

The Chemical Exploration of the Stratosphere.

HUGO MÜLLER LECTURE, DELIVERED BEFORE THE CHEMICAL SOCIETY AT BURLINGTON HOUSE ON MARCH 27TH, 1952, AND AT THE UNIVERSITY, MANCHESTER, ON APRIL 23RD, 1952.

By F. A. PANETH.

THE discovery of the stratosphere, and all research concerning it, belongs to this century; but the chief chemical problem involved goes right back to the period when our science was born, and it seems to me that even to-day we can learn something from the procedures, successes, and mistakes of the early chemists who probed into the nature of the atmosphere.

Modern chemistry arose in the middle of the eighteenth century from the scientific study of the historical four elements. It became clear that "earth" was too vague a term for analytical chemistry and that many different earthy substances had to be distinguished. The explanation of "fire," and of the accompanying phenomena of light and heat, was recognized as belonging to the realm of physics. A clear chemical answer could soon be given for "water"; James Watt was the first who stated that it could be synthesized by combining two gases, and thanks to the further researches of Cavendish and Lavoisier the question of its nature was soon definitely settled.

It proved to be much more difficult to come to a decision about "air". The work of Scheele, Priestley, and Lavoisier had shown that the atmosphere, like water, consisted of two gases; but was it also a chemical compound, or only a physical mixture? Some chemists, for instance, Dalton's friend Thomas Thomson,¹ strongly advocated for air the formula N_4O , and Dalton himself abstained as late as 1838 from a clear-cut decision between the two possibilities.² The majority of their contemporaries, however, considered atmospheric air to be a mixture of nitrogen and oxygen whose composition was dependent on meteorological conditions. It is well to remember that the "eudiometer", in accordance with its etymology, was originally an instrument for measuring the "goodness", *i.e.*, the oxygen content, of air.

To-day we know that the adherents of the view that air is a mixture, were right; but in their strongest argument, the variability of its composition, they were entirely mistaken. They over-estimated the accuracy of their methods and believed that changes in the results which were due to experimental errors indicated actual fluctuations in composition. We shall see that the same mistake was made much later in the analyses of stratosphere air.

If we remember on what methods the old chemists had to rely for the analysis of air, we are not astonished at the spurious figures found by many but are filled with admiration for the few who handled these methods so skilfully that correct results were obtained. At the beginning the nitric oxide eudiometer was used; the diminution of the volume of an air sample, when mixed with a certain volume of nitric oxide and kept over water, was taken to be a measure of the oxygen present. But the nitric oxide employed was far from pure, and each chemist chose his own factor for calculating the oxygen content from the decrease of gas volume. No wonder that the results varied widely, especially if the analysis had to be carried out under unusual conditions. As gifted a scientist as the young Alexander von Humboldt during a sea voyage reached the conclusion that the oxygen content of air rose to more than 30% on fine moonlit nights. Others observed that South Kensington air was much richer in oxygen than that of London, and that the weather had a marked influence. Cavendish, on the other hand, as early as 1781, with his uncanny experimental skill came to the conviction that no variations in the oxygen content of air occurred, although he too had no better instrument than the nitric oxide eudiometer which, according to a contemporary critic, was suffering from no less than 20 different sources of error.

It was a great step forward when Volta introduced the hydrogen eudiometer, especially after Gay-Lussac and Humboldt, by experimenting with it, had stated that exactly two volumes of hydrogen disappeared with one volume of oxygen when the two gases were exploded. Omitting a few other methods, *e.g.*, those based on the oxidation of phosphorus or iron sulphide, or the absorption of oxygen by pyrogallol, we want to single out the copper eudiometer, introduced by von Jolly in 1850,³ because we found this method most convenient in our own experiments. If metallic copper is heated to the right temperature, one can be certain that all the oxygen gas present in an air sample disappears.

Determining the oxygen content of air was a subject which for decades not only was a hobby

with many amateurs of chemistry and meteorology, but occupied the interest of almost every great chemist; we find, beside the famous names already mentioned, those of Berthollet, Regnault, Bunsen, and many others. In a review of the literature one fact becomes obvious: the better the method, and the greater the personal experience of each investigator, the smaller were the differences found. Outstanding in many respects was the world-wide survey carried out by Regnault⁴ in the middle of the nineteenth century. He enlisted the help of scientists in many countries who provided him with air samples; even though some of these showed slight variations—which Regnault took to be significant, although they were certainly due to faulty sampling or storage—he came to the conclusion that the percentage of oxygen in air is almost invariably 20.9. Amongst the later investigators two are specially to be mentioned in our brief survey: U. Kreisler,⁵ who in 1885 in Bonn by a very long and painstaking series of experiments proved that meteorological conditions are without influence; and F. G. Benedict,⁶ who in 1912 in Washington confirmed this statement with higher precision and expressed the main result very well in the illuminating sentence: "Air is a physical mixture with the definiteness of composition of a chemical compound."

Benedict's statement is, of course, not applicable to more or less closed areas in which the oxygen content may be reduced by the combustion of fuel and the respiratory exchange of organisms, or increased by the assimilation of carbon dioxide in plants; but, as in these processes almost equal volumes of oxygen and carbon dioxide replace each other, they leave the nitrogen percentage in air practically unaltered. We are, therefore, on still safer ground if we restrict Benedict's statement to this gas and, following A. Krogh,⁷ declare that the percentage of nitrogen in the atmosphere is a geophysical constant which can be determined with a high degree of accuracy.

"Atmospheric nitrogen" in older literature always means, of course, nitrogen plus argon, plus the negligibly small amounts of the inert gases helium, neon, krypton, and xenon. We shall see later than these inert gases are most useful standards in stratosphere research, and we are therefore interested in the question of their individual constancy in ordinary atmospheric air. Only for two of them, argon and helium, have direct investigations been carried out. Moissan⁸ analysed air samples from several towns and also from over the sea, and found—with one doubtful exception—no variations. The likelihood of geographical influences seemed somewhat greater in the case of helium because of the very large quantities of this gas entering the air in certain areas, as *e.g.*, the petroleum fields of Texas. As we intended in our stratosphere research principally to make use of helium, we thought it necessary to test the uniformity of its distribution over the surface of the earth. Regnault, in his world-survey of oxygen, had insisted that his samples be collected by aspiration of air and sealed in glass; that restricted the number of his helpers to fairly well-instructed persons. We extended their possible number by asking only that a bottle be filled with water, then the water poured out and the bottle well closed with a cork or rubber stopper. It is obvious that one cannot be sure of the oxygen content remaining unaltered in such a bottle, but we thought it anyhow much safer to base our research on the relationship of the inert gases to the nitrogen content. Thanks to the help given by the Meteorological Office of the Air Ministry and to many private persons we obtained samples from all over the world, as can be seen from the points indicated on the map (Fig. 1). Our subsequent analyses showed that the helium content of atmospheric air is as much of a geophysical constant as is the nitrogen content.⁹ There is no reason to doubt that what has been found for argon and helium holds also for neon, krypton, and xenon.

