STUDIES IN ATMOSPHERIC OZONE

ABSTRACT

of a Thesis

by

M. Grigge, B.A.

Oriel College.



It has been known for many years that the variations, annual and day-to-day, in total ozone are caused by air movements in the stratosphere. To follow these air movements in detail, it is essential to measure the vertical distribution of ozone in the atmosphere.

To date, only one instrument has been capable of measuring the fine structure of the ozone distribution. This is the transmogrifier developed by Brewer and Milford (1960). Unfortunately it is complicated in construction and is difficult to use.

A new detector, the bubbler, is described. It is similar in principle to the transmogrifier, but is much simpler in both design and use. The detector is a galvanic cell with a platinum cathode and silver anode in buffered potassium iodide solution. The air containing ozone is bubbled through the solution, and the ozone is removed:

$$2KI + O_3 + H_2O \rightarrow 2KOH + I_2 + O_2$$

The iodine reaches the platinum cathode by the mixing action of the bubbling, and the iodide ion is formed:

$$I_2 + 2e \rightarrow 2I^-$$

This iodide ion is then removed from the solution at the silver anode:

$$2I^- - 2e + 2Ag \rightarrow 2AgI.$$

Thus, each ozone molecule entering the solution causes the passage of two electrons through the cell and external circuit. The detector is coulometric and gives a continuous measurement of the ozone with an exponential response time of about 20 seconds. For atmospheric concentrations of ozone, the bubbler output current can be up to 7μa, which is easily measured.

The design of the bubbler, which is moulded in polystyrene, is perhaps unexpected, in that the air is taken through the pump and blown into the solution. In fact, little or no ozone is destroyed in the pump. Experiments were conducted to choose the best plastic materials, for the construction of the bubbler and pump, and the best lubricating oil for the pump. By certain treatments of the bubbler and pump, it is possible to keep the ozone losses below 8%. This is a small disadvantage

compared with the advantages of a blowing system which are listed.

The bubbler is incorporated into an ozonesonde, using much the same auxiliary equipment as used with the transmogrifier, although modification of the transductor which converts the d.c. ozone current into an audio signal for transmission by the Kew sonde, has given improved performance.

Investigation of the temperature effects on the ozonesonde shows that a correction for a change in sensitivity of the transductor must be made. This was not realised with the transmogrifier, and the results obtained with it may be up to 10% low near the top of the ascents.

The possible errors in the results are examined, and the maximum error in the absolute values is about ±20% or 1×10^{-3}cm/km, whichever is larger. Changes in ozone readings during a flight are significant if they are greater than ±15% or 1×10^{-3}cm/km. Analysis of the flights suggest that, in fact, the absolute accuracy of the results is better than indicated.

More than 60 flights, with very few failures, have been made at Liverpool, Nairobi and Malta. Most flights were made at Liverpool once a week for over a year. The

flights at Nairobi are the first to give detailed ozone structure near the equatorial tropopause, and they show only small ozone concentrations just above it.

Two approaches are made to extract as much information as possible out of the Liverpool series of ascents. The first is to consider the variations of ozone and temperature in stratospheric layers in conjunction with the changes in total ozone. The second method is to consider the ozone and vorticity changes at three pressure levels in the lower stratosphere.

Consideration of the ozone and temperature changes in layers enables a tentative discussion to be made about the mechanism of the day-to-day changes in the ozone distributions. The discussion is necessarily tentative due to the lack of a statistically significant number of ascents.

The discussion suggests that in the period August to January, before the breakdown of the polar vortex, vertical movement is the main cause of ozone changes between the tropopause and 50mb. Between 50mb. and 25 mb, the lower limit of the photochemical equilibrium layer, advection is the main cause. Advection from the north (south) is generally associated with ascent (subsidence) in the lower layers.

In the period January to August, it is suggested that advection is the main cause of ozone changes right up to 25mb., although vertical movement is playing a large part in the lowest levels of the stratosphere. The results for the stratosphere below 100mb. are confirmed in another tentative discussion based on the ozone-vorticity-temperature variations at 100mb, 150mb and 200mb.

A brief discussion of the equatorial tropopause is made on the basis of the Nairobi ascents, and it is concluded that the air is rising through the tropopause.

Finally, a brief discussion of the long-period use of a glass bubbler for surface measurements is given, along with some interesting results obtained in aircraft.

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M. Griggs, B.A.

Oriel College.

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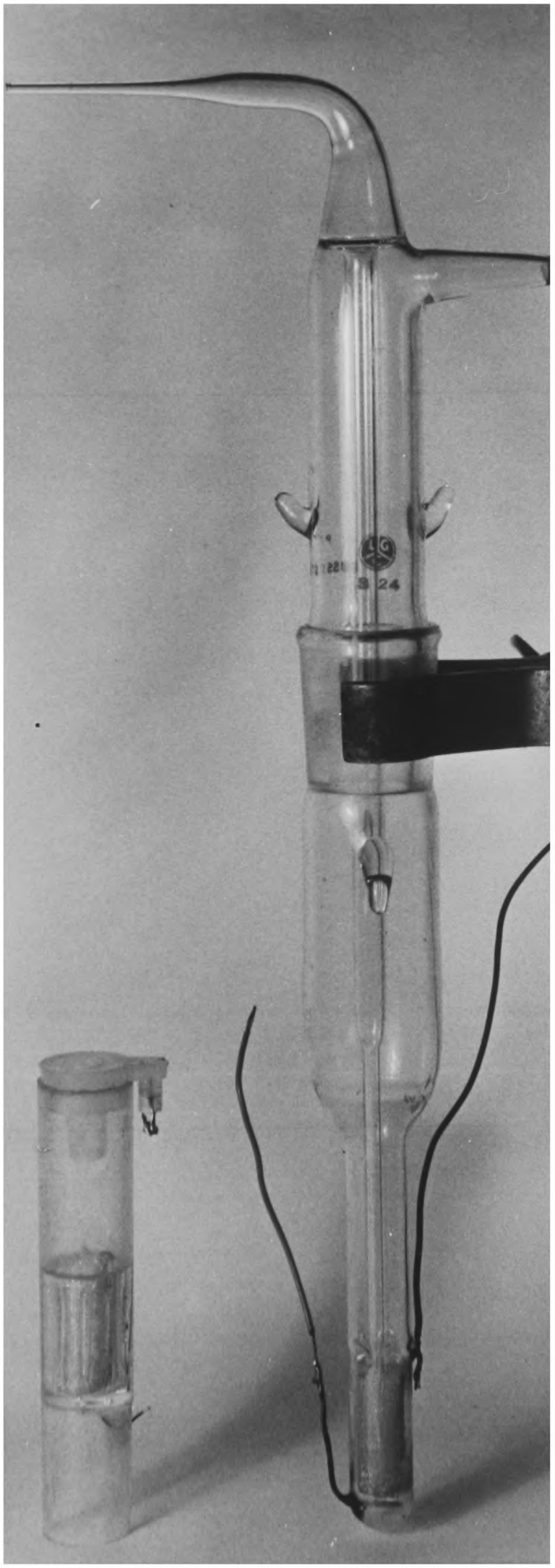
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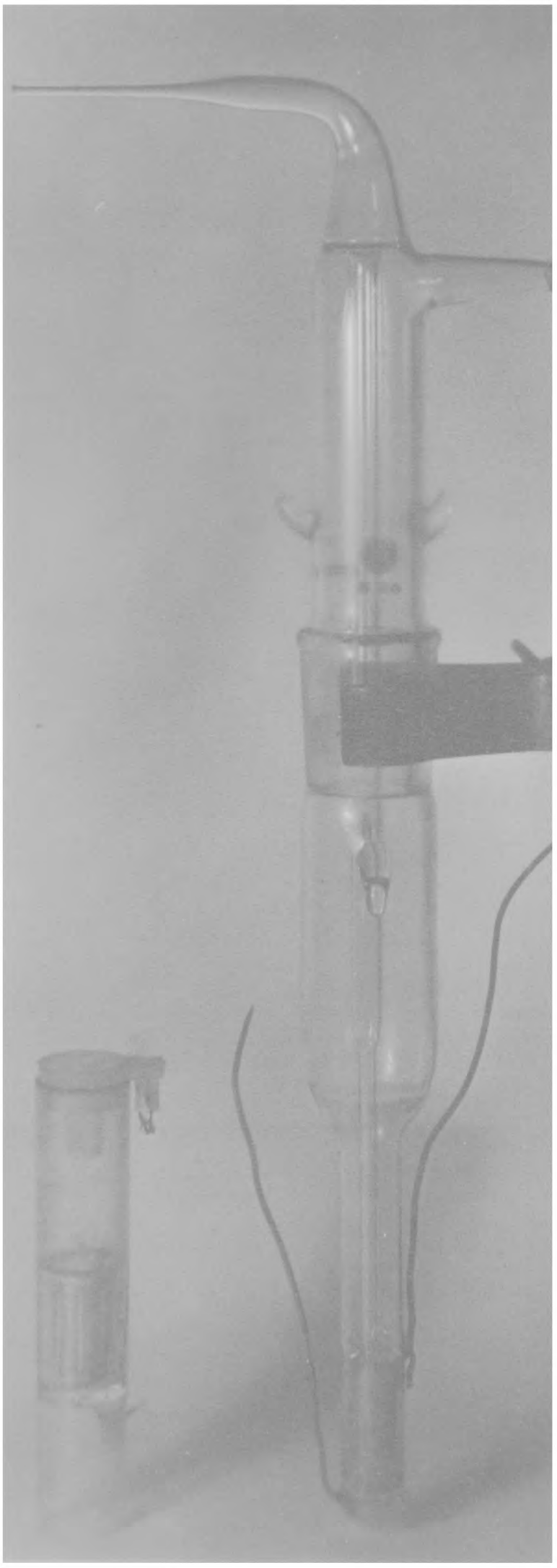
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CHAPTER I.

