcoal is placed in the sidearm of the gauges to prevent other gases given off by the walls or the tap-grease from interfering with the measurements. To achieve a high accuracy with small amounts of gases, the total volume inside the gauges were made as small as possible and both the gauges were immersed in liquid nitrogen.

A potential of exactly 1 volt is applied across the gauges when they are used, and a sensitive moving coil galvanometer is mounted across the bridge, the deflections being read on a 50 cm scale. The sensitivity of the Pirani gauges were altered by varying the galvanometer shunt.

When measuring the amount of gas, the mercury in the compression bulb is raised, this brings more than 99% of the gas into the measuring space. Readings of the position of the galvanometer spot was carried out every minute, before admitting the gas to the Pirani gauge until there was a steady drift. The gas was then admitted and when readings indicated a steady drift again, T_{20} was opened and the gas was pumped away while the readings were continued until the drift was steady. This method of reading allows for both the zero drift which always seems to be present and the slow approach to equilibrium when the gases are admitted or pumped away.

One further error had to be allowed for, namely the one due to the non-linear response of the galvanometer system.

Fig. 12



McLeod gauge for calibration and expansion system.

It was found that equal amounts of gas gave smaller deflections near the centre of the scale than near the ends. To estimate the size of this error, a megohm resistance was connected across one of the Pirani gauges with a mercury switch in the circuit, the turning of which gave deflections in the same way as the presence of a gas in the Pirani gauge. By adjusting the sensitivity of the gauge, the size of this deflection could be altered and readings were taken for various deflections over the whole scale. There was about 10% difference in the reading of equal angular deflections giving readings of 6 cms. at the ends of the scale when there was only 5 - 4 cms. deflection near the centre.

By plotting a graph of these deflections against position on the scale and fitting a parabola to it, a correction table was constructed showing the amount of correction to be applied to readings between any two points on the scale, thus reducing the readings to the values one would have obtained with a perfectly circular scale.

(xii) Calibration (Fig.12)

After the measurement of each sample, the Pirani gauge was calibrated absolutely with an accurately known amount of the same gas of the same order of magnitude as the unknown sample and as far as possible over the same range of the scale.

This was done by measuring a small amount of spectrally pure helium or neon in the McLeod gauge M' and expanding it into the previously evacuated sidearm O' and pipette K'L', the volume of which had previously been determined very accurately. By raising the mercury in J', the gas in K'L' was cut off from the McLeod gauge, and sidearm, and could be expanded again into the bulb I' from which another pipette-full in G'H' was obtained, and expanded into the compression bulb and thence brought into the pirani gauge. By this method accurately known amounts down to about 6×10^{-5} of the amount measured in the McLeod gauge can be measured on the Pirani gauges, and the whole calibration apparatus had a range of from 1×10^{-3} ccs NTP down to 3×10^{-8} ccs NTP which was quite sufficient for the present work.

As the gauges are not equally sensitive to helium and neon, separate calibrations were always carried out for both gases.

(xiii) General.

During each series of experiments control analysis were done with ground level air in such a way that each analysis of a stratosphere sample was sandwiched between two ground air analyses. This was done to keep a check on the experimental procedure as well as the efficiency of the apparatus.

Usually, two or three analyses were carried out for each sample for helium, neon and argon unless the initial amounts of samplewas too small to allow for this as was the case with the highest samples. Any air left over after this in the storage bulb G, Fig.7, was transferred to the previously evacuated bulb K by raising the mercury in the Toepler bulb and in the air-pipette and then opening T_3 and T_6. After sealing off, the bulb was then returned to the U.S.A. for other investigations, usually the measurement of the $^{14}N/^{15}N$ ratio or similar experiments.

3. Results.

In the following section, the results of all the stratosphere analyses are given as well as a summary of the determinations of helium, neon and argon content of ground level air, and also the results of the analysis of some test bottles filled with ground level air at Michigan and analysed at Durham.

The results are quoted as the abundance of the respective gases relative to nitrogen in the sample, compared to the abundance at ground level - denoted by α .

(a) Stratosphere samples.

TABLE 2.

(see Page 44).

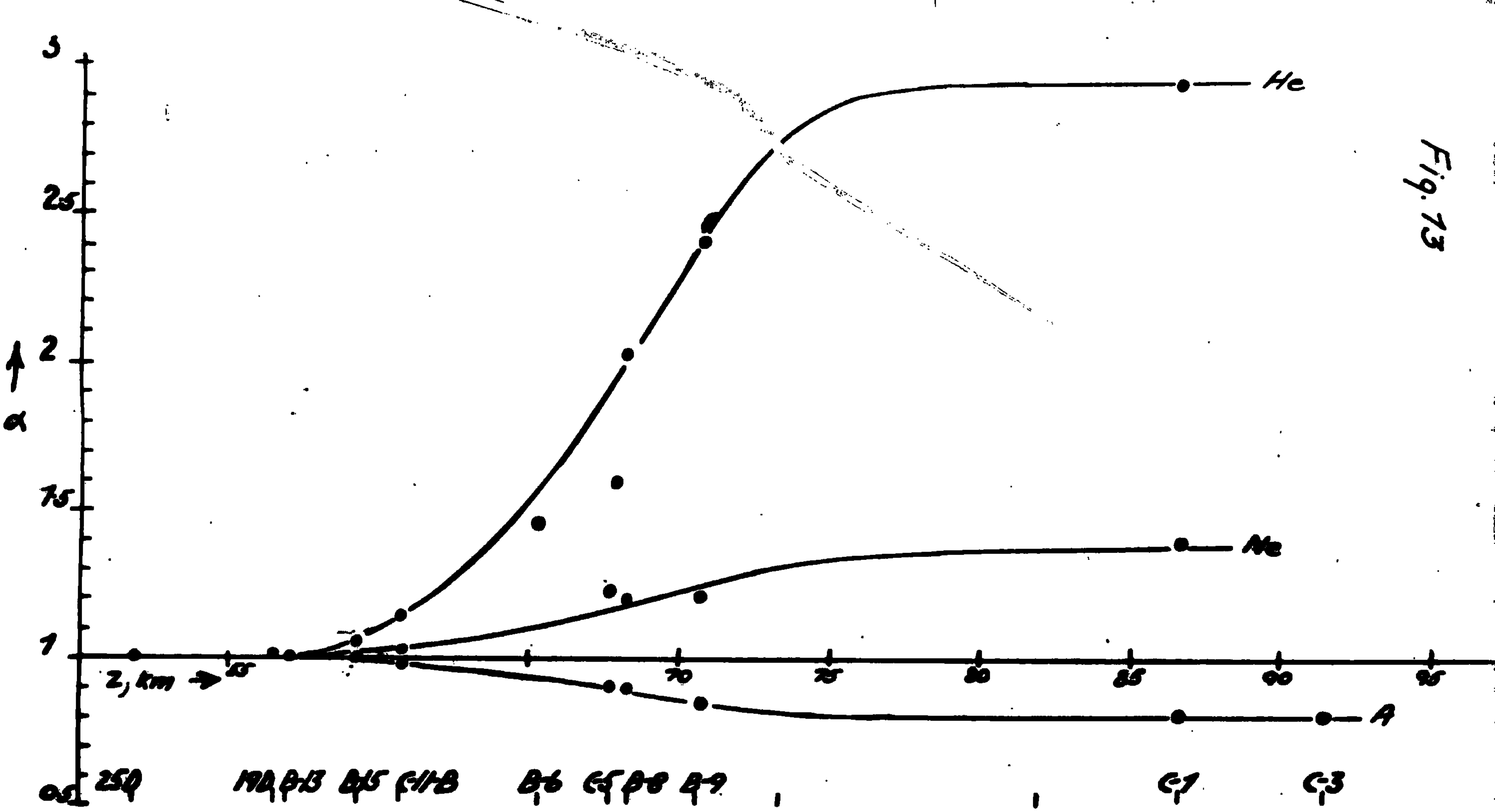

3
2.5
2
1.5
1
0.5
α
z, km
55
70
75
80
85
90
95
He
Ne
A
250
190
B-13
B-15
C-11-B
B-6
C-5
B-8
B-9
C-1
C-3

Fig. 13

TABLE 2.

Results on Stratosphere Air Samples.

No. of sample.	Height (Km)	Amount of gas in bottle (C) cc.N.T.P.	Ratio to ground level air			
			He.	Ne.	A.	O_2
25D	50.4 - 53.3	8.6	0.981	1.003	0.998	0.6
19D	54.7 - 58.3	2.04	1.013	1.450Ø	1.009	0
B-13	55.56 - 58.18	6.78	0.998	1.005	1.001	0.5
B-15	58.18 - 60.35	5.15	1.035	1.008	0.996	0.01
C-11-B	57.0 - 64.3	0.398	1.113	1.040	0.962	0.7
B-6	64.3 - 67.0	0.415	1.445	1.080	0.929	0.07
C-5	64.3 - 71.0	0.204	1.570	1.232+	0.90	0.10
B-8	67.0 - 69.6	0.218	2.02	1.177	0.886	0.25
B-9	69.6 - 71.8	0.535 0.185 corr.	2.41+	1.20+	0.85+	0.03
C-1	84.4 - 89.0	0.015	2.94	1.39	0.82	0.00
C-3	89.0 - 93.2	0.0032	-	-	0.82	0.00

Ø unreliable because of contamination by H_2 in original sample, confirmed by mass spectrometry.

\+ corrected for leakage.

+ suspected to contain small amounts of hydrogen as well.
(C)corrected for loss of oxygen.

Description of Samples.

(i) 19D and 25D.

19 D Sc 4 and 25 D Sc 3 were both analysed mainly for the reason that McQueen had found a slight separation of the nitrogen isotopes in these two samples (52). The results as shown below did not confirm McQueen's findings however (53), and he discovered later on that his results were due to an experimental error in the mass spectrometer.

The Ne result was found to be due to contamination with hydrogen which starts coming through towards the end of the neon fraction during the analysis. The presence of H_2 in the original sample was confirmed by mass spectrometer analysis (48).

(ii) B6; B8; B9.

The next samples to be analysed were B-6, B-8 and B-9. The results obtained for these have already been published, together with 19D and 25D (54), and later with B-13 and B-15 (36). They were the first samples which showed any conclusive evidence of a composition of stratosphere air different from that of ground level air.

When first analysed, B-6 and B-9 were shown to have nearly the same composition in spite of the fact that B-9 contained air from about 5 km above that of B-6. B-9 also contained more air, 0.535 ccs. as against 0.338 ccs. for B-6 and 0.231 for B-8, Because of this, experiments were made to find out if any of the bottles had leaked which, of course, would introduce an error in the results. Both B-6 and B-9 were therefore put back on the apparatus and pumped out again, and the pressure developed after a few days was measured. In the case of B-6, no leakage was found at all, even when the sealing wax was removed from the end of the copper tubing over the cold welded seal. With B-9 however an appreciable leakage was found as soon as this was was removed. The rate of leakage was found to be 3.4×10^{-3} ccs/hr, and it then appeared that a great deal of the air found in the bottle was in fact ground level air which had leaked in before the Glyptal wax had been applied to the seal. To correct for this it did not seem to be reasonable to extrapolate the values for the amounts of air in B-6 and B-8, as B-8 may not have collected all the air it should have done. Although B-8 sealed perfectly, the opening knife was found to be in a position only about half way across the tube on recovery, and may therefore have impeded the flow of air considerably. Instead, it was decided to take the amount of air in B-6 as correct and calculate the amount of air to be expected in B-9 from the formula

$$\underline{\underline{P = P_o \exp\left(-\frac{z}{H}\right)}} .$$

where z = height above z_o

H = scale height for

air with $T = 280^{o}K$

$R = 8.31 \times 10^{7}$ cm2/sec2 oK

$g = 980$ cm/sec2

$m = 28\ (N_2)$

The temperature of 280^{o} K was rather approximate, but the final results are not very accurate in any case.