There are, however, other constituents of atmospheric air which are certainly not constant. Water vapour is obviously so variable that for our purpose—not for meteorological questions—it is best to neglect it completely by referring always to dried air. Hydrogen is present in air only in such a small amount and is so difficult to exclude as a contamination that very little is known about its quantity,¹⁰ and less still about its constancy. In several instances traces of dinitrogen tetroxide, ammonia, sulphur dioxide, and carbon monoxide have been reported, but it may be that their occurrence is limited to the neighbourhood of human habitations and industrial activities. Recently, by spectroscopic means, methane and nitrous oxide have also been identified in the atmosphere,¹¹ in quantities not exceeding those of the rarest of the rare gases.

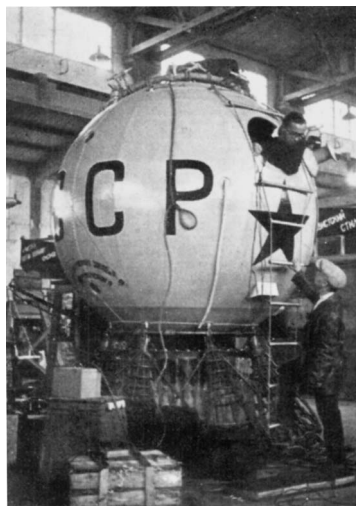
For our present survey we may neglect these constituents; it would, however, be incomplete if we did not pay attention to one gas which is rare near the surface of the earth but proportionately much more abundant in the upper atmosphere: the gas ozone. Schönbein, the discoverer of ozone, was also the first who believed in its presence in the air and in the possibility of measuring its quantity by the simple device of strips of paper soaked in solutions of potassium iodide and

PLATE I.



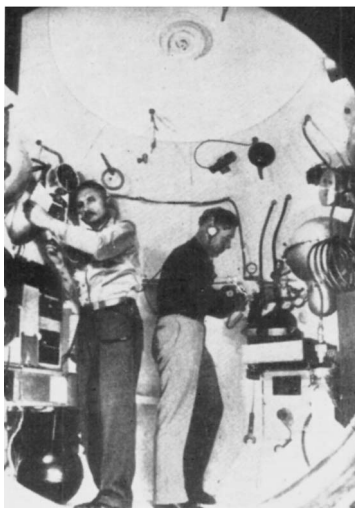
Gay-Lussac collecting air during a balloon flight in 1804, by turning the stopcock of an evacuated glass vessel. (The picture is included in J. Howard Appleton's "Beginners Handbook of Chemistry," Chauteauqua Press, New York, 1888; no reference to its origin is given.)

PLATE II.



Spherical gondola for the stratosphere flight of G. A. Prokofiev, K. D. Godunov, and Birnbaum in 1933 (see also ref. 30). [Reproduced, by permission of The New York Times, from G. Heard, "Exploring the Stratosphere," T. Nelson & Sons, Ltd., Edinburgh, 1936.]

PLATE III.



Captain A. W. Stevens (left) and Captain O. A. Anderson in the Gondola of "Explorer II" in 1935. The evacuated vessel for the stratosphere sample can be seen on the right (see also ref. 32). [Reproduced from G. Heard, "Exploring the Stratosphere," T. Nelson & Sons, Ltd., Edinburgh, 1936.]

PLATE IV.



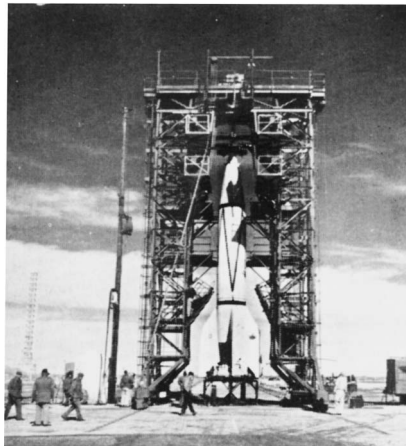
Mr. L. H. G. Dines launching a sounding balloon, with attached mechanism for air sampling, at Kew Observatory in 1936 (see ref. 26).

PLATE V.



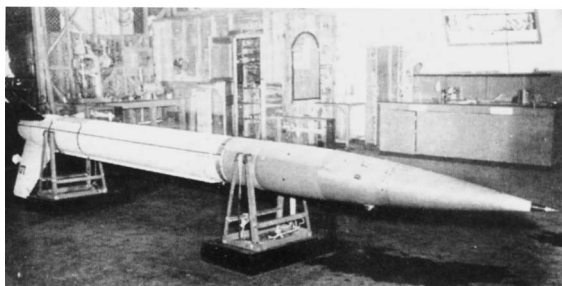
German V-2 rocket, converted in U.S.A. for scientific purposes.

PLATE VI.



German V-2 rocket standing on its fins inside a gantry for the final instrumentation and fueling. Before the flight the gantry is rolled away.

PLATE VII.



Aerobee rocket built in the Applied Physics Laboratory of Johns Hopkins University. Propulsion is accomplished in two stages. A solid propellant "booster" rocket brings the velocity to about 1000 ft. per second, then it falls away, and the sustaining liquid-fuel motor takes over, accelerating the rocket to about 4000 ft. per second (see ref. 27).

PLATE VIII.



Aerobee rocket standing inside the tower through which it is to be fired.

PLATE IX.

Aerobee rocket at the moment of being shot out of the tower.

PLATE X.

Front part of Aerobee rocket, with nose cone which is thrown off during the flight just before the sampling bottles are opened. The arrangement of the three bottles can be seen below the cone.

PLATE XI.

Arrangement for opening and closing of the copper tube which leads into the evacuated steel bottle. Both mechanisms are operated by the explosion of black powder; opening is achieved by a piston which breaks off the end of the copper tube, and closing by compression of two steel jaws which effect cold welding of the copper tube at a point nearer to the bottle (see also Plate XIII.)

PLATE XII.

Part of an Aerobee rocket, with the three bottles containing stratosphere air, after being landed by parachute.

PLATE IX.

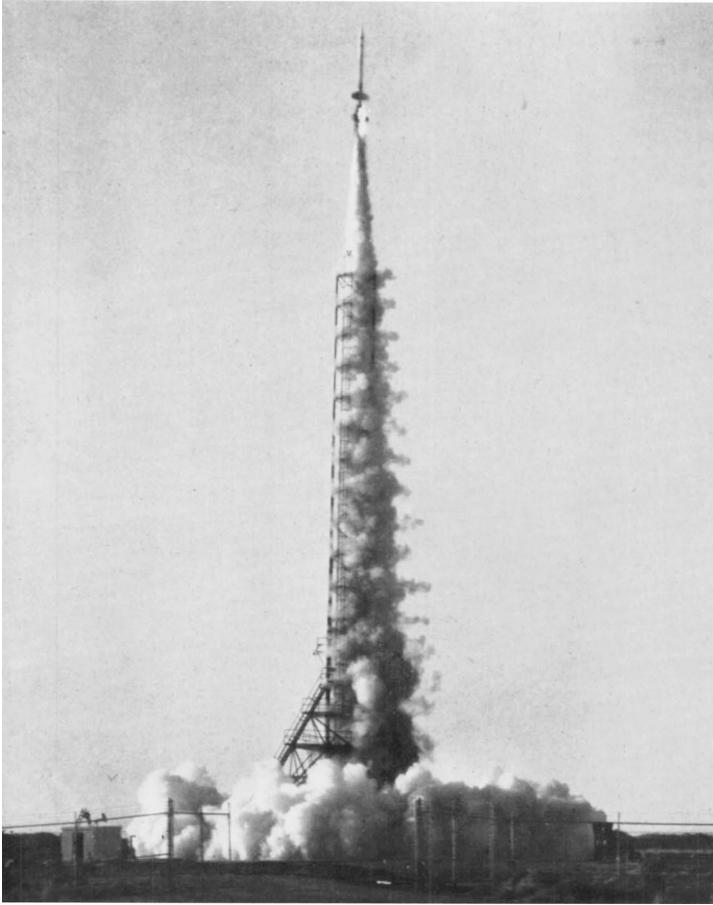


PLATE X.