AN INTRODUCTION

TO

ATMOSPHERIC OZONE.

Ozone is present in the atmosphere in only very small quantities (a few parts per hundred million of air), but is a useful, if not essential, constituent. In addition to its meteorological significance, it prevents much harmful ultra-violet solar radiation from reaching the earth and, being a powerful oxidizing agent, it has a cleansing effect on tropospheric air.

These optical and chemical properties enable atmospheric ozone to be measured accurately. The present work concerns a chemical method, but since most measurements have been made spectroscopically a brief outline of the absorption spectrum of ozone is given.

Gaseous ozone absorbs in bands in the ultra-violet, visible, and infra-red. In the ultra violet, absorption is mainly in the Hartley bands (2000 - 3200 Å). On the long wave side of these are the Huggins bands (3200 - 3600 Å) which are weaker but sharper than the Hartley bands. In the visible region, absorption on a lesser scale occurs in the Chappuis bands (4400 - 7400 Å). Then in the infra-red the main absorption is in the 9.6μ band.

Ozone was first suggested as a constituent of the atmosphere by the chemist Schonbein in 1840 and was proved,

chemically, to exist by Houzeau in 1858. However, it was not until 1913 that the ozone was shown conclusively to exist mainly in the upper atmosphere by Fabry and Buisson (1913) who estimated the amount of ozone in the atmosphere from measurements on the ultra-violet absorption by ozone.

Atmospheric ozone became of real meteorological significance as a result of Dobson's work. He developed the technique of Fabry and Buisson into a precise and convenient measurement of total ozone above an observer and used his method for world-wide observations (Dobson, 1930).

Dobson's work showed that the total ozone varies in two ways; there is an annual variation which is systematic, both with changing season and latitude, and there are large daily departures from the mean which are related to the synoptic meteorological conditions. Some details of these will be discussed later.

To explain the presence of atmospheric ozone, Chapman (1930) put forward a photochemical theory which has been developed by many authors, notably Lutsch (1946) and Craig (1948). The main predictions do not agree with observation, and the theory must be outlined before discussing the characteristics of atmospheric ozone.

Photochemical Theory of Atmospheric Ozone.

The photochemical production of ozone occurs in the

upper levels of the atmosphere through the dissociation of molecular oxygen by ultra-violet solar radiation. The dissociation energy of molecular oxygen corresponds to a wavelength of 2400 Å. Oxygen absorbs energy below this wavelength in the Herzberg, Schumann and Hopfield bands. This process produces atomic oxygen which can form an ozone molecule by combining with molecular oxygen in a three-body collision. A three-body collision is necessary to permit energy and momentum to be conserved. Ozone also, is dissociated by radiation. The minimum photon energy corresponds to a wavelength of 11000 Å, and dissociation occurs in the Hartley, Huggins and Chappuis bands. These opposing effects result in an equilibrium layer of ozone being established above about 30 km.

A mathematical model for the distribution of ozone may be obtained after rather complex computations involving these reactions and other properties of the atmosphere. The results indicate that there should be a maximum in the Summer and a minimum in the Winter, with a maximum at the equator decreasing towards the poles throughout the year. This latter effect should be more noticeable in the Winter. In the vertical, the ozone maximum at the equator should be at a lower level than at high latitudes.

These deductions are based on equilibrium conditions,

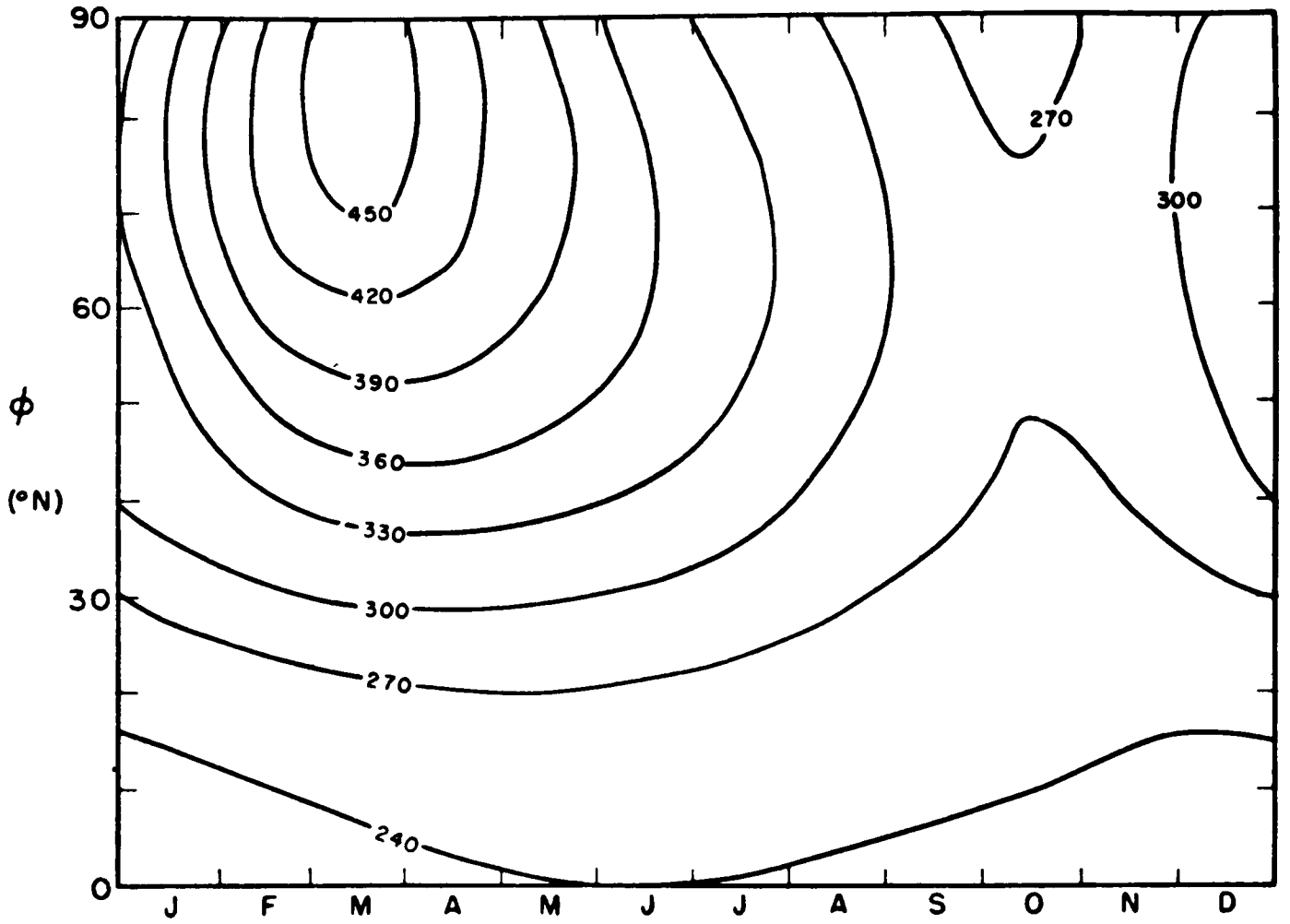


Figure 1. Mean distribution of total ozone as a function of month and latitude.

which may not exist except above the level of maximum ozone density. Calculations show that if the ozone were suddenly destroyed at any level, then the time for half the equilibrium ozone content to be restored photochemically would be about 1 day at 40 km., several days to several months between 30 and 25 km., and more than a year below 20 km.

Thus in the lower atmosphere the ozone, measured as an ozone/air mixing ratio, is a quasi-conservative property of the atmosphere.

Observed Characteristics of Atmospheric Ozone.

Annual variations.

Since Dobson's early work, a large number of total ozone measurements have been made with his spectrophotometer, and the same general results have been obtained. The results for the Northern hemisphere are summed up in fig. 1, adapted from Normand (1953). The total ozone shows an annual variation consisting of a roughly sinusoidal wave-form through the year with the amplitude increasing with latitude. The maximum of this seasonal variation occurs in the Spring and the minimum in the Autumn. Corresponding to the Spring maximum is a maximum latitudinal gradient of ozone, while in the Autumn the gradient is small.

In addition to these variations within the hemisphere,

there are differences between the two hemispheres, particularly in high latitudes. MacDowall (1960) found that the sharp seasonal increase of total ozone in the Antarctic occurs about three months later than in the Arctic. Also, in the early Spring months in the Southern hemisphere, less ozone is found at the highest latitudes, thus showing a reversal of the normal latitudinal gradient found in the Northern hemisphere. These differences may be due in part to the widely different climatology of the two polar regions, for Ramanathan (1960) found that there is a large geographical influence on the total ozone. However, the results suggest that there is a profound difference between the general circulations of the two hemispheres.

It is seen that observation, particularly in polar regions, is in complete disagreement with the photochemical theory, and in view of the quasi-conservative property of ozone in the lower stratosphere we must look to large scale air movements to account for these discrepancies. Since the time scale involved is a year, these air movements must be part of the general circulation of the atmosphere.

Hence ozone may be used as a tracer gas in the general circulation.

Day-to-day variations.

Dobson and Harrison (1926) showed that on individual

days, there is much deviation from the annual mean. Day-to-day variations in total ozone are related to the surface weather conditions, there being a tendency to high ozone values to the West of cyclonic centres, and low values within anticyclones.