The nitrogen pressure at 62 km was taken as 1, giving a N_2 pressure at 72 km of 0.3077. The O_2 - free volume of B-6 at 65.6 km is 0.338 ccs. and we should therefore expect 0.184 ccs. in B-9 at 70.7 km. Thus 0.347 ccs of ground level nitrogen appeared to have leaked in.

The experimental values for B-9 were:

$He/N2 = 1.49 \quad Ne/N_2 = 1.07 \quad A/N_2 = 0.95$

The true value is therefore for Helium:

$$\underline{1.49 = \left(\frac{\alpha He \;.\; 0.184 - 1 \;.\; 0.347}{0.531} \right)}$$

$$\therefore \quad \underline{\alpha He = 2.41}$$

Similarly $\underline{\alpha Ne = 1.20}$

and $\underline{\alpha A = 0.85}$

These "corrected" figures are entered in the summary of the results above, and although it is very unsatisfactory to apply such a correction, it is the only way to obtain the maximum amount of information from these analyses.

No correction has been applied to B-8 although it is quite probable that the sample is representative of somewhat higher layers than the mean height which is used throughout.

(iii) B-11; B-13; B-15.

The next rocket contained the samples B-11, B-13, and B-15. All of these were thought to have opened and closed perfectly, but when Bottle B-11 was opened it was found to contain air at atmosphere pressure and on close inspection a large pinhole was discovered in the coldweld seal on the copper tubing. It was in fact so large that when the tube was immersed in water only a small pressure of air was sufficient to produce a stream of bubbles from this point.

The other two sample bottles B-13 and B-15 both contained air at a pressure in accordance with that expected at their heights, and the highest of these two, B-15, again showed a distinct difference in composition as compared to ground level air.

(iv) C-1, C-3, C-4, C-5, C-6BL, C-11BL.

The last of the present samples was obtained with a rocket containing 7 sample bottles, sampling all the way from 57 to 104 km (46). Of these, 6 were of the usual size, 500 cu.ins. whereas the seventh, C-6-BL, was made 3 times as large in an attempt to overcome the difficulty of bringing down a sample from 100 km, height large enough for an analysis. This analysis has, however, not been attempted yet as it involves some considerable modifications to the air pipette because of the smallness of the sample, probably less than 10^{-3} ccs. NTP (43) (44).

Of the other bottles, however, five were opened. C-4 was found to have atmospheric pressure as a result of faulty seal made during the closing of the copper tube. The remaining four bottles were analysed and all of these contained air of a composition markedly different from ground level air, with He percentage up to 300% greater than in ground level,air.

The composition of C-11-B and C-5 were in accordance with previous results.

C-1 and C-3, although there was a greater difference in composition than in any previous samples, did not show a sufficiently large difference compared to their height. One reason for this may be that the vertical circulation in the air increases again at heights above 80 km. This may be due to ionisation currents set up in connection with the dissociation of O_2 molecules at present thought to take place between 80 and 100 km. Another reason may be a minute leak or slight degassing of the bottles during the time between sampling and analysis. C-1 was found to contain 0.012 ccs NTP of air, and C-3 0.0026 ccs. N.T.P. of air. As 248 and 263 days respectively elapsed between sampling and analysis, a leakage or degassing rate of 1×10^{-6} for C-1 and 2×10^{-7} ccs/hr for C-3 would account for as much as half the amounts of air found. Rates of this order of magnitude would be difficult to detect as they involve pressure increases of

2×10^{-7} mm Hg/hr and 4×10^{-8} mm Hg/hr. respectively and not too much importance should be attached to these two sets of results yet until further information is available about the composition of the air at these heights.

A further point about the results of the analyses for C-1 and C-3 is that the accuracy is much lower than for the rest of the samples owing to the small amounts of air available. They are certainly not better than 10% accurate in the case of the argon figures where the final amount of argon read on the McLeod gauge was 2.5×10^{-5} ccs NTP

(b) Results for Radio-active Carbon-Dioxide Monitoring.

TABLE 3.

Bottle No.	c.p.m.	Activity found in bottle compared to activity released from CO_2 contained.
C-5	160	1 part in 4×10^6
C-1	800	1 part in 10^6
C-3	10	-
C-11-B	360	1 part in 2×10^6

From the above table, it is quite clear that any possibility of the samples being contaminated by air swept up with the rocket from ground level has to be excluded. The active CO_2 was released in the sampling compartment only five seconds before the first bottle was opened.

(c) Test Samples.

In order to exclude the possibility of the results of our analyses being falsified by the adsorption of different gases on the inside of the steel bottles during storage, a few test bottles were prepared at the University of Michigan and shipped to Durham for analysis. Altogether six bottles were prepared, B-17-P, B-18-P, B-19-P, B-20-P, B-21-P, and B-22-P. Of these four were analysed, of which two were found to contain air of the same composition as ground level air. The other two, however, gave results which differed considerably from the others, showing a shift in composition in the same direction as that obtained with stratosphere samples; although the shift was not as great as in some of these and not with the same relative magnitude between Helium, Neon and Argon.

The reason for this change in composition is not yet clear and several more experiments are needed before one can decide whether it is due to the methods of making up the samples or due to some selective adsorption of some of the heavier gases on some part of the inside of the bottles during storage.

The methods used for introducing the air into the sample bottles were of two different kinds. The first consisted in having a glass vial of known volume filled with air from the roof of the building and sealed off. This was then put in a vacuum chamber with the evacuated sample bottle. After complete evacuation of the chamber the glass vial was broken and the bottle opened and closed again five seconds later in the same way as is usual during actual sampling in the rockets. This method was used for B-17-P, which showed a composition the same as that of ground level air.

The other method, used for B-18-P. B-20-P. and B-21-P, consisted in filling the glass vial with air and sealing it off. The vial was then placed inside the steel bottle which was pumped down and baked out at 150°C. The pressure was measured in the bottle to test for leakage after it was sealed off, and when satisfactory the vial was broken and the pressure read again. Two bottles filled by this method showed a composition different from that of ground level air when analysed, and one did not.

The exact details of the methods used for filling the glass vials are as follows:-

B-17-P.

The vial consisted of a spherical glass bulb connected to a 5 mm glass tubing through a capillary tube with internal diameter of ca. 0.08 cms. The volume was found by weighing the bulb before and after filling it with mercury. The mercury was removed on the roof of the building. The bulb was attached to another piece of glass tubing of equal size by a small rubber tube. This piece of glass tubing was previously pulled out to a capillary of same internal diameter as that on the vial. After emptying it of the mercury, the vial was returned to the laboratory where asbestos was placed over the bulb to prevent heating and the capillary was then sealed off.

B-18-P.

The vial was here made of 7 mm. glass tubing, one end of which had a small bead and could be suspended inside the steel bottle from a copper wire. The other end was pulled out for sealing off. The volume was determined by weighing before and after filling it with water. The water was then removed and the vial attached to a vacuum system. That portion of the apparatus was closed off from the rest, after it had been pumped down to less than 10^{-5} mm HG as measured on a McLeod gauge, and a small quantity of ground level air admitted by opening a mercury valve to the pumps for short intervals until the vial pressure was the one desired, when it was sealed off.

B-20-P and B-21-P.

The vials were filled in identical ways for these two bottles. Small sections of lime glass tubing were beaded on one end, and a capillary pulled out on the other, leaving a short section of open tubing at the end of the capillary opposite the vial. The volume was found with mercury as in B-17-P, and the vials filled by that method as well. They were both sealed off with a small alcohol torch at the capillary end of the tubing while still on the roof.

The various data in relation to these bottles, and the results of the analyses, are given below:-

TABLE 4.

Results for Control Bottles.

Bottle No.	Amt. gas in bottle. (cc.N.T.P.)	Ratio to ordinary laboratory air.				Bottle pressure (mmHg) as measured in Durham.	Bottle pressure (mmHg) of air put in at Michigan.
		He	Ne	A	O_2		
B-17-P	0.151	0.994	1.001	1.00	0	0.0189	0.0185
B-18-P	0.134	0.997	1.003	0.99	0	0.0165	0.0165
B-20-P	0.120	1.259	1.032	0.92	0	0.0150	0.0202
B-21-P	0.130	1.359	1.083	0.92	0	0.0112	0.0174

	Method of filling bottle.	Date of Filling.	Date of analysis.	Pressure decrease.
B-17-P	Chamber	15.10.52	17.12.52	-0.0004
B-18-P	Internal	15. 9.52	19.12.52	0.0000
B-20-P	Internal	23.12.52	3. 3.53	0.0052
B-21-P	Internal	23.12.52	1.5.53	0.0062

When comparing the analyses of these four bottles, it seems as if the method of filling the bottles is without influence on the results, the method of filling the vials however may be at fault in B-20-P and B-21-P. The important thing seems to be the fact that the pressures as measured in Durham and Michigan agree closely for B-17-P and B-18-P, but not for the two bottles which showed a different composition.

As the adsorption of nitrogen and argon on the walls of the bottles seems to be an unlikely cause of the observed separation, the direct cause of it can only be ascertained after several more test samples have been made up and analysed by the same method.

As B-17-P and B-18-P however show no change in composition, there is no reason as yet to discard the results of the stratosphere analyses, as there may have been some specific and as yet undiscovered peculiarity about the bottles themselves or the methods of filling them for B-20-P and B-21-P.

(d) Ground Level Air Samples.

During the experiments, each analysis of a stratosphere sample was "sandwiched" between the analysis of a ground level air sample from the laboratory immediately before and after. The results of these analyses are given below.

TABLE 5.

He (%x10^{-4})	Ne (% x 10^{-3})	A (%)
5.253	18.11	0.9292
5.311	18.15	0.9340
5.448	18.18	0.9350
5.214	18.39	0.9311
5.290	18.42	0.9378
5.364	18.28	0.9471
5.274	18.10	0.9350
5.411	18.51	0.9461
5.154	18.24	0.9340
5.290	18.28	0.9350
-	18.13	0.9330
5.218	18.03	0.9434
5.283	18.24	0.9350
5.290	18.28	0.9368
5.393	18.21	
5.228	18.23	
5.186	18.15	
Mean 5.285 ± 0.010	18.23 ± 0.020	0.937 ± 0.005

These figures are in fair agreement with those published by Gluckauf and quoted in section 1. (He: 5.239 ± 0.004 ;

Ne: 18.21 ± 0.04 and A: 0.934 ± 0.001) although he used 10 to 100 times the amount of air used in the present experiments. (32).

Section 4.

Theory.