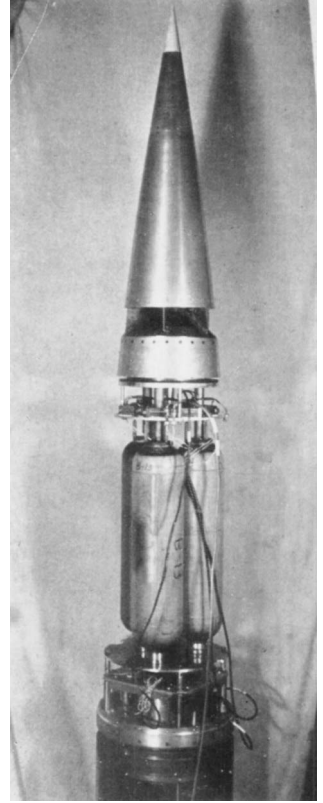


PLATE XI.

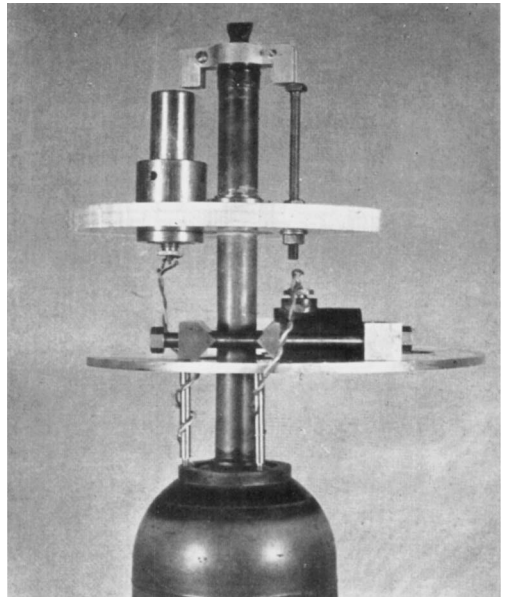
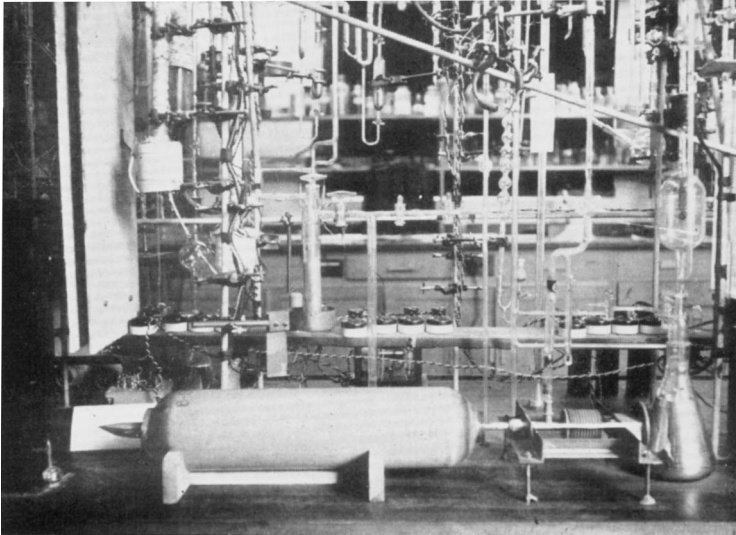


PLATE XII.

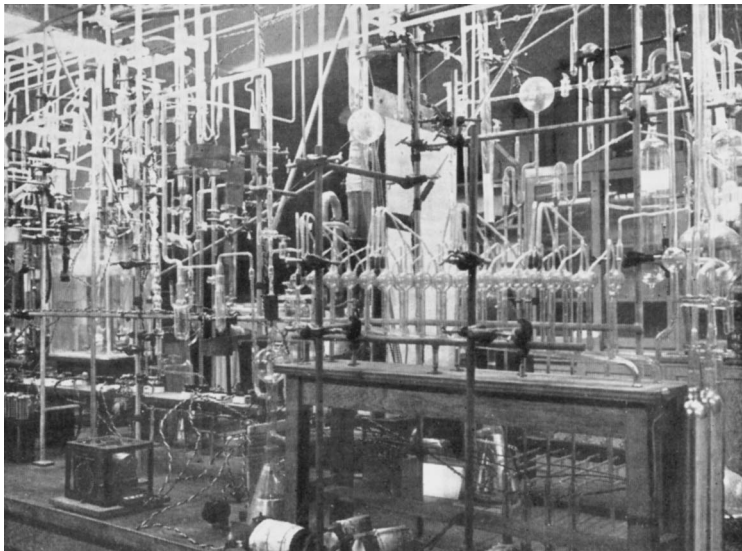


PLATE XIII.



Steel bottle containing stratosphere air connected with the gas-analysis apparatus. On the left can be seen the flat edge of the copper tube which was cold-welded during the flight of the rocket; on the right the metal bellows which allow a needle to be pressed against a copper membrane inside the steel bottle, thus making a hole through which the gases can be pumped into the apparatus for analysis.

PLATE XIV.



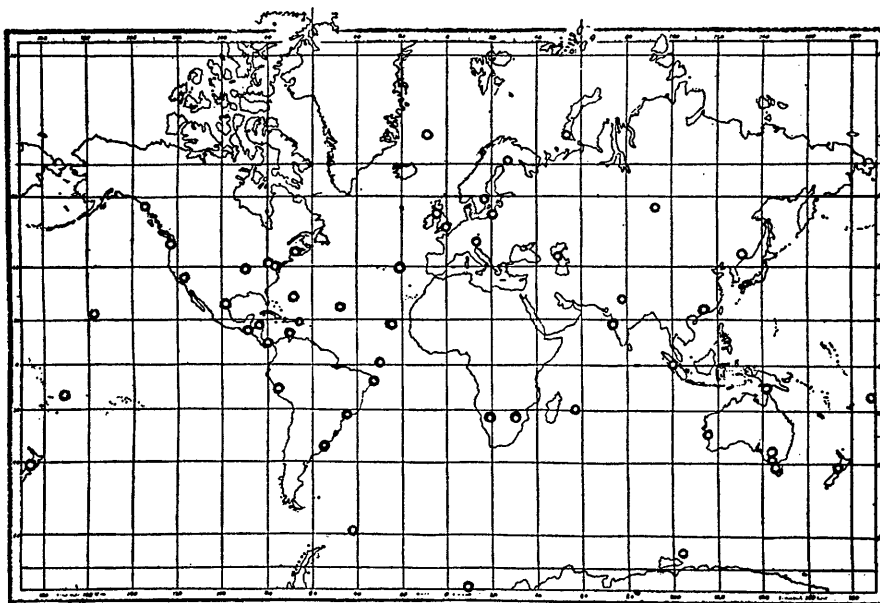
Part of the Durham apparatus for the micro-analysis of rare gases. In the foreground can be seen the fractionation column for the separation of helium and neon.