Photochemical processes cannot explain these phenomena, and the daily changes must result from the redistribution of ozone already present.

Advection was first proposed as the reason for these daily variations, but this simple theory cannot apply in the Autumn when the latitude gradient is low. However, since the amplitude of the daily fluctuations has a maximum in the Spring, corresponding to the seasonal maximum of latitudinal gradient, advection may play some part in the variations.

The variations may be explained by a combination of advection and vertical movement, subsidence or lifting. Reed (1950) estimated that for the maximum deviation of the total ozone from the mean, only one third could be due to vertical movement, the remainder being due to horizontal advection.

<u>The Vertical Distribution of Ozone.</u>

It is apparent from the preceding sections that the most important meteorological use of ozone is as a tracer

gas for following air movements. However, measurements of the total ozone alone are insufficient, and a knowledge of the vertical distribution of ozone in the atmosphere is essential. This is best achieved with measurements at a network of ozonesonde stations (comparable with that of the radiosonde stations) in conjunction with total ozone observations with the Dobson instrument. It should then be possible to distinguish between advection and dynamical effects in local day-to-day variations; and, on a global basis, to further the understanding of the general circulation.

Results of measurements.

Many measurements of the vertical distribution have been made by spectroscopic methods, both from the ground and from balloons and rockets. Unfortunately, as discussed in the next chapter, these methods can give only the broad picture of the distribution. They show a maximum concentration of ozone between 25 and 30 km., and above 30 km., where the methods are most accurate, the results show general agreement with the photochemical theory. In addition, they indicate that the annual variation in total ozone is almost entirely accounted for by variations in the amount in the lower stratosphere. The results of Brewer and Milford (1960), obtained with a chemical ozonesonde

confirm this, and demonstrate that much interesting fine structure is missed by spectroscopic methods.

The General Circulation.

To make the best use of ozone measurements in the problem of the general circulation, it is necessary to obtain regular meridional vertical cross-sections of the ozone distribution. This was not achieved in the present work, although results were obtained in England, Malta and Nairobi.

Of special interest is the nature of the equatorial tropopause, about which there is little information. Ramanathan (1954), Dobson (1956) and Brewer (1959) proposed meridional circulations based on the then-existing knowledge of the distribution of carbon dioxide, water vapour and ozone. Dobson and Brewer show an upward movement of air through the equatorial tropopause, while Ramanathan shows motion towards higher latitudes, parallel to, and on either side of the equatorial tropopause. Another variation is given by Staley (1957) in a general theory of the tropopause. He suggests that there should be downward transport through the tropopause.

Radiation Calculations.

There is another problem in meteorology for which the vertical distribution of ozone is required more precisely. This is the calculation of the radiative heat

exchanges in the lower stratosphere. Exchange of heat between different layers is by long wave radiation, and the 9.6μ band of ozone is a significant contributor. Data are available on most of the other contributions, particularly water vapour and carbon-dioxide. Calculations will be complicated by the wide variety of distributions found, but they will be more reliable if they can be based on more detailed observations than provided by spectroscopic methods.

Objects of Present Work.

The primary object was to perfect a more simple and more reliable ozonesonde than has been available in the past, for measuring the vertical distribution of atmospheric ozone. Having done this, the next aim was to follow the variations of total ozone in conjunction with changes in the vertical distribution. This would prove the instrument in field use over a long period, and it was then to be used in a large-scale programme to elucidate the problem of the general circulation.

The first two aims were achieved, and the third was attempted, but only partially fulfilled.

CHAPTER II.

MEASUREMENTS OF THE VERTICAL DISTRIBUTION OF ATMOSPHERIC OZONE.

Methods of measuring the vertical distribution of ozone in the atmosphere may be conveniently divided into two groups: spectroscopic methods for ground-based or airborne equipment, and chemical methods for airborne use.

Measurements in the Ultra-violet.

Ground-based apparatus

The Dobson spectrophotometer was designed to measure the total ozone between the sun and the observer, by finding the relative intensities of two wavelengths in the Hartley absorption band of ozone. The wavelengths are chosen so that the difference in emitted intensities is small, while the difference in absorption by ozone is large (e.g., 3110 and 3290 Å).

The Dobson instrument may be used to determine the vertical distribution by making measurements on the zenith sky instead of direct sunlight. This is the "Umkehr" method due to Götz, Meetham and Dobson (1934) who found that the ratio of the intensities of two wavelengths, chosen as above, changed with solar zenith angle. For large values of the zenith angle, ie., near sunset or sunrise, this ratio decreases with increasing zenith angle, reaches a minimum and then increases. It is this

"turned up" curve from which the method derives its name. The way in which the ratio of intensities changes depends upon the vertical distribution which can thus be determined. The computation involved is very complicated, and even then, the distribution is obtained only as mean ozone values in 4-9 km layers of the atmosphere, and is inadequate for determining any fine structure in the lower atmosphere. The Umkehr method cannot be used satisfactorily with cloudy skies, and the presence of haze in the atmosphere makes the results difficult to interpret.

Airborne apparatus.

A number of rocket-and balloon-borne spectrographs have been devised, using a system of filters to isolate the necessary wavelengths (Johnson et al (1952); Coblentz and Stair (1939); Paetzold (1954); Vassy (1958)). As the instrument ascends, it measures the total ozone remaining above it, and the ozone at any level is obtained from the differential of the measured quantity. In the lower atmosphere this leads to inaccuracies as the ozone is measured essentially by the difference of two large quantities. These instruments can be used only with the sun well above the horizon; also haze or cloud confuses the results in the lower atmosphere.

An attempt was made by Regener (1954) to obtain a more direct measurement of the vertical distribution,

using a spectroscopic method. He used a balloon-borne spectrograph carrying its own light source, a hydrogen discharge lamp, on an extended rig to give a light path of 300 m. The excessive practical difficulties prevented any useful results being obtained.

Measurement in the infra-red.

Ground level observations of the atmospheric emission spectrum in the region of the 9.6μ ozone band, have provided measurements of the vertical distribution of ozone, but are still unable to show any fine structure. Indeed, the distribution is obtained in terms of only three layers of the atmosphere, and the interpretation of the results is very subjective. Measurement cannot be made on cloudy skies.

However, some consider there to be merits in the method. Walshaw (1960), a prominent contributor, says "The observations are simple and the necessary equipment relatively inexpensive, while the interpretation of the results, though involving considerable computation, is fundamentally straightforward. The 'continuous' absorption over this spectral region is indeed a serious complication, but its origin has now been almost certainly identified with the absorption caused by accumulated wings of distant lines in water vapour bands. Against this may be set the very great advantage over the ultra-violet region in that

atmospheric haze is virtually negligible at these wavelengths".

Chemical Measurement.

Chemical sampling is very suitable for local measurement, for ozone is a strong oxidising agent and so, even in its very small concentrations, extraction from the air is no problem. Many devices have been made for measuring surface ozone, and in recent years both "wet" and "dry" chemical ozonesondes have been developed.

"Wet" Chemical Methods.

The reaction most commonly used is the oxidation of potassium iodide in aqueous solution to give iodine.

$$2KI + O_3 + H_2O = 2KOH + I_2 + O_2$$

The iodine produced is measured, and it is in the iodometry that techniques vary.

The usual method is that of titration with a standard sodium thiosulphate solution. In the method due to Paneth and Gluckauf (1941) the air, with ozone, is passed through potassium iodide solution, containing a known weight of sodium thiosulphate. The iodine formed reacts with the thiosulphate until eventually there is free iodine in the solution. The presence of this iodine is detected by the passage of a current between two platinum electrodes in the solution. A potential difference

is maintained between the electrodes, so that no current passes until free iodine is formed. The onset of this current indicates the end point of the titration.

This method was adapted for automatic measurements on the ground (Gluckauf et al, 1944). The current at the end point is amplified to trigger the injection of a fresh quantity of solution with thiosulphate into the reaction chamber. The time interval between successive triggerings gives a measure of the mean ozone concentration over that period.

Regener (1957) developed an ozonesonde based on this method. The resulting equipment was complex and bulky, and he achieved only a few ascents. A great disadvantage, apart from its complexity, is that it does not provide much more detail in the lower stratosphere than the airborne spectroscopic ozonesondes. This is because the ozone is measured as the average concentration in a layer whose thickness is dependent on the thiosulphate amount and ozone concentration. In the lower atmosphere where the ozone concentration is small, the thickness will be large and detail will be missed. The sensitivity cannot be improved without increasing the inaccuracies.

A great advance was made by Brewer and Milford (1960) who developed the transmogrifier, a continuous detector

for use on an ozonesonde. The transmogrifier is based on the familiar reaction of ozone with potassium iodide which yields one molecule of iodine for each molecule of ozone. The method of measuring this iodine is different. Each iodine molecule is brought to the surface of a platinum wire cathode, where it takes up two electrons, and is reduced to two iodide ions. The reverse reaction occurs at a platinum wire anode, and the iodide ions are oxidized to iodine:

Cathode $I_2 + 2e \rightarrow 2I^-$

Anode $2I^- - 2e \rightarrow I_2$

Thus with the passage of two electrons, one iodine molecule is transferred from cathode to anode.

The iodine made at the anode is prevented from returning to the cathode by the geometrical arrangement, and by continuous flow of the solution past the electrodes. So, only iodine made directly by the ozone will cause the flow of electrons.