When the results from the analysis of B-6, B-8 and B-9 were available, they were the first samples to show a composition greatly different from ordinary air, and attempts were made to fit these results into the usual simple theory, using the barometric formula (54). That is, in a turbulence free atmosphere, the height distribution of any constituent with molecular weight m in terms of the number concentration is given by:

$$n = n_0 \exp\left(-\frac{z}{H}\right) \qquad - \quad (1)$$

where n_o is the number of molecules per unit volume at the base of the layer. z is the height above this base, and H is the scale height.

$$H = \frac{RT}{mg}$$, where R is the molar gas constant.

The experimental results however did not fit in with this theory. It was then assumed that no sharp boundary layer existed, but a certain amount of mixing had taken place, and attempts were made to find out what amount of undisturbed air had been mixed with certain amounts of thoroughly mixed air, both amounts in terms of heights of layers, in order to give a separation of the gases approaching the experimental results.

The method adopted was a rather approximate one and consisted of drawing graphs of density against height for the different constituents at different temperatures, including ordinary air from 0-10 km below z_0. The densities were read at 1 km, intervals from 10 - 1 km below z_0 for air and from 0-27 km above for He, Ne, N_2 and Ȧ, and the figures arranged in a table. For the sake of simplicity, the density was put = 1 at z_0 in all cases. To find the ratio of $\frac{He}{N_2}$, say, where the air was a mixture of ordinary air from - 5 → 0 km. and separated air from 0 → + 10 km. the ordinates of ordinary air were added up from 0 → - 5 km. and those for He and N_2 added up from 0 → + 10 km. The ratio is then the sum of the He ordinates plus sum of the air ordinates divided by the sum of the N_2 ordinates plus the sum of the air ordinates.

This looked quite promising for a single result, that of B-6 where a mixture of ordinary air from -10 to 0 km. with separated air from 0 → + 26 km. would give the following ratios (the experimental values are shown in brackets) :

<u>He/N_2 : 1.45 (1.44)</u>, <u>Ne/N_2 : 1.09</u> (1.08), <u>A/N_2 : 0.93</u> (0.93)

The difficulty here, however, is what to do about B-8 and B-9, whose height of opening above that of B-6 is known. It is pretty well impossible to assign any mixture of mixed and unmixed air to these two samples on the basis of what is assumed for B-6.

The last attempts made then were to assign an opening height of B-6 in relation to z_o, the boundary height, and presume that the sample obtained was an average for the height in which the bottle had remained open. B-6 should then represent the average for (z) -- (z + 2.8) km, B-8 the average for (z+2.8) -- (z+5.4) and B-9 the average for (z+5.4) - (z+7.6). The values obtained for various heights and temperatures are shown in the table to be nowehere near the values obtained experimentally, and this method was finally abandoned with the conclusion that the results did not fit any simple theory of gravitational separation.

TABLE 6.

T = 280° K.

1st Bottle opened at Z_0 + x km.	He.	Ne.	A.	
x - 4 km.	2.90	1.43	0.588	B9
	2.28	1.32	.663	B8
	1.72	1.20	.765	B6
x - 3 km.	2.63	1.39	.615	B9
	2.06	1.27	.700	B8
	1.55	1.15	.804	B6
x - 2 km.	2.38	1.34	.65	B9
	1.87	1.23	.70	B8
	1.41	1.12	.80	B6
			T = 220° K.	
x - 1.5 km.	2.83	1.41	.60	B9
	2.02	1.26	.71	B8
	1.37	1.11	.86	B6
x - 0.4 km.	2.61	1.37	.63	B9
	1.85	1.23	.74	B8
	1.21	1.07	.90	B6
			T = 150° K.	
x - 0 km.	3.32	1.45	.56	B9
	2.08	1.30	.68	B8
	1.31	1.11	.92	B6
			T = 150° K.	
x - 0.6 km.	2.96	1.44	.59	B9
	1.96	1.27	.74	B8
	1.19	1.07	.96	B6

By the time the other samples had been analysed, however, there was available a treatment of the case of partial separation of the gases in the atmosphere of H.Lettau (38), whose theories are the basis for the following discussions.

4. Theory.

(b) The Theory of Partial Separation of Gases in the Atmosphere.

(i) General.

Previous calculations (56, 57, 58), have been based on the assumption that the atmosphere existed in one or other of two well-defined states; the first being a state of complete mixing caused by strong vertical movements in the atmosphere, whilst the second state implied the total absence of vertical movements on other than a molecular scale. In the first state (which certainly appears to obtain in the troposphere and lower stratosphere) no change in composition is to be expected with height. The second state will allow an approach to a gravitational-diffusion equilibrium in which the several components of the atmosphere will distribute themselves in accordance with the barometric formula (1); composition is consequently no longer independent of altitude.

These gravitational and diffusional forces will, of course, operate under all conditions, but it is clear that it may be necessary to consider also the situation where they are supplemented by macroscopic vertical movements which, although insufficient to ensure complete mixing, are large ~~enought~~ enough to disturb the equilibrium distribution predicted by the barometric formula. This intermediate case leads to a partial separation of the constituents of the atmosphere. It is also of interest to consider the influence of 'sources' and 'sinks' on the resulting distribution. This is necessary on account of the steady flow of helium through the atmosphere - radio-active substances acting as the "source" and outer space, into which it is possible for helium to escape from the upper reaches of the atmosphere, serving as a 'sink'.

(ii) General theory of Eddy Diffusion.

[A complete list of the symbols employed in this section will be found at the end of the chapter.]

Before proceeding to derive the expressions relating to this intermediate state, it is useful to consider briefly the concept of turbulence, and to find some parameter which can be used as a quantitative measure of the effects associated with it.

Large scale air movements take place broadly in a horizontal plane, but the flow is in general turbulent rather than laminar. The small "eddies" which results from this turbulence will give rise to mixing in a vertical direction on a scale much larger than the molecular scale on which 'ordinary' diffusion occurs, but still on a scale small compared to global distances. (59,(60),(61),(62). The effects of this 'eddy diffusion' are thus in many ways analogous to those of molecular diffusion, the differences arising from the larger masses of material which are transported, and the much larger distances covered by a single 'step' in the transport process; in the lower parts of the atmosphere these differences in magnitude are substantial, and eddy diffusion may be as much as 10^6 times as effective as ordinary diffusion in causing mixing. As the pressure decreases, however, ordinary diffusion becomes more important and we may expect an ultimate approach to the idealised Dalton atmosphere at very high altitude.

Provided sufficient time of contact is available, the masses of air transported by the eddy diffusion process will be able to effect an equalisation or exchange of properties ("Austausch") and it is clear that the same co-efficient will be relevant to the calculation of the transport of any property associated with the pockets of air which are exchanged. This concept has proved to be of great value in modern meteorology, and can be applied for example to the distribution in the atmosphere of dust particles, heat content, moisture content, or any other property which can be expressed in terms of the mass of air involved.

Consider a horizontal area f across which, in a time t, masses of air M; are being transported from a mean distance $\bar{\ell}$, measured from this boundary. Then if s represents some property of the air, expressed per unit mass of air (e.g. dust content /g. air, moisture content /g.air, etc.), then it can be shown that (59) the net flux of this property per unit area and unit time across this boundary is given by :

$$\underline{S(s) = -\frac{1}{f.t} \cdot \frac{\partial s}{\partial z}\,\bar{\ell}\sum M} \qquad - (2)$$

If we put $\underline{\frac{\bar{\ell}\sum M}{f.t.} = A}$. we get $\underline{\underline{S(s) = -A\frac{\partial s}{\partial z}}} \quad -(3)$

where A is the "Austausch" "Coefficient", and has dimensions g/cm.sec. A more exact analogy with ordinary diffusion is obtained if we replace the property s per unit mass of air by the corresponding property per unit volume. Then :

$$S\,(s) = -\frac{A}{\rho}\cdot\frac{\partial \bar{s}_v}{\partial z} = -D\cdot\frac{\partial s_v}{\partial z} \qquad -\ (4)$$

Where $D = A/\rho = \bar{l}\,\frac{\sum v}{f.t.}$ - (5)

D is the "coefficient" of eddy diffusion, with dimensions cm^2/sec.

It may be noted that the coefficient of ordinary diffusion is proportional to the product of molecular mean free path l_d, and molecular velocity w_d, whilst the coefficient of eddy diffusion is proportional to the product of the turbulent mixing path, $\bar{l}_D$ and the mean turbulent mixing velocity $W_D = \frac{\sum v}{f.t.}$

W_d and l_d are of course unique functions of the pressure temperature and composition of the region of the atmosphere considered. l_D and W_D on the other hand, depend on a variety of less well defined conditions; weather, season, latitude, as well as altitude (62). D has been estimated to have a maximum value of about 10^8 cm^2/sec. We are not, however, concerned with regions of very large D (where the mixing will be virtually complete) but rather with those regions where $D \approx d_{f.}$.

It is convenient to define also a'separation factor ' Q.

$$Q = \frac{d}{d + D} = \frac{d\rho}{d\rho + A} \qquad -\ (6).$$

which is more useful than the ratio d/D which could also be used as a measure of the general state of mixing at any point in the atmosphere.

Since d and D are both positive quantities, it is clear that $0 \leq Q \leq 1$

The two limiting cases are apparent; when $Q = 1$, $D = 0$, and the Dalton atmosphere, with maximum separation, results. When $Q = 0$, $D \rightarrow \infty$, and complete mixing is to be expected. The intermediate case, with $0 < Q < 1$ describes the state of partial separation which we will now discuss.

(iii) Gaseous Flow.

We shall restrict consideration to an isothermal atmosphere, with uniform gravitational field, and an assumed absence of horizontal variations in properties. Our interest centres upon three gases, He, Ne and A, which are present in such small amounts at least up to the heights so far investigated, that we can safely neglect their influence on the bulk properties of the atmosphere, especially on the density. Further, it would appear reasonable to regard the bulk properties of the atmosphere in which we are interested as being those of a pure nitrogen atmosphere with the same pressure and distribution. These simplifying assumptions resolve an impossibly complex multi-component system into three separate two-component problems.

By a simple hydrostatic argument, one can show that

$$\rho = \rho_0 e^{-z/H} \qquad - \qquad (7)$$

where H, the scale height $= \left(RT / m.g \right)$

The net flux of molecules of type s crossing a horiztontal unit area can be regarded as the resultant of several component fluxes:

$$S = S_G + S_D + S_A + S_0 + S_L \qquad - (8)$$

The ionisation flow, S_L, arises from the interaction between ionised gases and electric and magnetic fields in the upper atmosphere, and can only be of significance above the highest levels with which we are concerned. We shall therefore put $S_L = 0$ throughout.

The basic flow, S_0, may be of importance, as mentioned before, in a case where there is a steady transport of gas through the region considered.

Gravitational flow, S_G, is always present, and is given by:

$$S_G = n_s \cdot u_s = - n_s \cdot m_s \cdot g \cdot B_s \cdot \text{ mol/cm}^2\text{/sec} \qquad - (9)$$

Where B_s is the mobility factor for gas s in air, and represents the drift velocity under unit impressed force.