[Photographs from which Plates X and XI were made were taken by the photographer of the Engineering Research Institute of the University of Michigan; the other photographs of the V-2 and Aerobee Rockets are by U.S. Signal Corps photographers.]

starch. Similarly, as half a century earlier the salubrity of air was supposed to vary with its oxygen content, so now medical men ascribed it to the presence of ozone, and the apparent simplicity of its estimation from the intensity of the blue colouration of the paper strips inaugurated a period of "ozonometry" in which an even greater number of qualified and unqualified people participated. It has been calculated that literally millions of such ozone measurements have been made.¹² Although little of permanent value was achieved, it seems that some seasonal variations were correctly established, and as an influence of the ozone content of air on the human well-being¹³ is not *a priori* impossible, we must admit that ozonometry was not quite such a wild-goose chase as the old eudiometry.

There came, however, a reaction when it was realized that Schönbein's potassium iodide test, not being specific for ozone, may indicate other oxidising agents in air, especially dinitrogen tetroxide, and for a while only the well-known spectroscopic proof for atmospheric ozone was considered to be reliable. In 1938, J. L. Edgar succeeded in my laboratory in London in concentrating atmospheric ozone by condensing it on silica gel, and then in measuring the

FIG. 1. *Places from which air samples have been analysed for their helium content (see ref. 9, p. 94).*
[Reproduced, by permission, from *Proc. Roy. Soc.*, 1945, *A*, 185, 94.]



same sample in two ways—spectroscopically and by the iodide test. The agreement was very satisfactory, and he could also show that the danger of a confusion with dinitrogen tetroxide was small and could easily be avoided.¹⁴ These experiments paved the way to a trustworthy chemical measurement of atmospheric ozone. Between the years 1939 and 1941 in my Durham Laboratory E. Gluckauf, H. G. Heal, and G. R. Martin¹⁵ developed a self-recording chemical ozonometer. The basic idea was to liberate iodine by the ozone in a potassium iodide solution and to use its depolarizing effect on a platinum electrode for the production of a minute electric current which, after amplification, triggered an automatic burette; the apparatus measured the ozone content of air every few minutes and worked without supervision for 24 hours. These experiments had to be discontinued during the war, but it is gratifying to know that recently Bowen and V. H. Regener¹⁶ at the University of New Mexico have taken up our method and hope to use it, with slight alterations, for the automatic recording of ozone in the upper atmosphere. No results have so far been reported, but it is very likely that in the near future the measurement of ozone by this or another chemical method will have to be included in a report on the chemical exploration of the stratosphere.

If, returning now to the constant constituents of atmospheric air, we take it for established that their relative proportions do not change from place to place, or from day to day, have we to assume then that the total atmosphere has the same percentage composition? To be sure,

very few scientists expected that after Dalton's law of partial pressures had been formulated in 1826. Since the days of Descartes, Pascal, and Boyle it had been known that the density of air diminished with height according to the barometric formula and, if each gas behaved as if it alone were present, then the rate of this diminution had to be slower for the light than for the heavy gases; in other words, a sample of air taken from a certain height should be relatively enriched in the lighter constituents.

It is of some historical interest that even before Dalton's time this conclusion had been reached. In 1800 Berthollet, who was very sceptical about reports that variations of the oxygen-nitrogen ratio had been found in not very distant villages, added: "However, one has to make an exception for places high above sea level. The difference in the specific weight between oxygen and nitrogen gas, which have only a very feeble action on each other, explains the difference which has been found in their proportions."¹⁷ It is only fair to see, with Kreisler, in this passage a statement coming very close to an enunciation of Dalton's law; and similar considerations had apparently as early as 1798 prompted Humboldt to analyse air collected during a balloon flight at an altitude of 1300 metres, and de Saussure to do the same with air from several mountain tops. As a curiosity it may also be mentioned that about the same time a professor claimed that he had succeeded in separating the oxygen and nitrogen by simply allowing an air-filled glass tube of five feet length to stand undisturbed upright for a year; but this remarkable experiment which Chladni mentions in his famous book on acoustics,¹⁸ seems to have succeeded only once, in my native town Vienna.

For some reason or other in those early days one expected to find more spectacular changes in the composition of air on rising anywhere only a short distance into the air than by attaining, on the ground, great altitudes above sea level. It was, of course, known that on high mountains people can breathe with only little discomfort and without any damage to their health; but the first ascent into the air even in a captive balloon seemed so dangerous that experiments with various kinds of animals had to be performed first. So a cock, a duck, and a sheep were sent up in a wicker basket. When examined after their return it was found that the cock was clearly suffering from an indisposition; but the conclusion reached by the experts that the higher air had not been suitable for his respiratory organs had to be abandoned when his ailment was traced to the fact that during the flight he had been trodden upon by the sheep. Nevertheless, it was thought best that the first men to follow the animals should be two criminals under sentence of death; but in their place a very courageous young technician volunteered, spent five minutes at a height of eighty feet, and described his experience as exhilarating.¹⁹

These early ascents in 1783, including the first free flight undertaken by the same technician, Pilâtre de Rozier, together with a French nobleman, were mainly meant as public spectacles, and the hot-air balloons of the brothers Montgolfier never got beyond that stage. But simultaneously the French physicist Professor J. A. C. Charles developed the hydrogen-filled balloon and with it scientific aeronautics began. Charles himself made observations with a thermometer and barometer during the flights, and in a letter to Sir Joseph Banks at the end of 1783, a year so memorable for the history of science, Joseph Priestley expressed the hope that the balloons "though at present they only amuse the idle, may in time answer some important purposes in philosophy, enabling us to explore the upper regions of the atmosphere."²⁰

It is probably right to say that, in the minds of most scientists, foremost amongst these purposes was the wish to prove the correctness of the law of partial pressures by analysing air from the upper regions and to show that its oxygen percentage had decreased. This seemed to be almost a foregone conclusion, as this observation had been more than once reported on mountain air. But when in 1804 one of the very best chemists, Gay-Lussac, examined air which he himself had sampled in a balloon flight at a height of more than $6\frac{1}{2}$ km. (see Plate I) he found no difference.²¹

Gay-Lussac was to my knowledge the only scientist who applied himself to both the difficult tasks of collection of an air sample from as great a height as possible and its analysis with as great an accuracy as possible. Usually the analysis was entrusted to a chemist who had nothing else to do but to perform this job correctly; in most cases he probably did so and if, nevertheless, for decades the results were inconsistent and contradictory, the reason must be sought in the dangers inherent in the collecting and storage of air. Illuminating examples of this can be found in Dalton's protocols.²² Dalton always observed that air collected by himself on the tops of mountains, or sent to him by a friend from heights in Switzerland, contained a lower percentage of oxygen than Manchester air; but it did not occur to him that the longer time during which mountain air had been stored in wet bottles in contact with cork might have something to do with the observed effect. In at least one case he even noted that after two more weeks the

oxygen content had further decreased; this seemed to him incomprehensible in view of the fact that the bottles had been kept carefully corked. We shall see later that even to-day the difficulty in determining the oxygen content of stratosphere air does not lie with the analysis, but with the sampling.