An ozonesonde was developed around the transmogrifier, and many flights were made, measuring the fine structure of the vertical ozone distribution in the lower stratosphere for the first time. Unfortunately, the transmogrifier proved unreliable in field use, requiring lengthy preflight preparation and proving difficult for

inexperienced handlers to use.

A simpler and more reliable detector has been developed from the transmogrifier, and is described in detail in this thesis.

"Dry" Chemical Measurement.

There is a limitation to the altitude at which a "wet" chemical ozonesonde employing aqueous solutions can function without freezing. This has not proved to be a practical limitation, as balloons used on routine ascents seldom reach this limiting height of about 6 mb (34 km).

Recently, Regener (1960) has described a new ozonesonde which has the elegant features of being dry, and having a substantially instantaneous response. It employs the luminescence of a dry substance, luminol, in the presence of ozone. The intensity of light emitted by the luminol depends upon the ozone concentration, and is measured by a photomultiplier. This is not an absolute method, and the calibration of the instrument is difficult.

Comparison of Methods.

Little work has been done on direct comparison of methods to measure the vertical distribution, and the only published results are those obtained in 1958 at Arosa (Brewer et al, 1960). The Brewer-Milford and Paetzold sondes were compared with the indirect Umkehr

and infra-red observations. The distributions obtained generally agreed on the broad features, but there were some notable disagreements. These were probably due firstly to the subjective nature of the analysis of data from the infra-red observations and from Paetzold's sonde, and secondly, to the presence of haze or cloud in the atmosphere which can confuse these methods.

The overall results confirm that the optical methods are most useful at high levels, while only the chemical sonde will show fine structure in the lower levels.

Vertical Distribution Measurements in Practice

In addition to the necessity of accurately measuring the ozone, an ozonesonde must be suitable for extensive use, and a brief assessment of current and recent sondes is given in this respect.

The Paetzold Optical Sonde.

This is a complicated, heavy and expensive apparatus. It cannot be used at night. The evaluation of the flight data is complex and extremely subjective, and takes days rather than hours to produce the final ozone distribution. A fair number of successful flights have been made.

The Vassy Optical Sonde.

This is much simpler in design than the Paetzold sonde, but data reduction is still lengthy. Results have

not been published in detail.

The Regener Chemical Sondes.

"Wet". This is heavy and bulky due to complicated servo-mechanisms, and preflight preparation requires much skill. Evaluation of data is rapid, the ozone distribution being available within an hour of the ascent. Very few ascents have been made, and this sonde has been superseded by the "dry" chemical sonde.

"Dry". This offers great possibilities as it does not have the altitude limitation of the "wet" chemical sondes. However, it is heavy, expensive, and difficult to calibrate. It has yet to be proved in many flights, and much work must be done before it is capable of use on a routine basis.

The Brewer-Milford Chemical Sonde.

This is smaller, cheaper and simpler than the other sondes, but still requires a certain skill in preparation; it can take up to two hours to prepare for flight. Data reduction is rapid. Many successful flights have been made, but eventually the preparation difficulties and a high failure rate led to the abandonment of the transmogrifier and the development of the present detector - the bubbler.

The Bubbler Sonde.

This sonde is described in detail in this thesis, but a brief mention of it is made here to complete the comparison of ozonesondes.

The detector itself is most simple in design and use, with the result that preflight preparation of the sonde can be completed in less than fifteen minutes, making it markedly superior to the transmogrifier sonde. The auxiliary equipment of the bubbler sonde is essentially the same as that used with the transmogrifier, but modification and improvement has led to more accurate ozone data. The reduction of this data, as with the other chemical sondes, is exceedingly rapid. More than 60 successful flights, with very few failures, have been made.

CHAPTER III.

THE BUBBLER - THE SIMPLEST OZONE DETECTOR.

This new detector, the bubbler, is much simpler and more reliable, both in construction and in use, than any previous detector, and measures ozone continuously. It is easily adapted for use on an ozonesonde, and has satisfied a long-standing need for an ozonesonde which is easy to prepare and fly. The Brewer-Milford ozonesonde went far to meet this requirement, but the transmogrifier was still complicated and difficult to use. It was necessary to send four pages of instructions to users, and it could take up to two hours to make the transmogrifier work satisfactorily. This difficulty led to the development of the bubbler, which is made ready for use simply by pouring 2 cc of buffered potassium iodide solution through its open top.

Principles of Operation.

The bubbler relies on the potassium iodide-ozone reaction, and the method of measuring the iodine is similar to that of the transmogrifier. The method of removing the iodine is different.

The detector consists of a combined reaction and electrolytic cell containing 2 cc of 0.1 buffered potassium iodide solution. The cathode is a platinum gauze

and the anode a silver wire. This cell has a spontaneous e.m.f. which is balanced by an external e.m.f. of about the same magnitude. The air is bubbled through the solution and the ozone is removed according to the equation:

$$2KI + O_3 + H_2O \rightarrow 2KOH + I_2 + O_2.$$

The iodine reaches the platinum cathode by the mixing action of the bubbling, and the iodide ion is formed:

$$I_2 + 2e \rightarrow 2I^-.$$

This iodide ion is then removed from the solution at the silver anode to form practically insoluble silver iodide:

$$2I^- - 2e + 2Ag \rightarrow 2AgI.$$

Thus, for each ozone molecule entering the solution, two electrons pass through the cell and external circuit. The current in the circuit is then coulometrically equivalent to the ozone intake, giving a direct continuous measurement of the ozone. For atmospheric concentrations of ozone, this current can be up to 7μa, which is easily measured.

<u>Electrochemistry of the bubbler</u>.

The basic chemical reactions for the oxidation of potassium iodide in aqueous solution by ozone, and the conduction of electricity in such a solution when free iodine is present are as follows:

Firstly potassium iodide is oxidized to iodine:

$$2KI + O_3 + H_2O = 2KOH + I_2 + O_2 \qquad ...(1)$$

This iodine is reduced at the platinum cathode:

$$I_2 + 2e = 2I^- \qquad ...(2)$$

At the silver anode, silver iodide, which is effectively insoluble in dilute potassium iodide, is formed:

$$I^- - e + Ag = AgI. \qquad ...(3)$$

It is possible to use a mercury anode so that mercurous iodide, which is even more insoluble, is formed. However, a silver anode has always been used for practical convenience. Other base metals may be used as the anode, but the appearance of the metallic anion in the solution gives trouble.

These electrode reactions result in the electrochemical cell functioning as a galvanic cell i.e., the cell has a spontaneous e.m.f., and a current flows when the electrodes are connected externally.

Electrode Potentials.

It may be shown (e.g., Lingane 1953 p.29) that when the generalized electrode reaction

$$aA + bB + \ldots = cC + dD + \ldots$$

proceeds under conditions of thermodynamic reversibility, the potential of that electrode may be written as

$$E = E^O - \frac{RT}{nF} \ln L \qquad ...(4)$$

where R is the molar gas constant, T is the absolute temperature, n is the number of electrons associated with

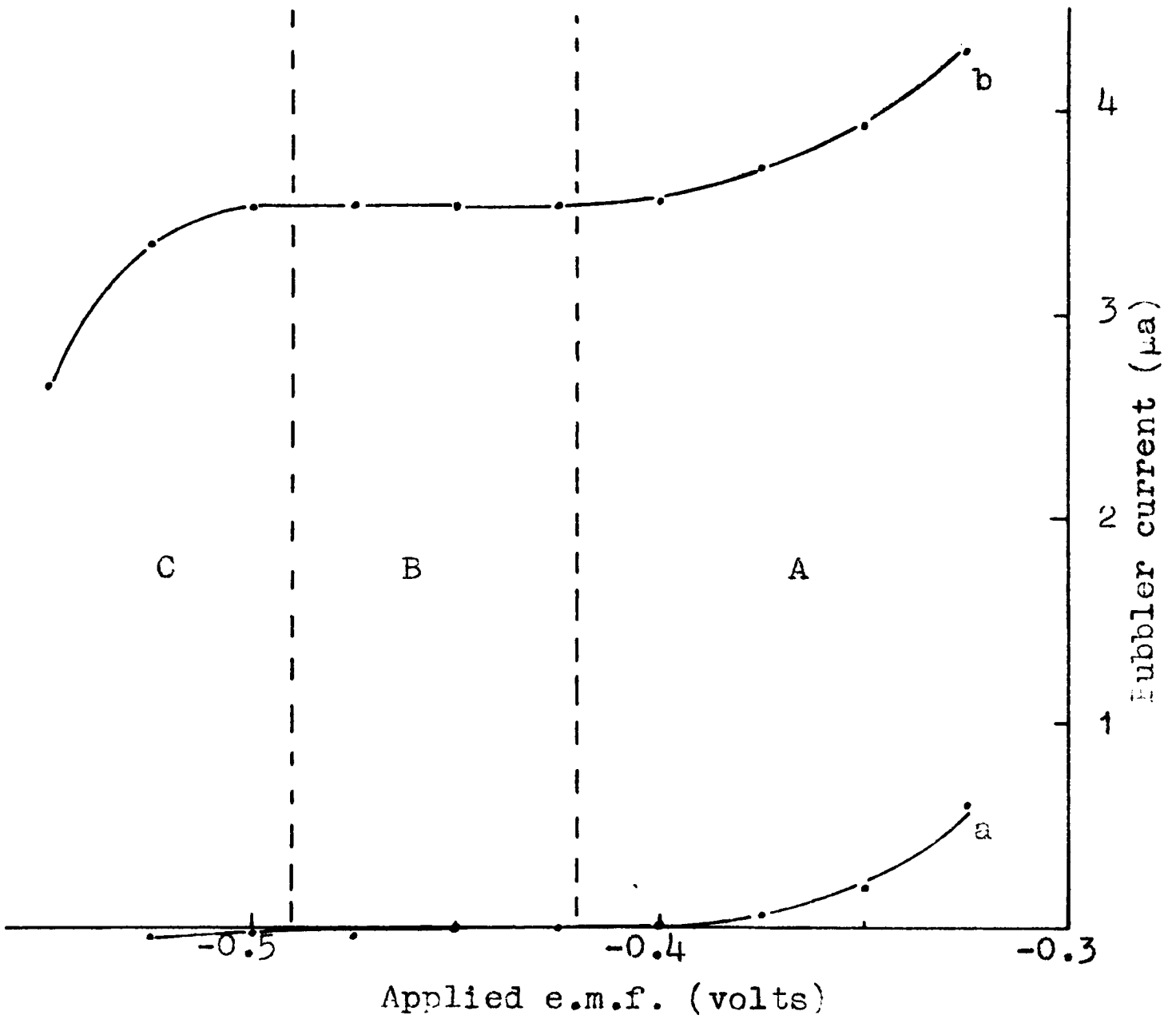


Figure 2. Variation of bubbler output current (b) and zero current (a) with applied e.m.f.