Molecular flow, S_D, acts in such a way as to tend to reduce concentration gradients:

$$S_D = - d_s \cdot \frac{\partial n_s}{\partial z} \text{ mol./cm}^2\text{sec.} \qquad - \qquad (10)$$

The flow due to turbulence can be expressed:

$$S_A = - A \, {}^{\partial s}\!/_{\partial z} \text{ mol/cm}^2\text{sec.} \qquad - \qquad (11)$$

$$\underline{S_A = -A\cdot\frac{\partial(n_s/\rho)}{\partial z}} \tag{12}$$

$$S_A = -A\left\{\frac{1}{\rho}\cdot\frac{\partial n_s}{\partial z} + n_s\cdot\frac{\partial(1/\rho)}{\partial z}\right\}$$

$$\underline{S_A = -\frac{A}{\rho}\left\{\frac{\partial n_s}{\partial z} + \frac{n_s}{H}\right\}} \tag{13}$$

Since $\rho = \rho_0\cdot e^{-z/H}$

(iv). StationaryStates For Permanent Gases.

For a quiet atmosphere , S = 0 ,and we have the case of pure gravitational-diffusinal equilibrium,where:

$$\underline{S_G = -S_D} \tag{14}$$

We then have:

$$n_s\cdot u_s = d_s\cdot\frac{\partial n_s}{\partial z} \tag{15}$$

From the hydrostatic argument, $n_s = n_{s_0}\cdot e^{-\frac{m_s g z}{RT}}$

so that: $\frac{\partial n_s}{\partial z} = -n_s\cdot\left(\frac{m_s\cdot g}{R\cdot T}\right)$

and $$\underline{u_s = \frac{n_s d_s m_s g}{RT}} \tag{16}$$

Putting $\underline{p_s = \frac{m_s - m}{m}}$,we have

$$\frac{m_s g}{RT} = \frac{(p_s+1)}{H} \tag{17}$$

Thus : $$u_s = -\frac{d_s(p_s+1)}{H} \tag{18}$$

And $$\underline{S_G = -\frac{n_s d_s(p_s+1)}{H}} \tag{19}$$

This downward flow, S_G, due to gravity, is balanced at equilibrium by an equal but opposite flow S_D, arising from molecular diffusion.

In table 7. are listed, for each of the relevant atmospheric gases, the molecular weights, m_s; the relative mass differences p_s; the molecular diameter, σ_s, in units of 10^{-8} cm; the mean molecular velocities $\bar{C}_s$ in 10^5 cm/sec; d_s in cm^2/sec. at N.T.P.; K_s (= $^{ds}/d$); and finally $(d_s\rho)$ in 10^{-3} g/cm.sec. (ρ for air at N.T.P. = 1.29 x 10^{-3} g (cm^3). Values for σ_s, and $\bar{C}_s$ are taken from Jeans; Kinetic Theory of Gases (63).

TABLE 7.

Gas	m_s	Ps	σ_s	$\bar{C}_s$	d_s	k_s	$(d_s\rho)$.
H_2	2.015	-0.93	2.72	17.0	0.664	3.71	0.857
He	4.00	-0.86	2.18	12.0	0.580	3.24	0.748
Ne	20.2	-0.31	2.60	5.38	0.275	1.54	0.355
N_2	28.02	0.00	.3.78	4.54	0.178	1.00	0.230
O_2	32	0.105	3.62	4.25	0.180	1.02	0.232
A	39.9	0.38	3.66	3.80	0.169	0.944	0.280.

When the contribution of eddy diffusion to the mixing process cannot be neglected, a further term must be added:

$$S_G + S_D + S_A = 0.$$

i.e.

$$-\frac{n_s d_s(\beta_s+1)}{H} - d_s\frac{\partial n_s}{\partial z} - D\left\{\frac{\partial n_s}{\partial z}+\frac{n_s}{H}\right\} = 0 \tag{20}$$

$$\frac{\partial n_s}{\partial z} = \frac{n_s}{H}\left\{\frac{d_s\beta_s}{(d_s+D)} + 1\right\} \tag{21}$$

Writing $Q_s = \frac{d_s}{d_s+D}$, we have $\frac{\partial n_s}{n_s} = -\frac{1}{H}(Q_s\beta_s+1)\,dz$ (22)

Integrating, and introducing a boundary condition, we have

$$\ln\left(n_s/n_s\right) = -\frac{\beta_s}{H}\int_0^z Q_s\,dz - \frac{z}{H} \tag{23}$$

Since $\ln\alpha_s = \ln\left(n_s/n_{s_0}\right) - \ln\left(n/n_0\right)$, and $\ln\left(n/n_0\right) = \frac{z}{H}$

we can write: $\ln\alpha_s = -\frac{\beta}{H}\int_0^z Q_s\,dz$ (24)

or, introducing: $\bar{Q}_s = \frac{1}{z}\int_0^z Q_s\,dz$ (25)

$$\alpha_s = -\frac{\beta\bar{Q}_s z}{H} \tag{26}$$

If α_s is not too different from unity, we find:

$$\alpha_s \approx 1 - \frac{\beta\bar{Q}_s z}{H} \tag{27}$$

Q_s is of course, a function of height, through the height-dependence of A.

$$Q_s = \frac{d_s\rho}{d_s\rho + A}$$

In general, one has no prior knowledge of A as a function of z, and it is therefore convenient to write Q_s as a Taylor series:

$$Q_s(z) = Q_s\left(\frac{z-z_0}{H}\right) = Q_{s_0} + Q_s'\frac{(z-z_0)}{H} + \frac{Q_s''}{2}\left(\frac{z-z_0}{H}\right)^2 + \cdots \tag{28}$$

We can choose z_0 as the height at which Q_s departs sensibly from its zero value. Then $Q_{s_0}=0$, and $Q_s(z)$ is defined only for z z_0. H is introduced in order to obtain dimensionless coefficients. From (24) and (28), we have:

$$\ln\alpha_s = -\beta_s\left\{Q_{s_0}\left(\frac{z-z_0}{H}\right) + \frac{Q_s'}{2}\left(\frac{z-z_0}{H}\right)^2 + \frac{Q_s''}{2\cdot 3}\left(\frac{z-z_0}{H}\right)^3 + \cdots\right\} \tag{29}$$

Q_{s_0}, however, is zero, and to a first approximation, terms in z of powers above the second can be neglected. Then:

$$\ln\alpha_s \approx -\frac{\beta_s Q_s'}{2}\left(\frac{z-z_0}{H}\right)^2 \tag{30}$$

or
$$-\frac{1}{\beta_s}\ln\alpha_s = \frac{Q_s'}{2}\left(\frac{z-z_0}{H}\right)^2 \tag{31}$$

With this approximation, it follows that:

$$A = (d_s\rho)\left[\frac{H}{Q_s'(z-z_0)} - 1\right] \tag{32}$$

or
$$D = d_s\left[\frac{H}{Q_s'(z-z_0)} - 1\right] \tag{33}$$

As remarked earlier, the value of D (or A) is essentially a property of the local circumstances at the particular point in the atmosphere being considered, and is influenced very little if at all by the nature of the transported property. (59,60). D should therefor be the same for all three gases considered, although Q_s (and hence Q_s') will vary through its dependence on d_s, which is, of course, a specific molecular property. It is convenient therefore to consider the "ordinary separation factor"

$Q = {}^{d}/(d+D)$ analogous to the "special separation factor", for the gas s.

$Q_s = {}^{d_s}/(d_s + D)$. These are simply related:

$$Q = \frac{Q_s}{[k_s + Q_s\,(1 - k_s)]} \qquad - \qquad (34)$$

or, for small values of Q_s,

$$Q \approx {}^{Q_s}/_{k_s}. \qquad - \qquad (35)$$

where $k_s = {}^{d_s}/_{d}.$

Equations (26) and (34) enable us to see readily the comparative sensitivity of the various constituents of the atmosphere as indicators of the degree of separation. Taking the ozygen/nitrogen separation as a standard, we find :

$$P = (p_s\overline{Q}_s) \;/\; (p_s\overline{Q}_s)_{O_2}.$$

is a measure of how much more sensitive than oxygen a particular gas is as an indicator of separation. For small values of $\overline{Q}$,

$$P = (p_s k_s) \;/\; (p_s k_s)_{O_2}$$

and this quotient is shown, for a number of gases, in Table 8. It may be noted that this factor involves the diffusion coefficients as well as the masses of the molecules concerned, a fact which is often overlooked.

Comparative separabilities of various atmospheric gases.

TABLE 8.

Gas	k_s	p_s	$p_s k_s$	$(p_s k_s)/(p_s k_s)_{O_2}$
H_2	3.71	-0.93	-3.45	(-) 32.5
He H	3.24	-0.86	-2.78	(-) 26.0
Ne	1.54	-0.31	-0.483	(-) 4.6
O_2	1.02	0.105	0.107	1.00
A	0.94	0.38	0.357	3.4

(v) Stationary States For Gases with Basic Flow.

Aterm S_0 must now be included in the equqtiom of continuity, which will now read, for a steady state:

$$S = S_G + S_D + S_A + S_0 = 0 \tag{36}$$

$$-\frac{n_s d_s (p_s + D)}{H} - d_s \cdot \frac{\partial n_s}{\partial z} - D\left\{\frac{\partial n_s}{\partial z} + \frac{n_s}{H}\right\} + S_0 = 0 \tag{37}$$

It is more convenient to work in terms of : $\nu_s \left(= n_s/n\right)$

so that $n_s = n \cdot \nu_s$

and $\frac{\partial n_s}{\partial z} = \frac{\partial}{\partial z}(n \cdot \nu_s) = n \cdot \frac{\partial \nu_s}{\partial z} - \nu_s \cdot \frac{n}{H}$ (38)

Then:

$$\frac{\nu_s n \cdot d_s \cdot p_s}{H} - (d_s + D) n \cdot \frac{\partial \nu_s}{\partial z} + S_0 = 0 \tag{39}$$

Whence, integrating and introducing $\nu_s = \nu_{s_0}$ at $z=0$

$$\underline{\nu_s = \nu_{s_0}\left\{\exp\left(-\frac{p_s}{H}\int_0^z Q_s\,dz\right) - \frac{H S_0}{\nu_s p_s n d_s}\left[1-\exp\left(-\frac{p_s}{H}\int_0^z Q_s\,dz\right)\right]\right\}} \qquad (40)$$

$$\underline{\alpha_s} = \left(\frac{n_s/n_{s_0}}{n/n_0}\right) = \frac{\nu_s}{\nu_{s_0}} = \underline{\exp\left(-\frac{p_s}{H}\int_0^z Q_s\,dz\right)\left\{1+\frac{HS_0}{\nu_s p_s n d_s}\left[1-\exp\left(-\frac{p_s}{H}\int_0^z Q_s\,dz\right)\right]\right\}} \qquad (41)$$

When $\underline{S_0=0,\ \alpha=\alpha_p = \exp\left(\frac{p_s}{H}\int_0^z Q_s\,dz\right)}$ (cf.eq.^{n}.(24),where

α_p is the separation expected for a permanent gas with no basic flow.When the expression in brackets is not too different from unity,we can write:

$$\ln\alpha = \ln\alpha_p + \ln\left\{1+\frac{HS_0}{\nu_s p_s n d_s}\left[1-\exp\left(\frac{p_s}{H}\int_0^z Q_s\,dz\right)\right]\right\}.$$

$$\underline{-\frac{p_s}{H}\int_0^z q_s\,dz = -\frac{p_s}{H}\int_0^z Q_s\,dz - \frac{HS_0}{\nu_s p_s n d_s}\cdot\frac{p_s}{H}\int_0^z Q_s\,dz} \qquad (42)$$

Whence $\underline{\int_0^z q_s\,dz = \left\{1+\frac{HS_0}{\nu_s p_s n d_s}\right\}\int_0^z Q_s\,dz}$ (43)

and since $\left\{1+\frac{HS_0}{\nu_s p_s n d_s}\right\}$ is independent of z,

$$\underline{q_s = Q_s\left\{1+\frac{HS_0}{\nu_s p_s n d_s}\right\}} \qquad (44)$$

q_s defined by (42),is the "apparent separation factor".