Although Dalton thought that qualitatively he had confirmed the expected diminution of oxygen content, he realised that the effect was far less than the theory of the independent behaviour of oxygen and nitrogen predicted, and he correctly ascribed this to the disturbing influence of winds.²³ He recognized for the first time how important the chemical investigation of the composition of the atmosphere may be for the meteorological problem of the efficiency of winds. It is this importance, much more than the purely chemical interest, which inspired the many difficult, and also very expensive, researches on the constituents of the atmosphere at ever greater heights.

Gay-Lussac's balloon ascent was followed by a few others from which air samples were brought back. In more recent times the analysis of these samples was undertaken in the expectation, not of finding a decrease in the oxygen content—which was known by then to be at the best very small—but a much more marked increase in the light gases hydrogen, helium, and neon (see Table 1). But if the carrying balloon is filled with hydrogen, no sampling

TABLE 1. *The constant constituents of the atmosphere.*

	Mol. wt. (O = 16.000)	Density (Air = 1.000)	Percentage in air
Hydrogen	2.016	0.0695	5×10^{-5}
Helium	4.003	0.138	5.2×10^{-4}
Neon	20.183	0.695	1.8×10^{-3}
Nitrogen	28.016	0.967	78.09
Oxygen	32.000	1.105	20.95
Argon	39.944	1.379	0.93
Carbon dioxide	44.01	1.529	0.03
Krypton	83.7	2.868	1×10^{-4}
Xenon	131.3	4.525	9×10^{-6}

device in the gondola will be safe against contamination from this overwhelming source, and the analytical technique of most of the chemists was not good enough to allow them to determine separately hydrogen, helium, and neon in small quantities of air; so they confined themselves to the statement that at an altitude of no more than eight or nine km. they had found a light "residual" gas which, they thought, indicated the presence of helium and neon. In most cases this ill-defined "residual" gas seems to have consisted of hydrogen from the balloon, and it is rather astonishing that well-known meteorologists in the twenties of this century declared themselves satisfied that the prediction of an increase of the lighter constituents of the atmosphere with height had been proved correct by these superficial analyses.¹⁰ Even the purely meteorological knowledge of the constant mixing of the atmosphere by winds should have made them sceptical about the chemists' findings.

Since the early part of this century it has, however, been known that we have to distinguish at least two different regions of the atmosphere. When thermometers were sent up in sounding balloons, they registered a fairly steady decrease of the temperature up to a height—in our latitude—of about 11 km.; but from there onwards the temperature remained constant, at approximately 219° K (-54° C), up to the greatest height accessible to direct measurements. It was then assumed that no large-scale mixing of the atmosphere could occur in such a region without temperature gradient; this supposedly quiet layer was, therefore, distinguished as the "stratosphere" from the lower "troposphere," the place of all meteorological changes.

To-day we know that the structure of the atmosphere is much more complicated. Indirect evidence, collected mainly from observations on meteors and measurements on the propagation of sound and radio-waves, makes it certain that the region of constant temperature reaches only up to about 25 km.; from that height onwards the temperature rises, but after attaining a maximum of perhaps 280° K at 50 km. it falls again, passes through a minimum of about 190° K at the height of 80 km., and finally rises, uninterrupted, to more than 1000° K.

The explanation of these temperature changes presents a very difficult problem for the meteorologist and theoretical physicist. The help of the chemist is essential because the heating effect of solar radiation depends on the nature of the gases, and it is for this and similar reasons important for them to know the chemical composition of the atmosphere at all heights. We have seen that all reports about an increase of the lighter constituents in the upper part of the

troposphere have been erroneous; but if in the stratosphere, or in certain layers of the stratosphere, stillness should reign, we may hope to find the long-sought effect of gravitational separation, and we may even expect to detect in the highest strata the rare gas helium as the predominant constituent.

Fig. 2, after J. Bartels,²⁴ shows the height-dependence of the partial pressures of argon, oxygen, nitrogen, and helium, calculated on the assumption that from 12 km. onwards the atmo-

FIG. 2. Diminution, with height, of the partial pressures of the atmospheric gases, on the assumption that there is stillness from 12 km. upwards (see ref. 24, p. 135).

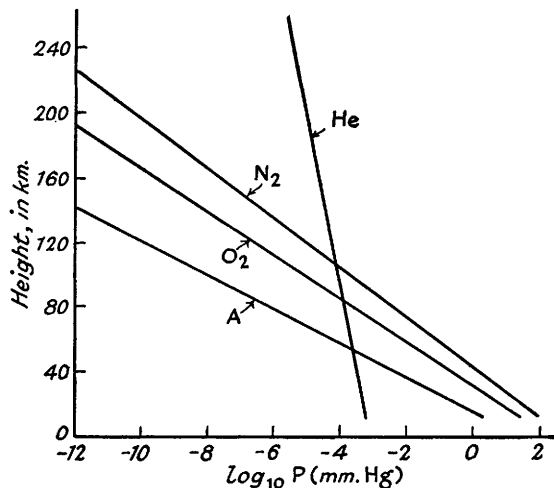


FIG. 3. Composition of the atmosphere at different heights, on the assumption that there is stillness from 20 km. upwards (see ref. 25, p. 379).

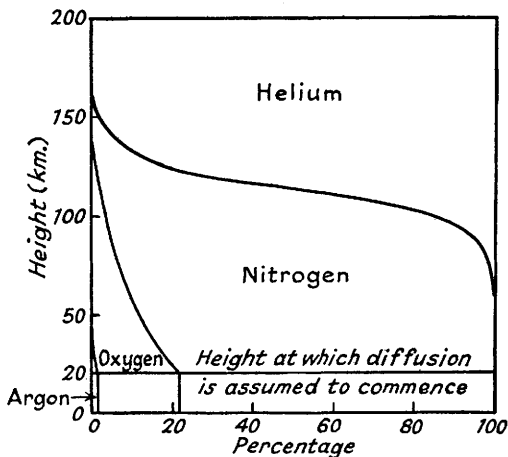
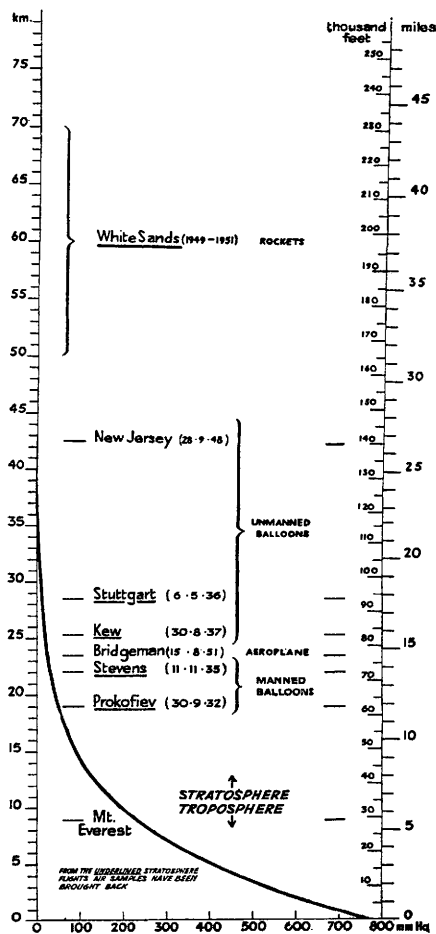