the reaction, F is the faraday and $L = \frac{(C)^c(D)^d \ldots}{(A)^a(B)^b \ldots}$ (A) (B) (C) (D) ... denote molar activities which, in dilute solutions, are approximated by concentrations. E^o is the standard potential and is the value of E when L = 1 At 25°C $E = E^o - \frac{.059}{n} \log L$.

For the reaction (2) at the platinum cathode E^o = 0.62V with respect to the standard hydrogen electrode, and so

$$E = 0.62 - \frac{.059}{2} \log \frac{(I^-)^2}{(I_2)}$$

For the anode reaction (3) E^o = 0.15V, so that

$$E = 0.15 - .059 \log \frac{1}{(I^-)}$$

The electrode potentials are not the same and the cell has a spontaneous e.m.f. given by the difference of these potentials.

$$E = 0.47 - \frac{.059}{2} \log \frac{(I^-)^2}{(I_2)} + .059 \log \frac{1}{(I^-)}$$

Since (I^-) is constant this equation reduces to

$$E = \text{Constant} + \frac{.059}{2} \log (I_2) \qquad \ldots(5)$$

It is observed that for a tenfold change in (I_2) the e.m.f. changes by about .03 volts.

This spontaneous e.m.f. is opposed by an equal external e.m.f., so that no current passes except when iodine due to ozone (equations (1) (2) and (3)) changes the spontaneous e.m.f.

If this external e.m.f. is varied while the ozone input is kept constant, then curve (b) in fig. (2) is obtained.

If the ozone input is zero, and air only is bubbled

through the cell then curve (a) is obtained.

Explanation of fig. 2.

In aqueous potassium iodide solution there exists the reversible reaction:

$$4KI + 2H_2O + O_2 \rightleftharpoons 4KOH + 2I_2 \qquad \ldots(6)$$

This reaction will normally be in equilibrium, and there will be an equilibrium value of the iodine concentration.

In ad ition to this chemical equilibrium there is an electrochemical equilibrium between the cell e.m.f. and the opposing external e.m.f. Thus there will be an electrochemical equilibrium value of the iodine concentration. This will vary with the value of the external e.m.f. according to equation (5).

It is found that the cell is in equilibrium with an external e.m.f. of about 0.4V. The iodine concentration necessary for this electrochemical equilibrium will be that concentration which provides chemical equilibrium by reaction (6).

Zero Ozone Current.

In region A, the external e.m.f. is low, and for electrochemical equilibrium to exist the cell e.m.f. must be reduced by reducing (I_2) according to equation (5). This is achieved by a current passing according to equations (2) and (3). This disturbs the chemical

equilibrium, equation (6), and the reaction proceeds left to right to form iodine to restore equilibrium. Thus there is chemical production of iodine and electrochemical removal, resulting in a steady current.

This current is larger than the reverse current at corresponding high e.m.f's and is probably due to other reactions adding to this zero ozone current, such as:

$2H^+ + 2e \rightarrow H_2$ (cathode)

$I^- - e + Ag \rightarrow AgI$ (anode)

In region C, the external e.m.f. is high and iodine must be produced to maintain electrochemical equilibrium. A current passes in the reverse direction by the reverse of equations (2) and (3).

In region B, the cell is not far removed from electrochemical equilibrium, and in the dilute KI solution used, reaction (6) is too slow to produce any significant iodine changes for small disturbances of equilibrium. In concentrated KI solution the curves in fig. (2) would be displaced to a higher e.m.f. and the plateau in the curves, which are essential to the simplicity in the bubbler operation, would disappear.

Ozone curve.

When iodine is formed by ozone in the cell, the cell e.m.f. is raised according to equation (5), and a current

passes as shown in equations (2) and (3). This current passes in order to reduce the iodine concentration to its electrochemical equilibrium value.

The ozone current, curve (b) in regions A and B, is merely the sum of this ozone current and the zero ozone current.

In region C however, the ozone curve has a greater reverse current than would be expected from the zero ozone curve. This is because for zero ozone a reverse current flows in the external circuit, and the external opposing e.m.f. is reduced. Thus the iodine required for equilibrium is less, and a current smaller than expected at first sight, will pass. For the ozone curve, however, there is a forward current and the opposing e.m.f. is increased. Thus more iodine is required, and a greater reverse current flows.

Dilute KI Solution.

The KI solution must be dilute in order to obtain the plateau of the current e.m.f. curve, as was shown above. In addition to this, there are other reasons which may be mentioned.

(1) In KI solution, the following equilibrium must be considered:

$$I^- + I_2(aq) \rightleftharpoons I_3^- \; ; \quad K = 710.$$

In concentrated iodide solutions, much of the iodine exists as the triodide ion, with the result that the iodine concentration gradient at the cathode is reduced and the response time increases (see Chap. IV).

(2) Silver iodide is more soluble in concentrated iodide solution, and would interfere with the anode reaction.

Effect of Sunlight.

The cell must be protected from sunlight for two reasons.

(1) In acid medium the following reaction occurs:

$$4I^- + 4H^+ + O_2 \rightarrow 2I_2 + 2H_2O$$

In neutral medium it is extremely slow, but is greatly accelerated in direct sunlight.

(2) Also photolysis of the silver iodide on the anode occurs in sunlight.

A negative current passes if the bubbler is placed in direct sunlight, or even just daylight. This effect cannot occur in the ozonesonde unit, which is always in the dark.

Effect of Reducing Agents.

Two types of reducing agents have been observed when using the bubbler for surface ozone measurements.

(1) A negative current has passed due to iodine being removed from the solution by the reducing agent.

(2) Reducing agents have been stored in the KI solution without iodine being reduced. However, these reducing agents reduce ozone, and the bubbler does not register ozone until the stored reducing agent has been exhausted.

These effects have been observed on three or four occasions with the ozonesonde.

General Chemistry of O_3 - KI reaction.

This reaction has been examined thoroughly in the past, and is now well understood (e.g., Bowen and Regener (1951), Gluckauf et al (1944)), so only a brief summary is given here.

Specificity.

The oxidation of KI solution is not specific to ozone. The only substances in the atmosphere which will liberate iodine from KI solution are H_2O_2, SO_3 and NO_2. These are slow reactions, and it has been shown that only NO_2 is likely to be effective in neutral solutions. Even then NO_2 is only 2% as efficient as ozone in liberating iodine.

Stoichiometry.

Equation (1) is stoichiometrically correct only in neutral solutions with pH ranging from 5.5 to 8.

A phosphate buffer is used to preserve neutrality of the solution in the bubbler. It consists of 0.1 M solutions of sodium hydrogen phosphate and disodium hydrogen ortho-phosphate.

THE BUBBLER.