From (44), we see that:

$$S_0 = \left[\frac{q_s - Q_s}{Q_s}\right] \cdot \frac{\nu_{s_0} \cdot \beta_s \cdot nd_s}{H}$$

or, in terms of the ordinary separation factors q,Q,

$$S_0 = \left[\frac{q - Q}{Q}\right] \cdot \frac{\nu_{s_0} \cdot \beta_s \cdot nd_s}{H} \qquad - \qquad (45).$$

It is thus possible to inter-relate the basic flow, So, and the relative extent to which the apparent separation factor, q, differs from the separation factor Q, for a permanent gas.

It may be noted that when $\left(HS_0 / \nu_{s_0} \cdot \beta_s \cdot nd_s\right) = 1, \alpha$ is identically unity at all heights. This critical source strength, at which the basic flow just balances the gravitational flow, can be calculated for H_2 and for He (the only atmospheric gases for which there is a genuine basic flow) from the data given in Table 9 . It is clear that, given a sufficiently large basic flow, it is easily possible to achieve a situation where the lighter gases do not become the major constituents at any altitude. A similar cancellation of the gravitational flow can be effected by ionisation flow, although as pointed out earlier, this does not become significant until one reaches altitudes much greater than those studied in the present work. For positive values of S_0 (that is, upward flow) we see from (44), that $q_s < Q_0$ for gases lighter than air, and $q_s > Q_s$ for gases heavier than air.

TABLE 9.

Calculation of critical values of basic flow for H_2 and for He.

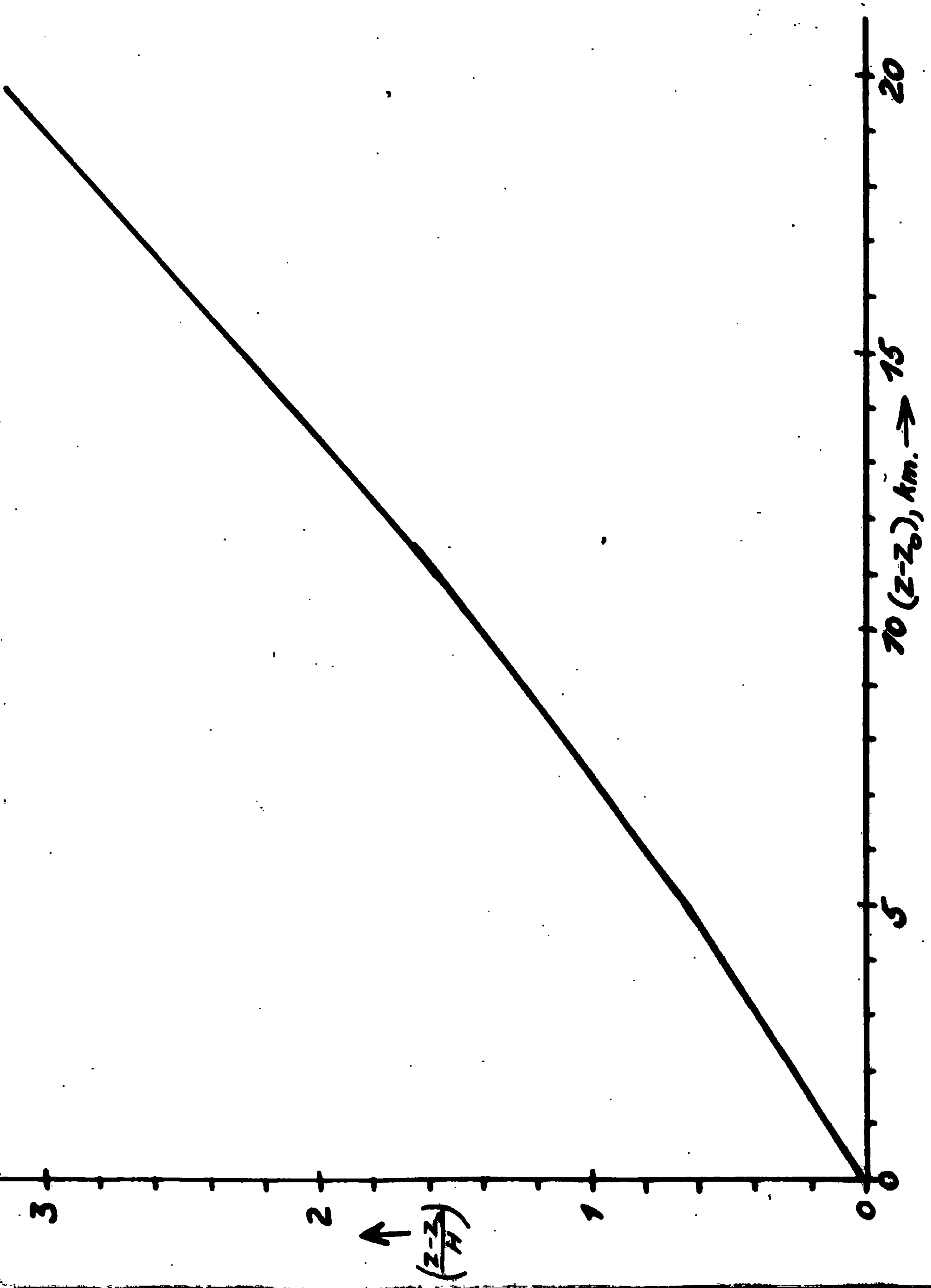
	H_2	He	
n_0 at N.T.P.	13.5×10^{12}	14.2×10^{13}	mol/cm^3
d_s	0.664	0.580	cm^2/sec.
p_s	-0.93	-0.86	
ν_{s_0}	5×10^{-7}	5.24×10^{-6}	
So critical	1.1×10^{-7}	9.5×10^{-7}	mol/cm^2/sec.
(S_0/n_0)"	2	17	m^3/earth's surface/ sec

The significance of these results will be discussed later.

5. Calculations.

Of the samples with a composition different from ground level air, only the first seven have been used in these calculations; that is, the theory has only be applied between 55 and 71 km. Two samples were available from greater heights, but these were excluded since the rate of change of composition appears to fall off rather sharply above 71 km. This may be due to an increase in turbulence in the 70-80 km region, but may, on the other hand, simply reflect the greater experimental errors resulting from the extremely small quantities of air available (2.5 mm^3 NTP from C.3)

Fig. 14



For each of the seven samples, the value of $-1/p_s \ln \alpha_s$ s has been calculated from the values of α_s quoted in Table 2 of Section 3. The respective mean heights of these samples have been reduced to the dimensionless form $(\frac{z-zo}{H})$ using $z_o = 55$ km. this height being chosen as a suitable datum level according to Fig.13. The scale height H was taken from the compilation by the Rocket Panel (67) (see Figure 14). The neon value for C-5 has been disregarded on account of a suspected contamination with hydrogen.

TABLE 10.

	He.		Ne.		A.		$\frac{z-zo}{H}$.
	α_s	$-1/\beta \ln \alpha_s$	α_s	$-1/\beta \ln \alpha_s$	α_s	$-1/\beta \ln \alpha_s$	
B-13	1.000	0.000	1.005	0.016	1.000	0.000	0.244
B-15	1.035	0.041	1.008	0.026	0.996	0.011	0.565
C-11-B	1.133	0.135	1.040	0.126	0.962	0.103	0.765
B-6	1.44	0.424	1.080	0.248	0.93	0.192	1.495
C-5	1.57	0.523	(1.23)	(0.668)	0.90	0.276	1.865
B-8	2.02	0.816	1.18	0.536	0.89	0.308	1.988
B-9	2.41	1.022	1.20	0.587	0.85	0.428	2.415

The results for each of the three gases were then fitted to equations of the type

$$Y = A + Bx^2$$

by the method of least squares. The constant A was introduced to allow for any uncertainty in Zo.