FIG. 4. Sampling of stratosphere air at different heights. The curve indicates the barometric pressure.



sphere is free from disturbances and its temperature throughout 219° K. Fig. 3 gives, after S. Chapman and E. A. Milne,²⁵ the percentage composition of air at various heights for the same temperature and the case that disturbances cease at 20 km. It is true that spectroscopic and other observations make an effect of this magnitude unlikely; the light of the aurora, for instance, indicates that at heights of several hundred km. nitrogen and oxygen are still the main gases of the atmosphere. But even a small change in composition, if established by chemical analysis, would be important because it would indicate the absence of air currents—not only for minutes or hours, but, depending on the density and temperature of the atmosphere at the

height in question, for weeks, months, or years. The establishment of an equilibrium in the gravitational field of the earth according to the law of partial pressures is a very slow process: its disturbance by winds is a very fast one. If, therefore, the chemists should find at least an approximation to this equilibrium, we may safely conclude that we have reached a region, or the neighbourhood of a region, of long-lasting stillness. Such a discovery cannot fail to be of consequence to meteorology and atmospheric physics.

All attempts at analysis of stratosphere air have to face two difficulties: the collection of reliable samples, and their exact analysis. Let us first consider the various methods by which the samples can be obtained.

The first men to enter the stratosphere were, in 1931, A. Piccard and his assistant. Their technique of the closed spherical gondola was copied in subsequent stratosphere flights. One of them, undertaken by Russian explorers (see Plate II), brought air back from 18.5 km. This height was surpassed by an American stratosphere balloon flight in 1935, which attained 22 km. and from which also air samples were delivered to a chemical laboratory; one of the evacuated vessels of 22-l. capacity which were used by the pilots for this purpose, is visible on the right side of Plate III, attached to the wall of the gondola.

From Fig. 4 it can be seen that the greatest height reported for aeroplanes is above the last-mentioned record flight of a manned balloon. But aeroplane flights at maximum height are so difficult and demand the attention of the pilot so completely, that he cannot be expected to work any scientific apparatus. The little he might be able to do can quite as well be performed by automatic devices attached to an unmanned balloon, and these sounding balloons can far surpass any altitude within reach of men. Furthermore, these flights can be done at very low cost and may therefore be arranged frequently—a very essential point in all meteorological investigations where the collecting of a statistical material is necessary. Such balloons are either made of rubber, closed, and expand as they go up; or they are fabricated of a plastic material, open at the bottom, and have constant volume. The higher the altitude they are meant to reach, the smaller has to be their payload, but up to 30 km. they can carry apparatus of the order of 100 lb.

These pilot balloons have been very useful in collecting air samples up to about 30 km.; Plate IV shows the launching of a rubber balloon, carrying an evacuated glass vessel of 300-c.c. capacity which was to be opened and closed at the top of the flight by a simple electrical device ²⁶ (see Fig. 5). As will be explained later, the analyses of these samples still failed to solve the main problem as to the presence or absence of gravitational separation, and air from still greater heights had to be provided.

This became possible when some of the 100 odd V-2 rockets seized by the American Army in Germany in 1945 were converted in such a way that instead of the explosive charge they could carry automatic scientific apparatus in the war-head (see Plates V and VI). The successful firing of such a transformed V-2 rocket, which is undertaken at the White Sands Proving Ground in New Mexico, is a very difficult and costly operation, and a smaller, simpler rocket, called the Aerobee, has therefore been constructed in the Applied Physics Laboratory of the Johns Hopkins University ²⁷ (see Plates VII, VIII, and IX). V-2 and Aerobee rockets have lately been used with great success in many different branches of stratosphere research. The devices developed by American scientists for the opening, near the top of the flights, of evacuated metal flasks, and for their closing a few seconds later ²⁸ can be seen in Plates X and XI. The rocket is disintegrated during the flight and the part which contains the flasks is brought down by parachute (Plate XII).

If by these devices a representative sample of stratosphere air has been obtained, the question of its analysis arises. In view of the great rarefaction the analysis may have to be performed on less than a tenth of a c.c. of air, measured at normal temperature and pressure. It is, of course, not necessary to analyse all the constituents in order to find out if a gravitational shift in composition has taken place. It will, however, be very useful to examine at least one which is lighter and one which is heavier than nitrogen because their concentrations in respect to the latter gas must change in opposite directions, and such a fact, if established, would at once rule out several possible sources of error. As mentioned before, we consider the inert gases as by far the most reliable test, since only with them are changes due to chemical reactions completely excluded; the procedure we adopted was to determine in the stratosphere samples the ratios of helium, neon, and argon to nitrogen, and to compare these values with the corresponding ones in ground-level air. From the densities of the various atmospheric gases shown in Table 1, and from Figs. 2 and 3, it is obvious that in gravitational equilibrium the shift should be greatest for the ratio helium : nitrogen; another factor in favour of the helium shift is the high diffusion velocity of this gas which allows it to approach this equilibrium quicker than neon or argon. ²⁹

However, before we deal with our own experiments a few words have to be said about attempts made earlier in other laboratories to detect a gravitational separation in stratosphere air. All of them were confined to analysis for oxygen. Now oxygen is no doubt the easiest to determine of the constituents of air, but at the same time the most difficult to sample correctly. We are, therefore, very sceptical about a few statements in the literature that at heights below 30 km. a deficit of oxygen has been found. Russian chemists, analysing air from the stratosphere flight reaching 18.5 km., came to the conclusion that the oxygen content was unaltered;³⁰ but E. Regener³¹ claimed that in a sample collected by a pilot balloon from the same height there was already a noticeable decrease in the oxygen content, and he believed that, in the air from a pilot balloon reaching 28—29 km., the percentage of oxygen had dropped from 20.92 to 20.39. However, it appears that even at ground level Regener found slightly less oxygen than the accepted standard figure of 20.95; an examination of his arrangements

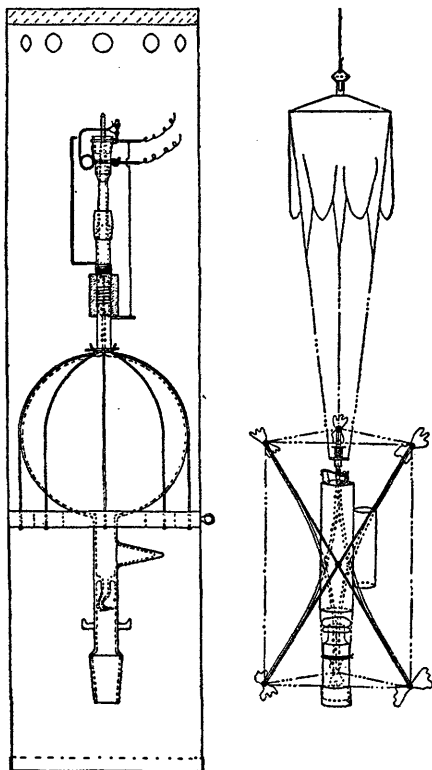


FIG. 5. Sampling of stratosphere air by sounding balloons. When the rubber balloon bursts, an electric circuit is closed and the tip of the evacuated glass vessel is broken off by the release of a spring. Another electric circuit heats a capillary restriction of the glass tube nearer to the vessel and seals it within a few seconds (see ref. 26). [Reproduced, by permission, from *Proc. Roy. Instn.*, 1937, 29, 350.]