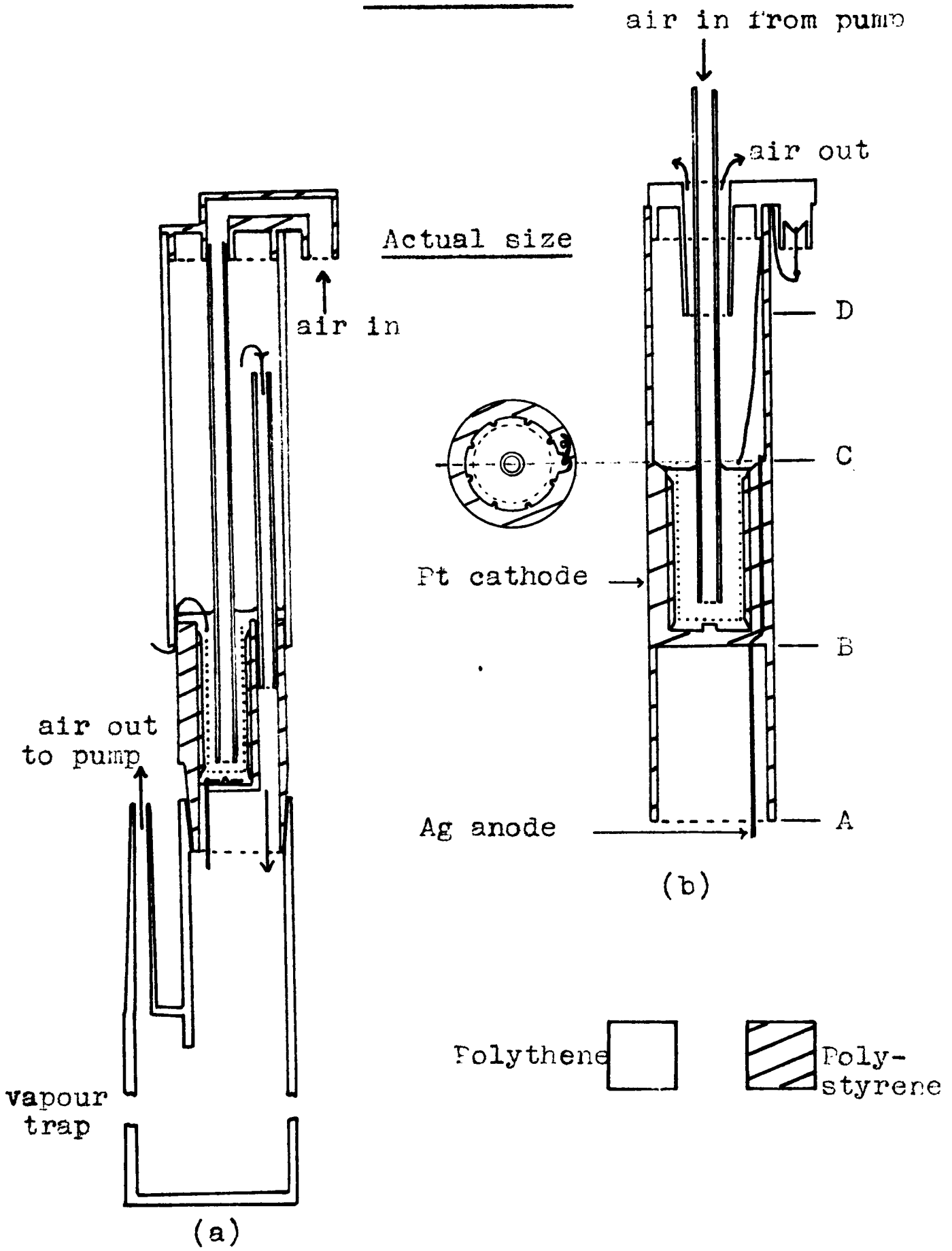


Figure 3. (a) Prototype sucking bubbler.
(b) Blowing bubbler.

CHAPTER IV.

DESIGN AND CONSTRUCTION OF THE BUBBLER.

The Prototype Bubbler.

In the original design for the bubbler (fig. 3a) as used on the ozonesonde, the air was sucked through the bubbler. This was used on several flights.

It was seen that much simplification in design and use could be achieved if the air were blown through the solution, passing through the pump before entering the solution.

The advantages of blowing may be listed:

(1) An airtight system is not needed. This is the main advantage, as the bubbler does not have to be touched in order to fill with solution at the ozonesonde station.

(2) Construction is much simplified, and the vapour trap, which is necessary to prevent water vapour being drawn into the sucking pump, is eliminated.

(3) The blowing pump will work at lower atmospheric pressures, since the blowing pump can always build up a pressure to force the air through the solution, whereas the sucking force is limited by the vapour pressure of the solution becoming comparable with the atmospheric pressure (see Chap. IX).

The only disadvantage, and it is a grave disadvantage at first sight, is that ozone will undoubtedly be lost as

the air passes through the pump.

It was decided that the advantages to be gained outweighed even this disadvantage.

Before the changeover could be made, it was necessary to carry out much experimental investigation into suitable materials to keep the ozone loss in the system to a minimum. The choice of these materials is described in chapter VI.

The results of this work are remarkable, in that the ozone losses in the system may be kept as low as 0-8%, and that scarcely any of this is lost in the pump.

The Final Bubbler.

The final design of the bubbler using a blowing pump is shown in fig. 3(b).

The diagram is self-explanatory, but some comments on detail are necessary.

Reaction Cell.

The bubbler is moulded in polystyrene. The moulding of this and other components of the ozone assembly is done in the laboratory, using a small hand-operated injection moulding machine.

The dimensions of the cell are chosen so that a minimum response time, and complete ozone extraction are obtained (see fig. 7, chap. V). The length AB below the

reaction cell plugs into a hole in the cork of the ozone assembly and retains the bubbler in an upright position.

The length CD above the reaction cell is made quite long, so that bubbles of solution carried up the side of the bubbler burst before reaching the open top.

Non-spill cap.

The cap of the bubbler is also moulded, but in polythene. Its design is based on the familiar non-spill inkwell, and the bubbler may be inverted without spilling the 2 cc of KI solution.

The cap carries a tag to which the platinum lead (42 S.W.G.) from the cathode is fixed. This lead is gripped between the cap and bubbler wall when the cap is pushed into position.

Cathode.

The platinum cathode cup, made of .003" × 80 mesh gauze, is kept slightly away from the walls of the reaction cell by ribs on the side, and a projection on the bottom. This is essential so that there can be free flow of solution through the gauze.

The cathode, after being cleaned by heating to white heat, is lowered by its lead into position in the reaction cell.

Anode.

The anode is a .025 in. diameter silver wire and is moulded into the bottom of the reaction cell. It is taken upwards in a groove between two of the ribs, and hooked round a small moulded projection at the top of the cell. The anode is arranged in this position as it was found that when coiled beneath the gauze as in the prototype, a bubble of air could form in the small space below the gauze, thus isolating the anode from the solution, and preventing the passage of a current.

Inlet Nozzle.

The inlet tube is polythene tubing, 2.5 mm. bore, 0.65 mm. wall thickness. It is 10 cm. long and is connected directly to the pump. The nozzle must be 1-3 mm. from the bottom of the gauze cup. It cannot be closer than 1 mm. without restricting the bubble formation and causing an undesirably large back pressure. The nozzle must not be further away than 3 mm. as this reduces the depth of solution in which the ozone is extracted from the air.

Design of Bubbler Reaction Cell

The bubbler cell must be designed to give the quickest exponential response time for changes in iodine concentration, consistent with complete ozone extraction from the air as it passes through the cell.

The response time depends both upon the external e.m.f. and upon the physical design of the cell. The best electrical configuration is found by experiment as shown in chapter V. The best physical design is based upon theory and experiment.

It is shown in Lingane (1953, p.191) that

$i_t = i_o e^{-kt}$ $\quad i_o$ = initial ozone current

i_t = current at time t.

and that the exponential response time is given by

$T = \frac{1}{k} = \frac{V\delta}{DA}$ where V = volume of KI solution

δ = thickness of diffusion layer

D = diffusion coefficient of I_2 in KI

A = cathode area.

Thus for a minimum value of response time T, δ and $\frac{V}{A}$ must be small and D large.

Cathode Area A.

The iodine formed by ozone must be brought to the cathode before a current can pass. This is achieved by stirring the solution - the bubbling action does this in the bubbler - to bring the iodine into the vicinity of the cathode, where it then diffuses across the diffusion layer. The rate of extraction of iodine from the solution, i.e., the response time, will be increased by presenting a large cathode area to the iodine, and a finely meshed platinum

gauze is used to make a cylindrical cup for the cathode. The cathode design is determined by solution flow considerations, as well as by maximum area requirements, and is discussed fully later in this chapter.

Solution Volume V.

Reduction in the volume of solution is limited by the extraction of ozone from the air. The bubbles of air must pass through a minimum depth of solution for the ozone to be completely extracted (see fig. 7, chap. V).

The diameter of the cell cannot usefully be reduced beyond a certain limit, determined by the bubble formation at the inlet nozzle. If the cell diameter is too small, then the formation of bubbles is impeded. This results in a large back pressure which reduces pumping efficiency; also the flow of solution is not so smooth and continuous, and the response time becomes worse.

Diffusion Layer δ.

This is kept small by the vigorous agitation of the solution by the bubbling action. δ decreases with increasing temperature as it varies directly with the viscosity.

Diffusion Coefficient D.

The diffusion coefficient cannot be controlled except by temperature changes. If the temperature is increased, D increases by about 2% per degree centigrade. No attempt is made to control D in the bubbler, except in so far as

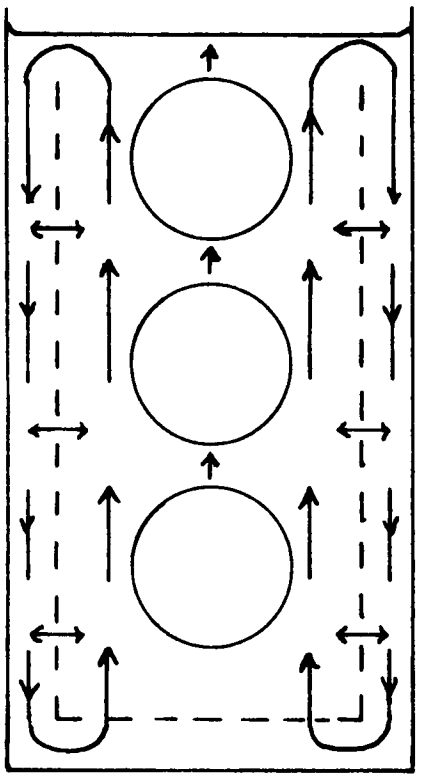


Figure 4. Diagrammatic illustration of motion of solution in the reaction cell due to the bubbling action.

dilute iodide solutions are used (see chap. III).

Extraction of I_2 from solution at the cathode.

As explained earlier, the response time of the bubbler depends on the rate of extraction of iodine from the solution at the cathode. This rate is increased by bringing the solution into contact with the maximum surface area of cathode and by continuous movement of the solution. The importance of a fine mesh gauze for the cathode and free flow of solution was investigated experimentally and theoretically.

Experimental.