The equations obtained were:-

Fig. 15

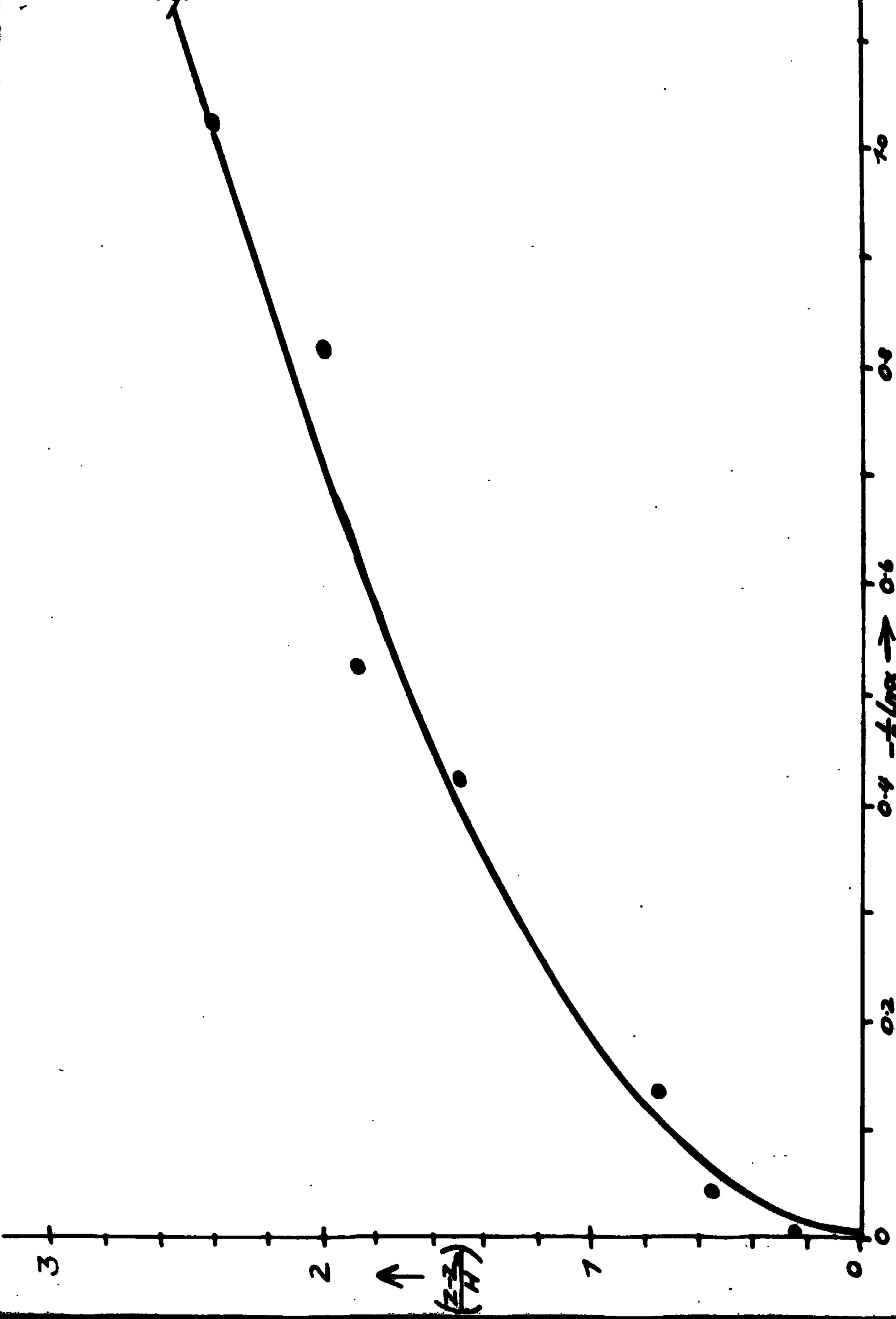


Fig. 16

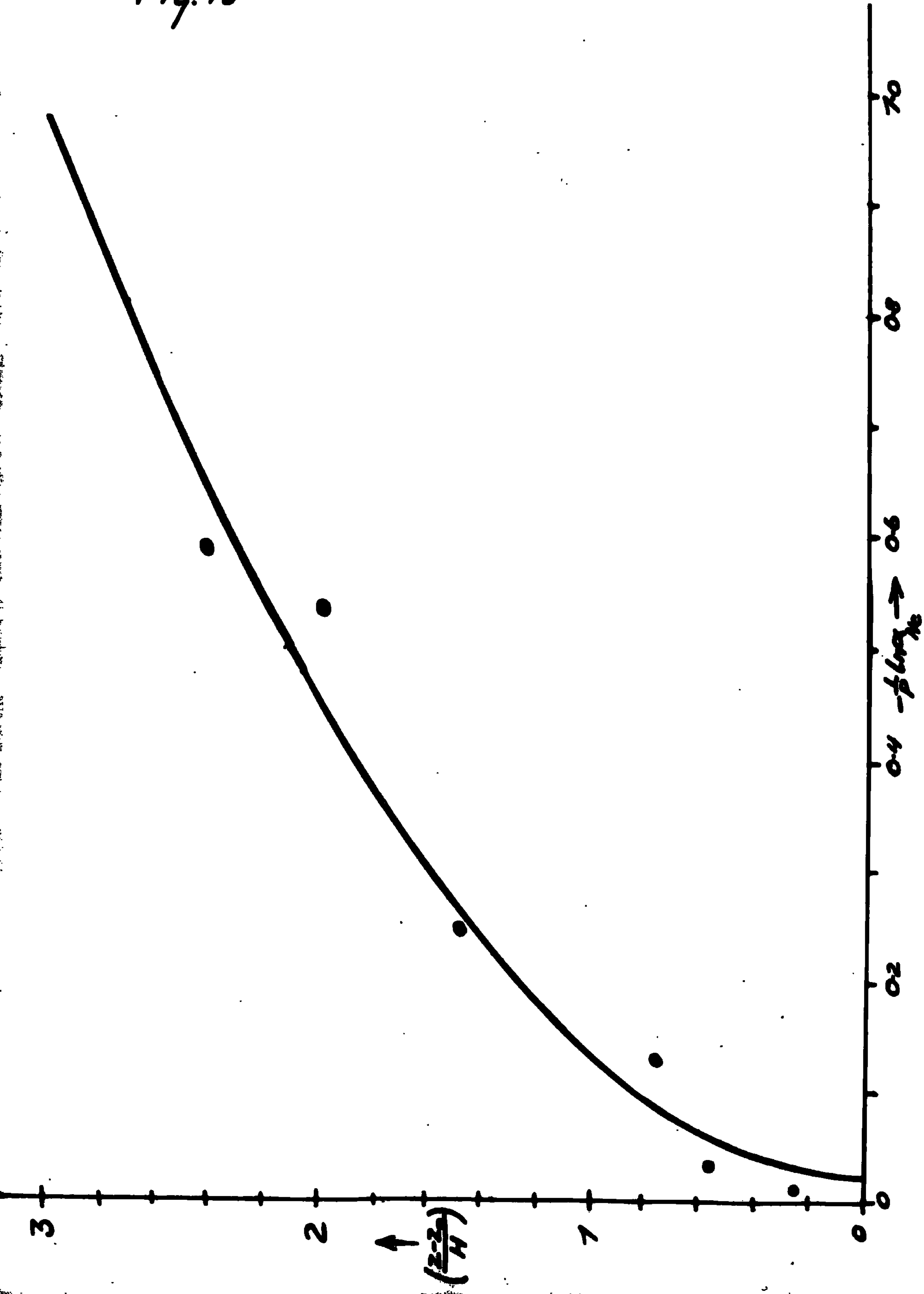
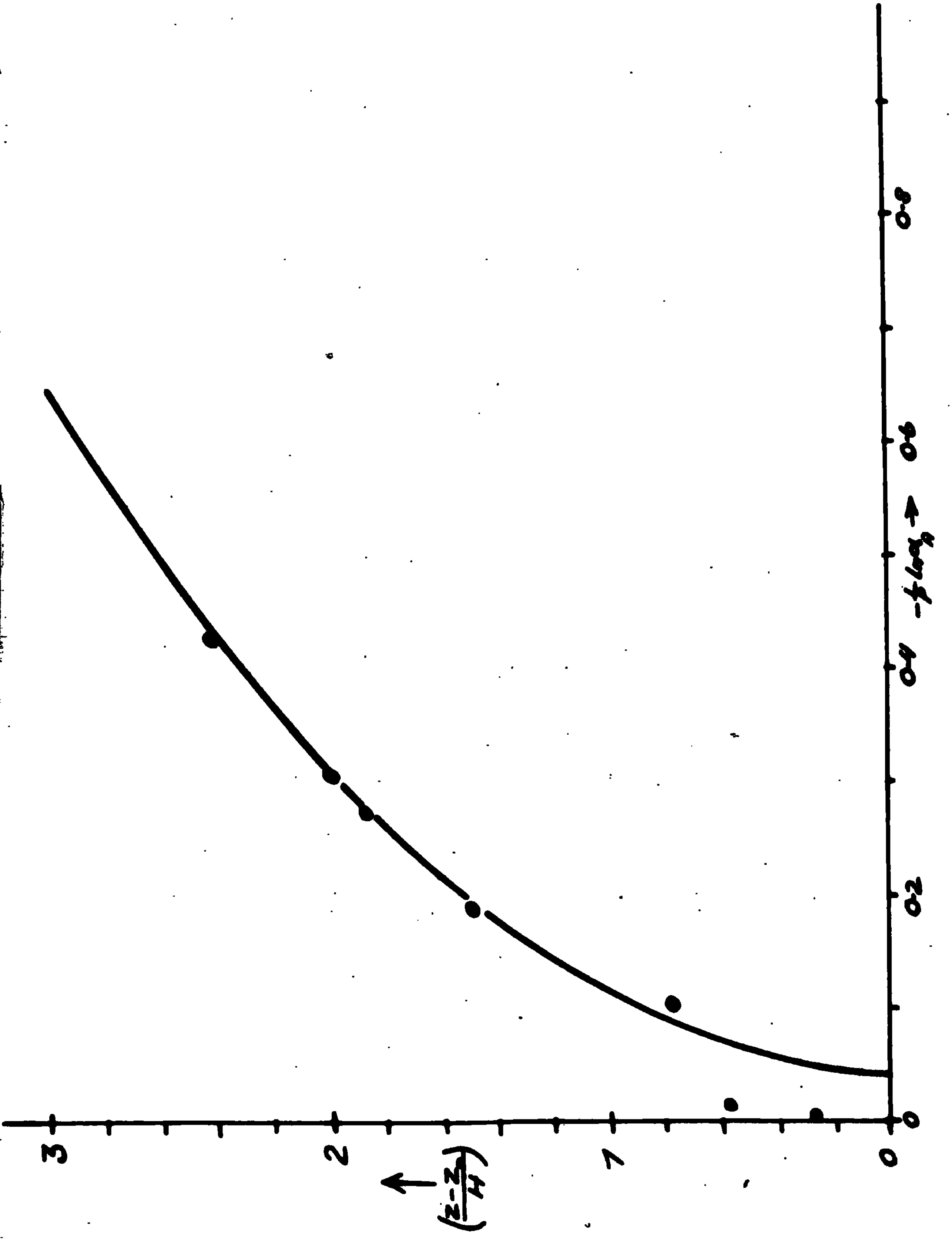


Fig. 17



Helium: $-{}^{1}/_{p_s} \ln \alpha_s = 0.010 + 0.175 \left(\frac{z-zo}{H}\right)^2$

Neon: $-{}^{1}/_{p_s} \ln \alpha_s = 0.026 + 0.106 \left(\frac{z-zo}{H}\right)^2$

Argon: $-{}^{1}/_{p_s} \ln \alpha_s = 0.046 + 0.067 \left(\frac{z-zo}{H}\right)^2$

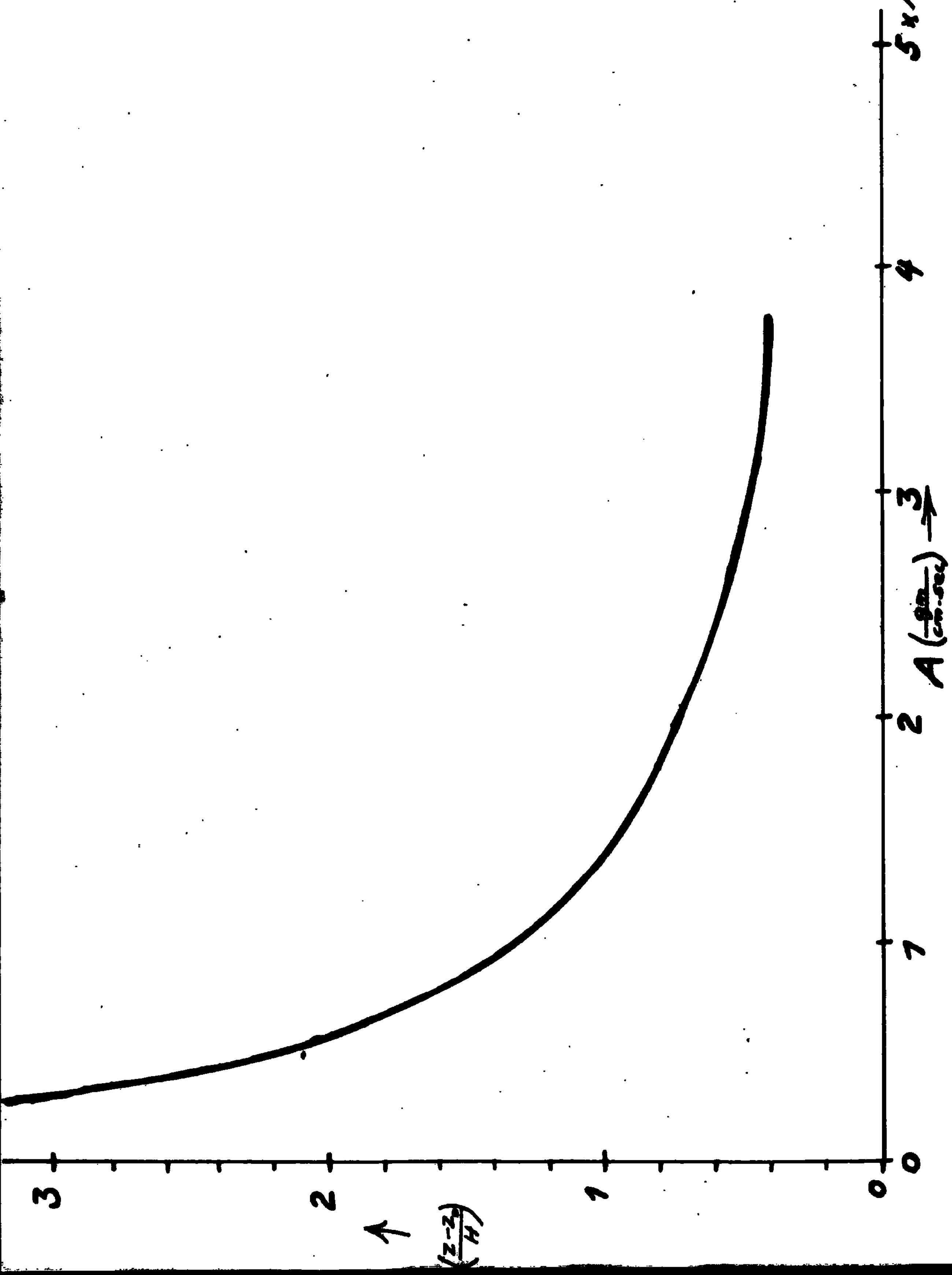
Curves drawn with these coefficients are drawn in Figures 15, 16 and 17, with the corresponding experimental points superimposed.