reveals that the oxygen entered the vessels through a greased stopcock and was then in contact with a clean copper surface. Both grease and copper are known to absorb oxygen even at room temperature, and it is obvious that this effect must become more marked as the quantity of air in the bottle decreases, *i.e.*, the samples from the greatest height must show the biggest deficit. It is likely that the same source of error, to a smaller extent, was operative also in M. Shepherd's analyses of the larger quantities of air brought back from 21 km. by the Americans.³² There too lubricated taps were used, and it is our experience that they immediately reduce the oxygen content of air by an appreciable amount if the measurements are made with the high accuracy reached by Shepherd. The decisive control experiment, which, unfortunately, does not seem to have been carried out by either Regener or Shepherd, would have been to fill an identical vessel with ordinary air at the same low pressure as that of the stratosphere sample, and analyse it after the same lapse of time.

When, as in our procedure, not the oxygen content but the inert gases are determined, there is a different source of error which has to be carefully watched. Helium dissolves readily in glass;³³ the usual hard glass (Pyrex, Hysil) shows this effect so strongly that its use in an apparatus for sensitive helium determinations is completely precluded but even soft glass, if

previously exposed to air, may give off helium into the vacuum or, alternatively, if it has been carefully degassed it is able to dissolve helium and thus to falsify the analyses in the opposite direction. In the experiments carried out before the last war we sent glass vessels in sounding balloons up to the height of 23 km. and observed slight and irregular increases in the helium content. We were inclined to consider these changes as an indication that from about 20 km. onwards there was a slight enrichment of helium in the stratosphere, but in view of the uncertainty introduced by the glass—which we could not avoid using, in our very lightly built sampling apparatus—we could not be sure, and in our final publication³⁴ we expressed the view that neither our helium results nor those obtained with oxygen in other laboratories were reliable enough to prove gravitational separation between 20 and 30 km., and that samples from considerably greater heights, and preferably in metal containers, would have to be collected in order to settle the question.

The possibility of obtaining such samples was provided by American rocket research after the war. These rockets can easily reach 70 km., and air is collected in metal bottles; however, the first samples we received were not in the original containers but had been pumped into glass vials. We were not too astonished to find that the helium values did not show the same consistency as those of neon and argon, and that some samples had even less helium than ground-level air (see Table 2). We therefore urged our American collaborators to send us the original steel bottles and our latest analyses were made with samples which right to the moment when we introduced them into our glass apparatus had only been in touch with steel and copper and could, therefore, not have lost or gained any helium. The results of our analyses, which are presented below, will, therefore, be divided into two groups: stratosphere samples from glass vessels and from steel bottles.

Not much need be said here about our methods of analysis as they have been described in a series of papers³⁵ (see Plates XIII and XIV). After removal of oxygen and carbon dioxide the argon, containing also the insignificant amounts of the other inert gases, is freed from nitrogen by heating it with barium in a steel furnace. Neon and helium, after removal of the heavier gases, are separated by fractional adsorption and desorption from charcoal; their measurement is accomplished by a refined Pirani gauge which permits the determination of a millionth of a c.c. of helium and neon with an accuracy of 1%. Some attention may be given to the oxygen figures in our tables which confirm our previous statement that even cold copper surfaces—the steel bottles are connected with copper tubes and contain copper membranes for the purpose of opening (see Plate XIII)—absorb this gas to an appreciable extent; it can be seen that in several of the samples hardly any oxygen gas was left when the bottles reached us.

Table 2 shows the results of air analyses from glass vials; they can be easily summarized by saying that the neon and argon figures prove the constancy of atmospheric composition. It should be added that a few of the samples were also analysed for neon at the University of Michigan, with the same result, apparatus modelled on the Durham one being used. As regards the height from which these samples came, we have to take into account the fact that in these early experiments the altitude range during which the steel vessels were kept open was rather considerable, and it is, therefore, not easy to say exactly to what heights these experiments

TABLE 2. *Analyses of stratosphere air from glass vials.*

No. of sample	Height (km.)	Date of		Ratio to ground-level air			
		sampling	first analysis	Oxygen	Helium *	Neon	Argon
16A	49.6 to 53.6	2.6.49	4.8.49	0.61	0.96	0.98	1.00
25D	50.4 to 53.3	6.12.49	17.4.51	0.60	0.98	1.00	1.00
15B	53.6 to 57.7	2.6.49	25.7.49	0.12	1.00	1.00	1.01
19D	54.7 to 58.3	21.7.49	6.3.51	0.00	1.01	—	1.01
3B	55.4 to 65.5	27.5.48	1.12.48	<0.02	0.98	0.99	0.99
1B	61.1 to 72.0	9.10.47	4.1.18	<0.02	0.93	1.00	1.01

* Figures uncertain on account of storage in glass.

should be allotted; careful calculations by Professor S. Chapman³⁶ make it likely that the vessels were filled soon after opening, and that during the further flight air escaped. For instance, the sample 1B should not be taken to represent the composition of air half way between 61 and 72 km. but probably corresponds to the height of only 62.5 km. This point is essential for comparison with the heights shown in the next table.

The experiments reported in Table 3 were all made on air from steel bottles and are particularly interesting because here for the first time changes of atmospheric composition can be

clearly recognized in different samples; they are shown not only by one constituent, but by three simultaneously, and in every case are in the direction predicted. B-15 comes from a height where alterations in the neon and the argon content, if present at all, are still too small to exceed the limits of possible errors by an amount sufficient to make us sure of their reality. The

TABLE 3. *Analyses of stratosphere air from metal flasks.*

No. of sample	Height (km.)	Date of		Amount of air (c.c., N.T.P.)	Ratio to ground-level air			
		sampling	first analysis		Oxygen	Helium	Neon	Argon
B-13	55.56 to 58.18	26.9.51	23.11.51	6.10	0.50	0.998	1.005	1.001
B-15	58.18 to 60.35	26.9.51	18.12.51	4.13	0.01	1.035	1.008	0.996
B-6	64.3 to 67.0	19.12.50	12.6.51	0.338	0.07	1.44	1.08	0.93
B-8	67.0 to 69.6	19.12.50	25.6.51	0.231	0.25	2.02	1.18	0.89
B-9	69.6 to 71.8	19.12.50	9.5.51	0.535	0.03	2.41 *	1.20 *	0.85 *

* Figures corrected for leakage.

helium figure, however, 1.035 instead of 1.000, which has been determined several times—always bracketed between analyses of ground-level air—must be considered as indicating a slight, but real, increase.³⁷ More convincing still are the next three samples, B-6, B-8, and B-9, collected during the same flight at successive heights. All of them show a marked increase in the helium and the neon ratios, and an equally obvious decrease in the argon ratio. It should be noted that the helium content in bottle B-8 was found to be as much as twice as high as in normal air. Unfortunately, bottle B-9 did not close perfectly and the small leak which we detected in it explains that in spite of the greater sampling height the total quantity of air was considerably bigger than in the two other bottles. This was most likely due to ground-level air seeping in after the flight, and before the bottle was found and the leak stopped by a protective layer of glyptal wax; no leak was apparent in the bottle when we received it; but, when the glyptal was carefully washed off the sealed end of the copper tube, a very small leak was found, of the right order of magnitude to account for the extra air in the bottle. The figures found for helium, neon, and argon in this bottle showed, in spite of this leakage, still very clear deviations from those of ground-level air, approximately to the same extent as those detected in B-6; since it is fairly well known what quantity of air should have been sampled at the height of B-9, we could attempt to correct for the contamination by ground-level air.