The motion of the solution in the reaction cell was observed by adding to it, fine aloxite particles, the movement of which traced out the motion of the solution. It was apparent that there is a pulsating motion of solution in and out of the gauze, as well as the vertical motions (see fig. 4). This motion is due to the bubbling action. It was found, by observation under a stroboflash, that about 700 bubbles per minute are formed by the pump used on the ozonesonde. These bubbles cause the solution close to the walls of the cathode cup to pass into, and out of, the mesh once per bubble, i.e., more than 2[illegible] times per second.

It is thought that this pulsating motion is mainly

responsible for the reasonable response times (about 20 sec) obtained in practice. Indeed, experiment showed that the passage of solution through the mesh is essential for a good response. If a cylindrical cathode of platinum foil is used, then the response time is about 90 seconds. This response improves as pinholes are made in the foil.

Calculation.

It is possible to calculate the approximate rate of the extraction of iodine by diffusion, as the solution passes through the mesh gap, by analogy with the problem of heat conduction in a solid. Carslaw and Jaegar (1959, p.98) give graphical solutions for heat conduction in a parallel-sided slab. The iodine extraction problem may be simplified, and these curves applied, using the appropriate constants. The curves indicate that less than 2% extraction occurs each time the solution passes through the mesh. Thus, it is seen mathematically, that the solution must pass through the mesh many times to give the observed response time.

Optimum Mesh for the platinum cathode.

There are two opposing effects which determine the mesh for optimum response time. The mesh must be fine so that the iodine is more easily extracted by diffusion. At

the same time the mesh must not be so fine that the flow of the solution is restricted.

Precise mathematical calculations based on the diffusion and flow equations are impossible, due to the uncertainty of the exact conditions, and experiments were conducted to supplement simplified calculations.

Experiments with meshes of different sizes and with platinum foil for the cathode indicate that the finer the mesh the better the response, but as the mesh is made finer, so the diameter of the wire in the mesh must be decreased, so that the overall area available for flow through the mesh is not decreased to the point of restricting the flow.

With the bubbler, a .003" x 80 mesh has been used as it is the finest commercially available. The experiments and calculations suggest that a .002" x 160 mesh would be necessary to improve the response from 20 sec. to about 14 sec.

A mesh of this size would have the additional advantage of containing less platinum by weight, and would be cheaper, providing it was used on a sufficient scale to justify the manufacturing costs.

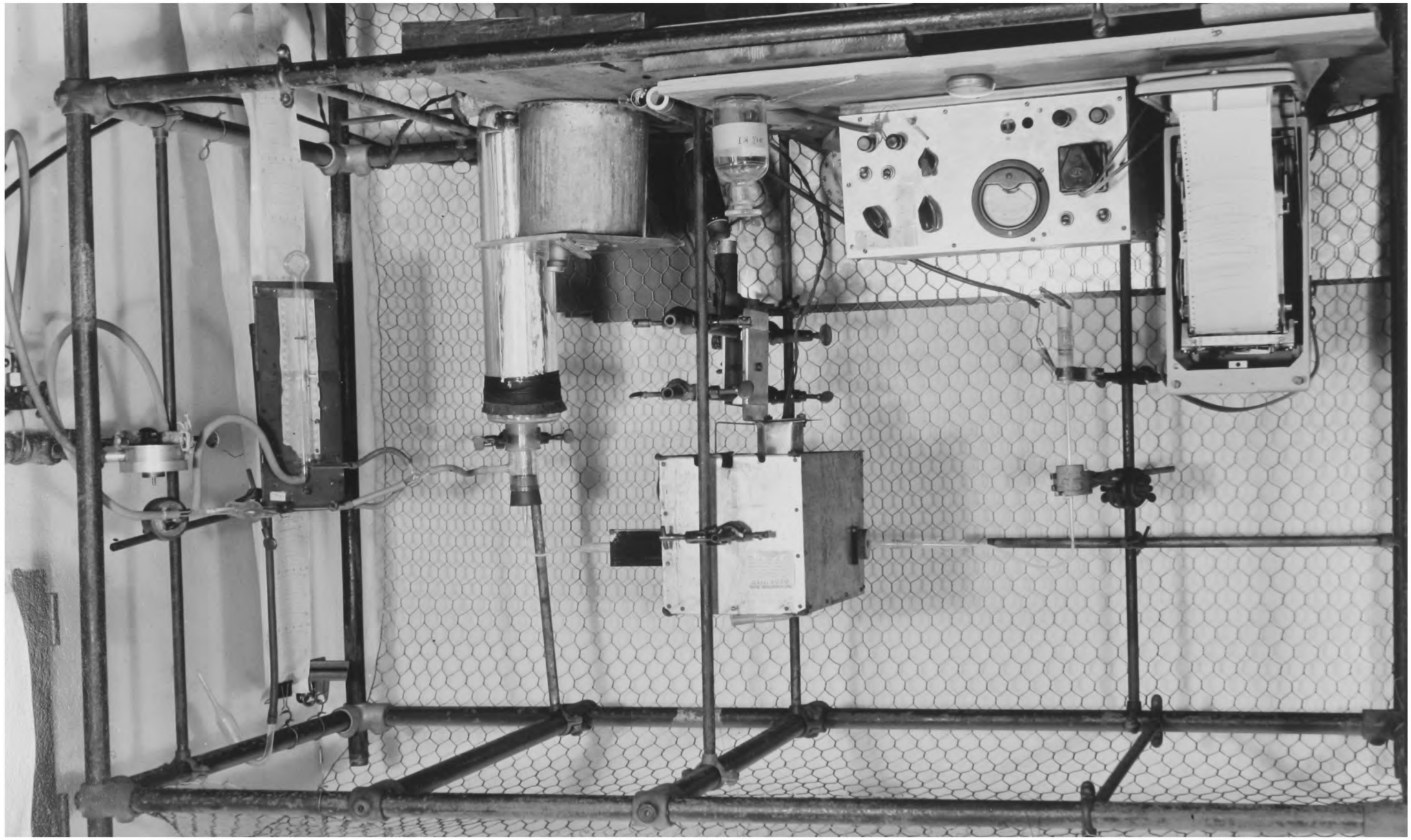
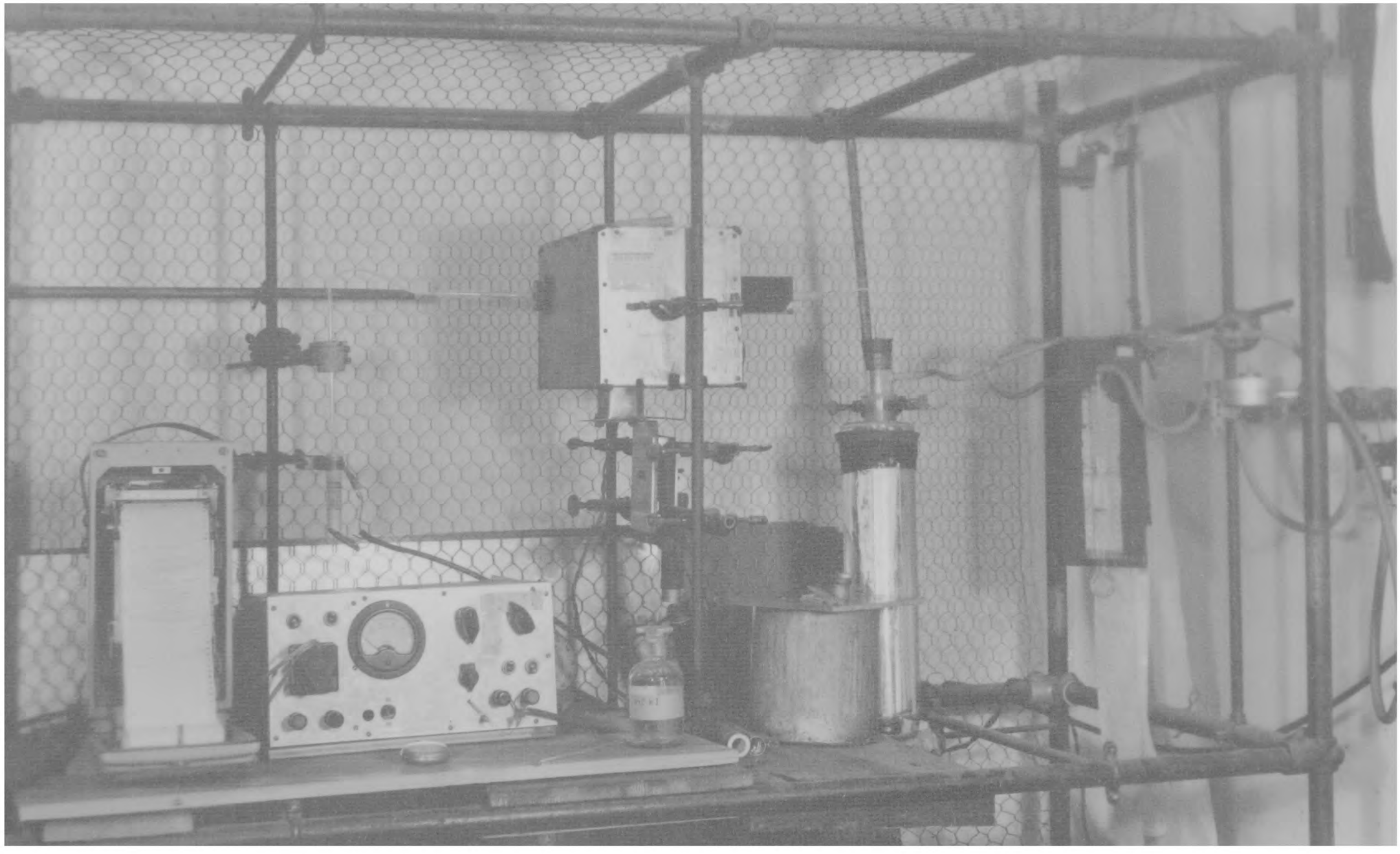


PLATE 1. THE TEST RIG.