According to equation (31) $-1/_{p_s} \ln \alpha_s = \frac{Q_s'}{2} \left(\frac{z-zo}{H}\right)^2$, and we can therefore identify the co-efficients of $\left(\frac{z-zo}{H}\right)$ with the corresponding Q_s' values. Using equation (35) to relate Q_s' and Q', we obtain the following data:

	Q_s'.	Ks.	Q'.
He	0.350	3.24	0.108
Ne	0.212	1.54	0.138
A	0.134	0.94	0.142.

For neon, which has no basic flow, and for garon, whose basic flow is negligible, the values of Q' are in good agreement. Helium, on the other hand, which is produced in large amounts by radioactive decay of materials in the earth's crust, and which is certainly subject to loss from the upper atmosphere into outer space, yield a value of q' which is significantly lower, as is to be expected for a gas with appreciable basic flow. Applying equation (45) we can deduce the magnitude of this basic flow:

Fig. 18



$\left(\frac{z-z_0}{H}\right)$ ↑
0
1
2
3
$A\left(\frac{gm}{cm\text{-}sec}\right)$ →
0
1
2
3
4
5×10^{-3}

$$\left(S_o/n_o\right) = \left(\frac{0.140 - 0.108}{0.140}\right) \times 17 \text{ m}^3/\text{sec.}$$

$$\left(S_o/n_o\right) = 3.9 \text{ m}^3/\text{sec (from the whole globe).}$$

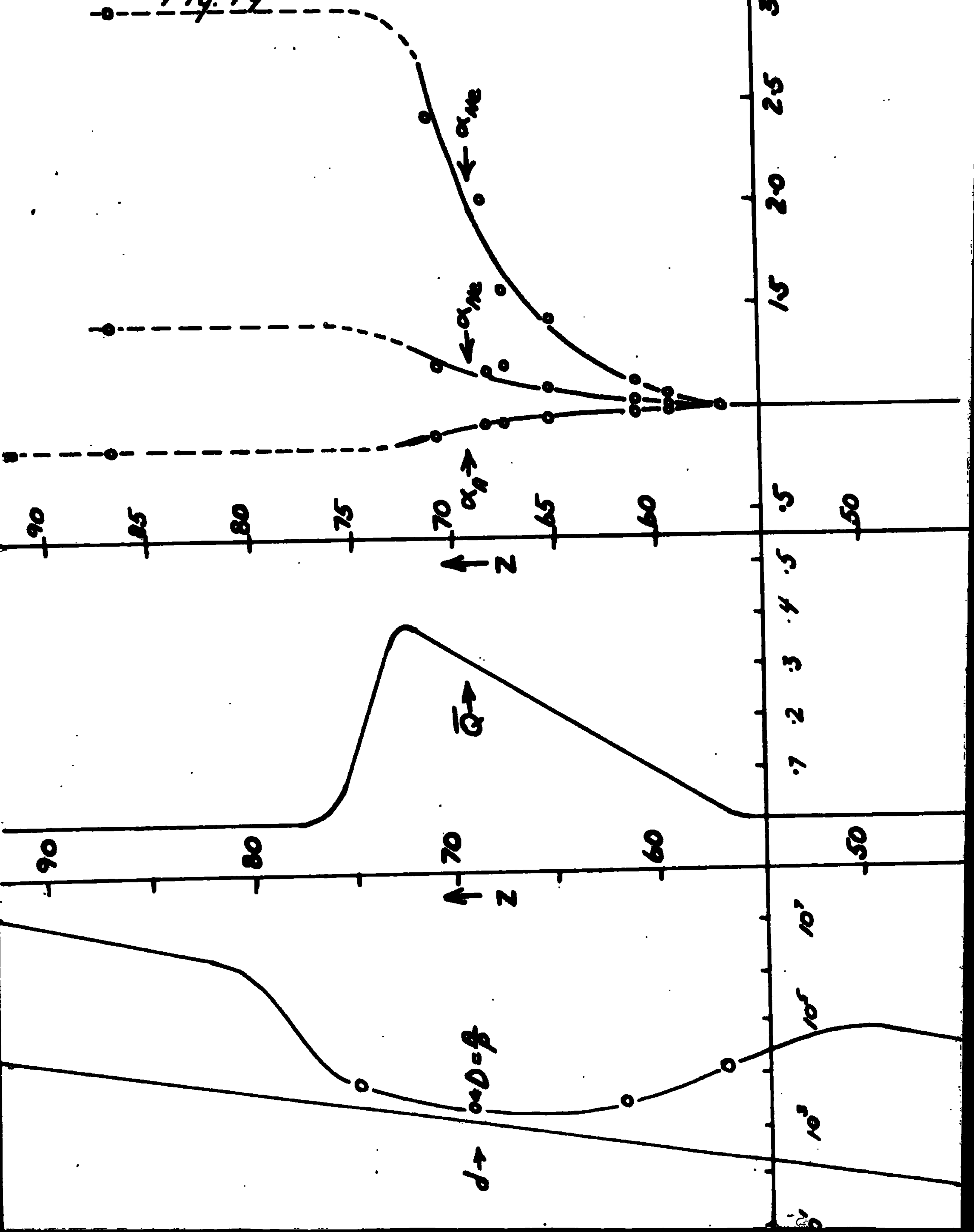
It is difficult to obtain an accurate estimate of the total rate of production of helium. It has been estimated by Rogers (66) to lie between 0.25 and 1.0 m^3/sec and by Gutenberg (58) at 10 m^3/sec. These figures are roughly confirmed by a calculation based on the averahe uranium and thorium contents of the earth's crust (4×10^{-6} % and 13×10^{-6} % respectively) (65). Taking the mass of the earth's crust as 4.7×10^{25} g, this yields a rate of helium production of 1.3 m^3/sec. The value deduced above is seen to lie within the range of these estimates.

The current rate of addition of argon by radioactive decay of ^{40}K is negligible compared to the argon content of the atmosphere. In any case, the basic flow treatment cannot be applied in an unmodified form, since the gravitational forces acting on an argon atom are sufficiently effective to prevent its escape from the top of the atmosphere.

The values for the Austausch coefficient have also been calculated for $\left(\frac{z-z_0}{H}\right) = 0.2 - 3.0$ and the results are shown on the accompanying curve (Fig.18), using the average value of 0.140 for Q' and $(d\rho) = 0.231 \times 10^{-3}$ gm/cm sec.

From these values of A the coefficient of eddy viscosity was estimated, using the values for density adopted by the Rocket Panel (67). The result is shown graphically in Fig.19, together with values for d which increases exponentially with height. On the same

Fig. 19


3.0
2.5
2.0
1.5
.5
α_{He}
α_{He}
α_H
90
85
80
75
70
65
60
50
Z
.5
.4
.3
.2
.1
$\bar{Q}$
90
80
70
60
50
Z
10^7
10^5
10^3
$D = \frac{\rho}{\rho}$
d

curve is also shown Q and the theoretical curves for He, Ne and A calculated from the equations above. The points shown by circles are the experimental results from the present series of experiments. The dotted lines on Figure 19 indicate expected values assuming vertical circulation to increase materially from about 73 km. onwards. It can be seen from this that the results from C1 and C3 may not be inconsistent with the theory of eddy diffusion.

6. Discussion.

(a) General.

The results outlined above seem to point strongly to the conclusion that, in the region between 55 km. and 70 km. there is a marked reduction in the extent of turbulent mixing in the atmosphere, so marked in fact, that a significant state of partial gravitational-diffusional equilibrium exists. Below 55 km. our results indicate that effectively complete turbulent mixing occurs, whilst above about 70 km. it seems probable that the same state is found.

Lettau (38) (62) has based calculations on determinations of atmospheric oxygen by Regener (40) and deduced that a similar partial separation occurs between 14 and 27 km. Helium analyses by Glückauf and Paneth (37,31), do not show the corresponding variations in this region, and Lettau has used this information to prove that the basic flow of helium must approach the critical value. The present analyses for neon and argon (which are not subject to uncertainties arising from basic flow) show that this interpretation cannot be correct. At 55 km. both neon and argon are present in proportions which agree with the ground level values to within 1%. As mentioned before, the sampling and measurement of oxygen is a notoriously difficult and unreliable prodedure, and it now seems clear that Regener's results are not truly representative of the composition of the upper atmosphere.

One of the main objections that have been raised against the existence of a comparatively quiet layer of air between 50 and 80 kms. is the fact that the temperature gradient is negative in just this region, whereas it is positive both above 80 and below 50 kms. However, as long as the rate of decrease of temperature is less than that obtaining during adiabatic conditions the air masses are perfectly stable although not to the same extent as for a layer with increasing temperature. As the temperature decreases by about 2° per km. between 50 and 80 kms (67) it can be seen that, as this is much less than the adiabatic gradient, this cannot itself cause strong vertical movements in this region.

Physical evidence about vertical winds at high altitudes are rather scanty as most experimental methods are based on the assumption that the vertical components of the air movements are small (68). Weisner states that this is reasonable on theoretical grounds for most altitudes in the range between 30 and 80 kms (69) and then proceeds to calculate horizontal wind speeds from acoustic data obtained by exploding grenades at different heights. The thing worth noting about his results is perhaps the fact that he finds a maximum in the wind speed at about 50 kms. in every instance after which there seems to be a gradual decrease to about 70 kms. after which the horizontal wind speed tends to increase again.