[Of the three steel bottles, B-6 opened and sealed perfectly. B-8, so we are informed, may not have opened fully, as the knife was, at the time of recovery, in an unexpected position, but sealed well. Thus to determine the correct amount of air to be expected in bottle B-9, it does not seem correct to extrapolate through the values for B-6 and B-8, as B-8 probably collected a smaller volume of air than it should have done. Instead, it was deemed best to take the amount of air in B-6 as correct, and to calculate the amount of air to be expected in B-9 from a pressure decrease according to the barometric formula, $P = P_0 e^{-mgh/RT}$ where $T = 280^\circ \text{K}$,³⁸ $R = 8.3136 \times 10^7 \text{ cm.}^2/\text{sec.}^2/^\circ\text{K}$, $g = 980 \text{ cm./sec.}^2$, and $m = 28 (\text{N}_2)$. The temperature 280°K is rather arbitrary, but the final results are not very dependent on the choice.

Correcting the sample volumes for the varying oxygen percentages, we obtain :

	Ht. (km.)	O ₂ , %	Net N ₂ content (c.c.)
B-6	65.6	1.875	0.332
B-8	68.3	6.81	0.215
B-9	70.7	0.7	0.531

If the nitrogen pressure at 62 km. is taken as 1, then the nitrogen pressure at 72 km. will be 0.3077 (from the above formula). From this it is apparent that if the nitrogen volume at 65.6 km. is 0.332 c.c., at 70.7 km. it will be 0.184 c.c. Thus 0.347 c.c. of ground-level nitrogen leaked in.

Since the experimental value of the helium : nitrogen ratio was 1.49, compared with 1 at ground level, we have :

$$1.49 = (R_{\text{He}} \times V_{70.7} + 1 \times V_g) / V_{\text{total}}$$

where R_{He} is the true helium ratio at 70.7 km., $V_{70.7}$ is the volume of nitrogen from 70.7 km., V_g is the volume of nitrogen from ground level, and V_{total} is the total volume of nitrogen in the bottle.

$$\text{Whence } R_{\text{He}} = [(1.49 \times 0.531) - 0.347] / 0.184 = 2.41$$

$$\text{Similarly, } R_{\text{Ne}} = 1.20 \text{ (experimental value, 1.07)}$$

$$\text{and } R_{\text{A}} = 0.85 \text{ (,, ,, 0.95)}$$

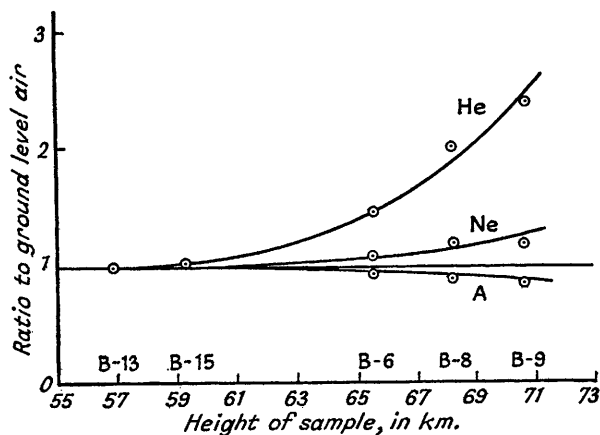
Further, the assumption that bottle B-8 did not open fully, but collected its sample slowly with the knife stuck across the copper tube and therefore probably yielded air from a greater average height than would be consistent with full opening, seems to be borne out by the helium figure. If the height from which B-8 is assumed to come is increased by 0.5 km. the three helium values are now all on the theoretical line, and the actual nitrogen volume of B-8 also comes much closer to the volume expected.]

These "corrected" figures are entered in Table 3. It need not be emphasized that such a correction is highly unsatisfactory but it is the best we can do at the moment to get the maximum possible information from the small number of analyses available.

Fig. 6 shows the results in graphical form. It can be seen very clearly that the decrease in the argon and increase in the neon ratio, although quite marked, are much less than the increase in the helium ratio, and that is exactly what one would expect. That the neon : nitrogen ratio shows a larger shift than the argon : nitrogen ratio, in spite of the smaller density difference, may be due to the fact that neon, with half the atomic weight of argon, approaches diffusive equilibrium faster.²⁹

If we try to make a more strictly quantitative comparison of the shifts found in our analyses with theoretical predictions for still air, it appears that they are approximately of the right mag-

FIG. 6. Variations in the inert-gas content of stratosphere air between 59 and 71 km.



nitude. It is too early to draw definite conclusions from these experiments, which are still far too few, but we believe that at present one can summarize our results as follows:

Up to a height of 57 km. no change in the chemical composition of the atmosphere could be detected. In two flights over New Mexico, December 1950 and September 1951, it was found that from about 59 km. onwards the ratios of helium, neon, and argon to nitrogen, changed in a way consistent with the assumption that in this region of the stratosphere gravitational separation is effective, essentially undisturbed by large-scale mixing.

The analyses recorded in Table 3 are, in our opinion, at present the only reliable ones which indicate any variation at all in the composition of the terrestrial atmosphere. So we see that the technique of both sampling and analysing air had to be developed a great deal further since the days when John Dalton climbed Helvellyn and Snowdon and believed that the air brought back in a bottle from some 3000 feet high was poorer in oxygen. The modern results were achieved by the very satisfactory collaboration between the team of physicists and engineers in the University of Michigan who succeeded in obtaining the air samples with rockets, and the chemists in the University of Durham who did the microanalyses of the rare gases. The workers on the American side, sponsored by the U.S. Army Signal Corps, were L. M. Jones, L. T. Loh, H. W. Neil, M. H. Nichols, and E. A. Wenzel; those in Durham, K. F. Chackett, P. Reasbeck, and B. S. Wiborg. The analytical methods have been developed successively in four different University Laboratories, Berlin, Koenigsberg, London, and Durham, and the work done by the Durham group would not have been possible without the previous efforts of their predecessors; it seems appropriate, therefore, to add here the names of those who during the last 25 years in an unbroken tradition have contributed to the development of the techniques now applied in Durham: K. Peters, H. Gehlen, P. L. Gunther, Wm. D. Urry, W. Hofeditz, K. Loleit, E. Gluckauf, and W. J. Arrol.

Many more analyses, and from still greater heights, will be needed before we can hope to obtain a clear insight into the working of gravitational separation in the stratosphere. The present technique for sampling and analysing ought, with some improvements, to be applicable up to altitudes of about 100 km.

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