More substantial evidence is available in the conclusions drawn by Liller and Whipple, from their investigations into high altitude winds by meteor train photography (70). They found the winds changed rapidly with altitude, having a maximum shear of 50 m/sec. per km. on average and suggested that about half the available kinetic energy of the high altitude winds is contained in large scale systematic motions, the other half in small horizontal eddies of the order of 50 kms. in diameter and a vertical turbulence of a few kms. Turbulence elements as small as 1 km. they state, are just possible over the range of altitudes covered by their observations, 80 - 130 kms. This last piece of evidence, therefore, although it may not actively support any assumption about a partially separated atmosphere between 55 and 70 kms. does not disprove it either when considered together with Weisner's results More data on the subject are needed, however, before any further conclusions can be drawn.

One objection to the state of partial separation, however, is rather serious, namely the time it would take for a fully mixed atmosphere to change into one which is partially separated. This time is quite considerable for heights below 10^{0} kms. according to the calculations of Lettau on the basis of the eddy-diffusion theory. Table 12 gives some of the results taken from his graph (62) of the height variation of minimum values of the transition period Δt_s

for argon in two different cases of initial and final diffusion conditions. The two cases are: (a):from $\overline{Q} = 0$, (a fully mixed atmosphere) to $\overline{Q} = 1$, (a fully separated atmosphere); (b):from $\overline{Q} = 1$ to $\overline{Q} = \frac{1}{3}\cdot 10^{-5}$. The times needed in the case of helium and neon would of course be less (58,46).

For the sake of comparison, we give also the times calculated by Epstein (71) for 50% attainment of the equilibrium separation, starting from a fully mixed atmosphere.

T A B L E 12.

Ht. km.	Δt_s		
	$\overline{Q}=0$, $\overline{Q}=1$ (Lettau)	$\overline{Q}=1$, $\overline{Q}=1/3 \times 10^{-5}$ (Lettau)	50% separation (Epstein)
1	~ 10000 yrs.	~ 10 days	-
1o	~ 5×10^4 yrs.	~ 80 days	-
25	~ 10^4 yrs.	~ 30 days	-
50	~ 500 yrs.	~ 8 days	-
100	~ 1 yr.	~ 5 hours	6.4 years
120	~ 30 days.	~ 1 hour	180 days
150	~ 1 day	~ 5 mins.	7 days
200	~ 6 mins.	~ 10 secs.	12 mins.

It can be seen from this table that although it would take several years for the state of complete mixing to change into a state of maximum separation in the region under consideration, this time is probably not as long as previously assumed, and that the reverse process will also need some time. Whether a change can take place under these conditions may seem doubtful at the moment, but it is not possible to state anything for certain as yet until more data are available about the vertical circulation at these altitudes.

(b) Reliability of Sampling.

As previously mentioned, we have ruled out from the start any consideration of the oxygen content of our samples; the area of metal accessible to the gas in the sample bottles is more than is needed to absorb all the oxygen as a monolayer. In most of the samples, certainly very little oxygen was found. We have concentrated attention entirely on the noble gases and nitrogen. Chemical effects, which are not to be expected with nitrogen anyway, can be excluded by the fact that the deficiency of argon and surplus of neon correspond quite accurately; had any nitrogen been irreversibly adsorbed on to the surface of the steel bottle, this result could not have been achieved.

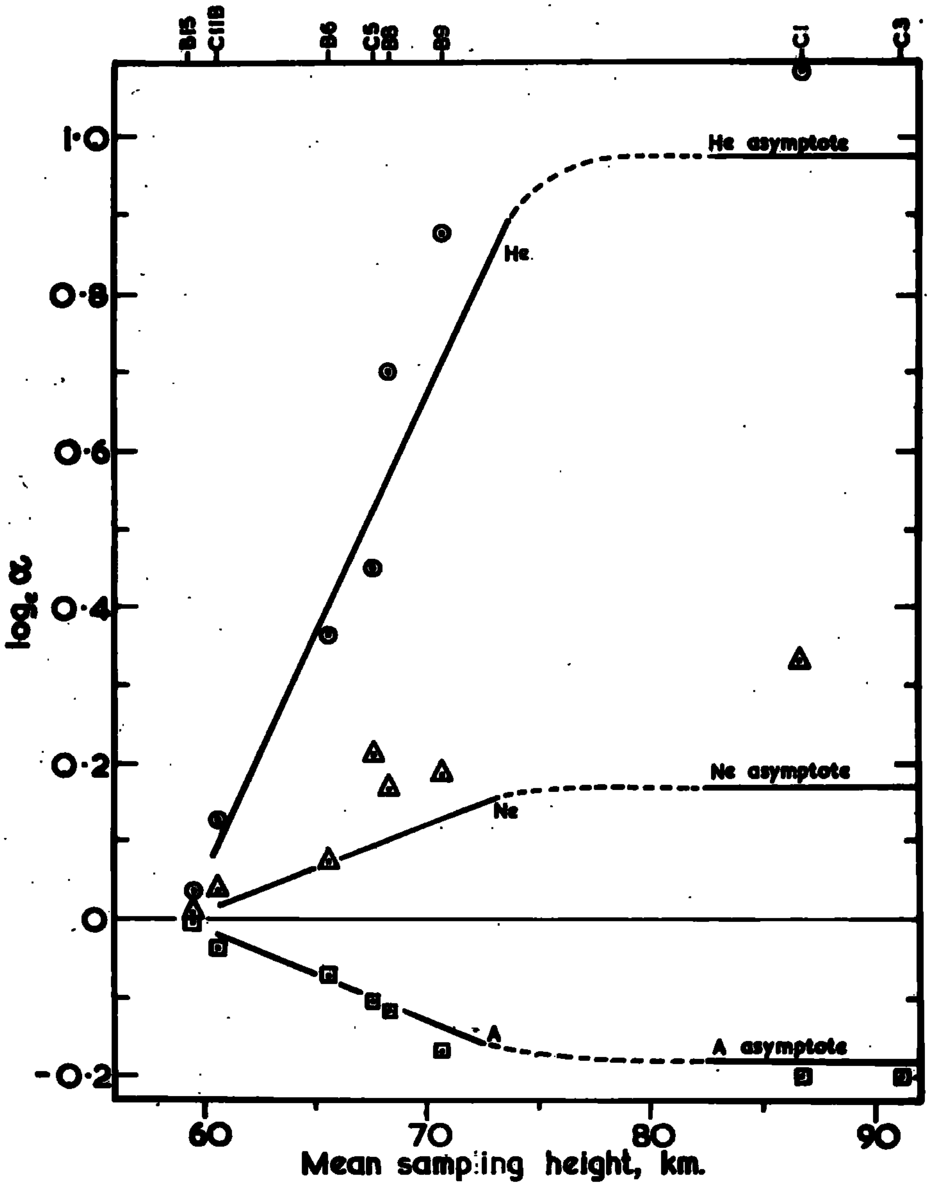
The other objection which has been raised against some previous work refers to the possibility of effusive separation by the inlet tube. In the present work, the diameter of this inlet tube was chosen so large (3 cm) to eliminate this possibility. It is disturbing, nevertheless, to find that the amounts of gas collected fall short of the quantities predicted from the known ambient pressures and rocket velocities. The relevant information is collected in Table 13. A consideration of these data has led Martin (45) to suggest the possibility that mass discrimination by

TABLE 13.

Pressures expected and actually observed in sample bottles from various altitudes. All pressures recorded in microns of mercury; ambient pressures taken from the smoothed curve given by the Rocket Panel (67).

Bottle Number.	Mean Mach Number.	Mean ram factor f	Ambient pressure at closing height. p_c	Ram pressure at closing height $p_c.f.$	Observed bottle pressure. p
B-13	1.54	3.57	321	1150	628
B-15	1.38	2.98	182	541	477
C-11-B	3.30	14.50	105	1522	37.1
B-6	1.77	4.54	72	327	38.5
C-5	3.20	13.67	38	519	18.9
B-8	1.73	4.36	48	209	20.2
B-9	1.49	3.37	36	121	21.6
C-1	2.64	9.48	2.2	21	1.4
C-3	2.36	7.67	1.2	9.2	0.3

Fig. 20



Experimental points: ⊙ helium; △ neon; ⊡ argon.
Theoretical lines deduced on the basis of Knudsen formula.

the inlet tube is present in spite of its large diameter. The results of his calculations are drawn in Figure 20, in which $\ln\alpha$ is plotted against height on the assumption that the increasing separation with height is due to the increasing importance of the "molecular flow" contribution to the passage of gas along the inlet tube.

The agreement between experiment and Martin's predictions is tolerable, but is not so good as that provided by the theory outlined in this thesis. Furthermore, Martin's suggestion implies the existence of some higherto unknown aerodynamic phenomenon which results in the effective 'choking' of the inlet tube at the high supersonic velocities which are involved. It is only fair to add that no experiments have yet been made to prove the existence or otherwise of such an effect.

At present, the balance of evidence seems to suggest that these separations are indeed genuine, although a definite conclusion should rest upon a decision between the two conflictory explanations; partial gravitational equilibrium, and mass-discrimination by the sampling system. A rocket flight which should provide such a decision is currently planned; it is intended to take three stratosphere samples at the peak of the rocket's trajectory. The three sample bottles will be opened simultaneously; one will be left open for a longer period than normal, and one will have a larger-than-normal sampling orifice. At the peak height, the rocket velocity will be definitely subsonic, and it is hoped in this way to demonstrate the existence of any discrimination by the inlet tube.

Unfortunately, the planning of such an experiment is a lengthy matter, and the results are not likely to be available for a considerable time.

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LIST OF SYMBOLS.

A	Austausch Coefficient ^{gm}/cm. sec.
B	Mobility Factor.
$\bar{C}$	Mean Molecular Velocity ^{cm}/sec.
D	Coefficient of Eddy Diffusion, cm^2/sec
d_s	Coefficient of Molecular Diffusion for gas s through N2, $= \dfrac{\sqrt{\bar{C}^2 + \bar{C}_s^2}}{3\pi n \left[{}^1/_2 (\sigma + \sigma_s)\right]^2}$ cm^2/sec.
f	Area, cm^2
g	Acceleration Due to Gravity, ^{cm}/sec.
H	Scale Height, cms.
k_s	$= \left({}^{d_s}/d\right)$
l_d	Molecular Mean Free Path, cm.
$\bar{l}_D$	Turbulent Mixing Path, cm.
m	Molecular Weight.
n	Concentration, molecules/cm^3 N.T.P.
p	Molecular Weight Factor.
Q	Secparation Factor.
q.	Apparent separation Factor.
R	Molar Gas Constant.
S.	Flux, molecules/cm^2.sec.
s.	Property of Air, expressed per unit mass of air.
T.	Temperature ^{o}K.
t	Time, secs.
u.	Molecular Velocity, ^{cm}/sec.

w_d	Molecular Mean Free Velocity, $^{cm}/sec.$
W_D	Turbulent Mixing Path, $^{cm}/sec.$
Z	Height, km.
α	$= \left(^{n_s}/_{n}\right) \div \left(^{n_{so}}/_{n_o}\right)$
σ	Molecular Diameter, cms.
ρ	Density, $^{gm}/cm^3$
V_s	$= \left(^{n_s}/_{n}\right)$

The symbols when used without subscripts refer to the atmosphere generally (taken as N_2) at heights $z > z_o$.

The subscripts :

o : refers to the datum level, $z \doteq z_o$

p : refers to permanent gases in the atmosphere.

s : refers to molecules of the kind s.

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