CHAPTER V.

CHARACTERISTICS OF THE BUBBLER.

Test Rig.

All the testing of the bubbler has been done on a simple ozone-producing apparatus which enables the ozone input to the bubbler to be readily changed within the limits 0 - 100 parts per hundred million by volume (p.p.h.m).

The layout of this test rig is shown in plate 1. Air (or oxygen) from the piped laboratory supply is passed through a constant pressure valve. The flow rate, which may be adjusted at this valve, is measured on the manometer of a capillary flow-meter. The air then passes through a filter of wet glass wool, which may be cooled with liquid air if a dry supply is required. From the filter, the air passes into the ozonizer. This consists simply of a length of clear quartz tube about 1 cm. in diameter and 8 cm. long, through which the air passes. This is irradiated by ultra-violet light from a mercury discharge lamp. he ozone is produced in the same way as in the upper atmosphere, by dissociation of the oxygen molecules. The distance of the lamp can be adjusted, or a shutter can be interposed, to vary the ozone output.

To measure and record the output current from the bubbler, a three-stage d.c. transistor amplifier is used to drive a 0-1ma. direct writing recorder. Each stage is

a "long-tailed pair" and the gain is stabilized by overall feedback. Variation of this feedback provides three ranges giving full scale deflection of 1, 5 or 10μa.

Standardization of the ozone source.

The ozone source was standardized by the method of Paneth and Gluckauf. The apparatus used consists of a glass tube with two platinum wire electrodes sealed into the bottom. About 5 cc. of buffered 2% potassium iodide solution containing a weighed quantity of sodium thiosulphate are placed in the tube, and an e.m.f. of about 20 mv. applied. The output of the ozone source is bubbled through. No current passes until all the thiosulphate has been oxidized and free iodine appears. From the time it takes before the current appears, and the weight of thiosulphate, the ozone output is simply calculated.

It was found that this method is difficult to perform. Repeatable results were obtainable only by using solutions freshly made with very good deionised water, and very clean apparatus. The results agreed with the bubbler reading to within 4%, and a glass bubbler, with which repeatable results are easily obtained, has subsequently been used as the standard.

Bubbler Characteristics

Tests have been carried out to determine the characteristics of the bubbler, and hence the optimum working con-

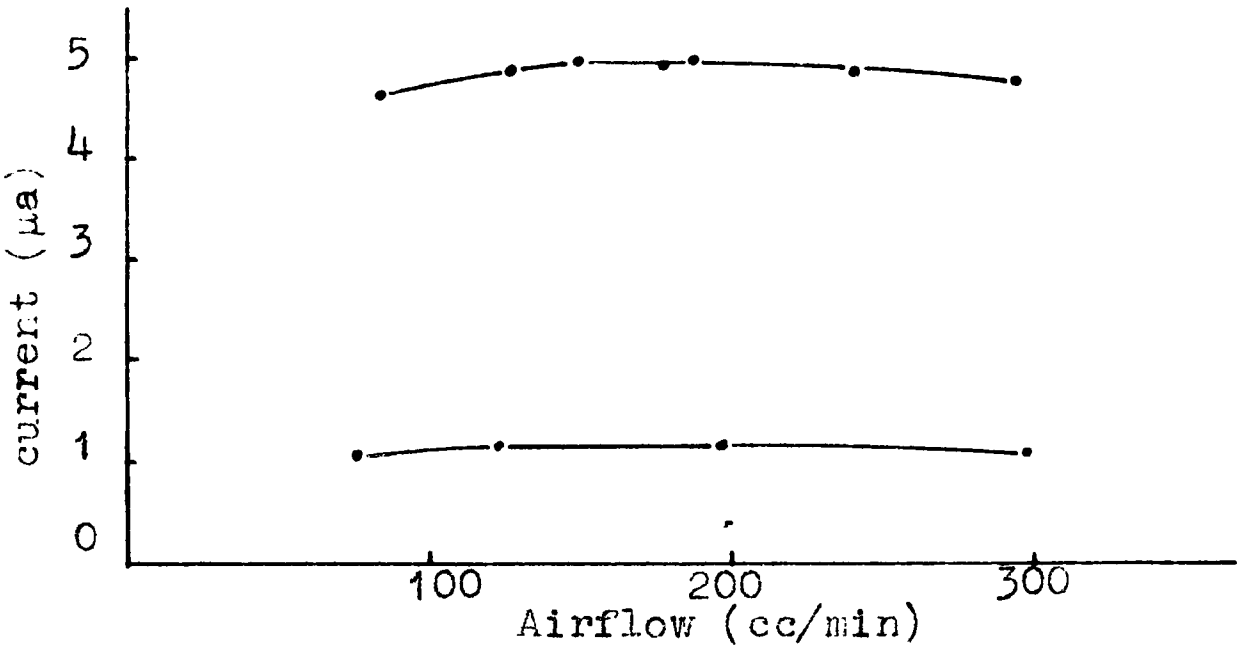


Figure 5. Variation of output current with air flow for two lamp settings.

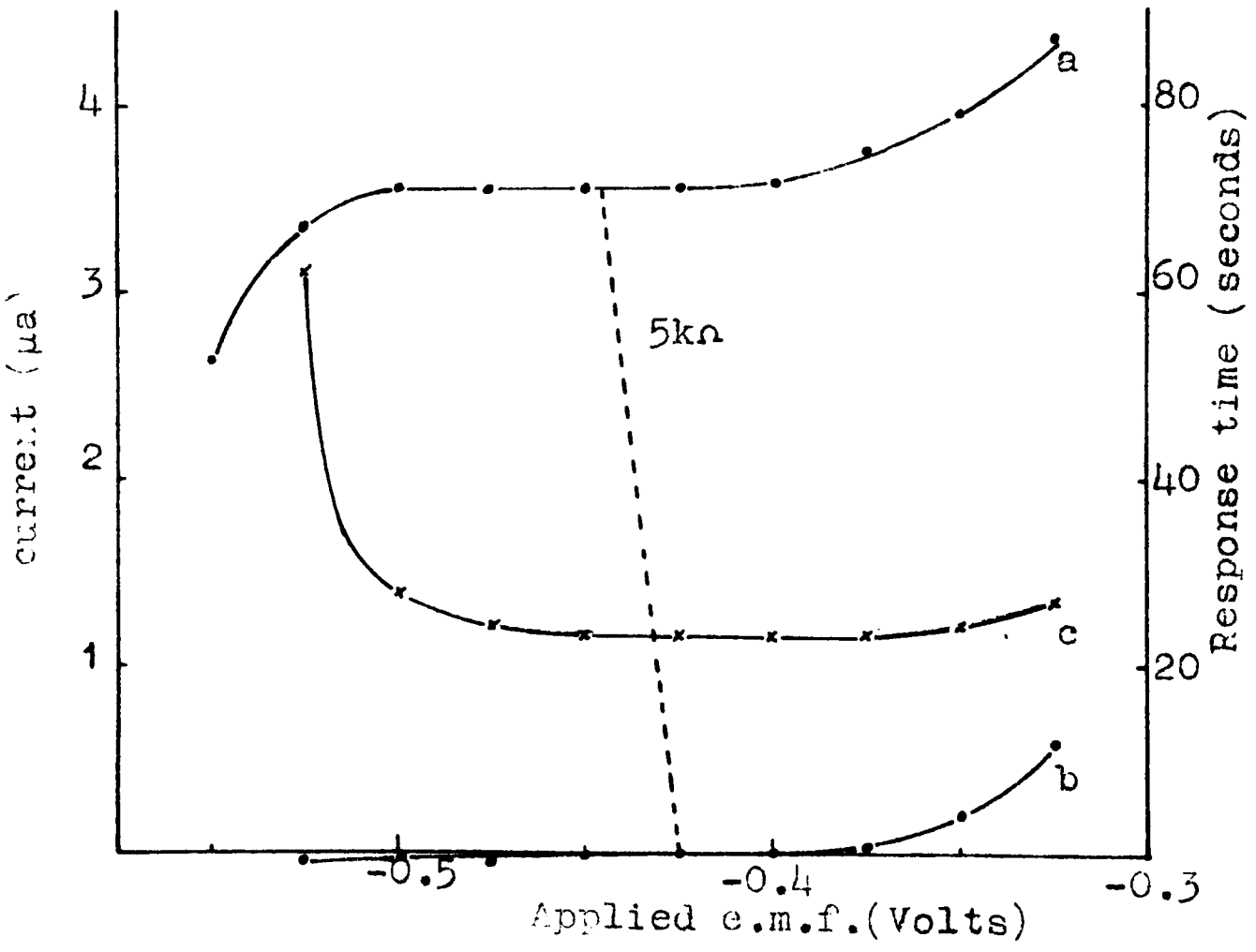


Figure 6. Variation of bubbler current and response time with applied e.m.f.

a: ozone current; b: zero current;
c: response time.

ditions. All the characteristics shown were obtained at room temperature and atmospheric pressure, and relate to the final form of plastic bubbler used on the ozonesonde.

Current vs.Air-flow

The curves in fig. 5 show the variation of bubbler current with airflow, with constant setting of the lamp and shutter. It is seen that the current is constant over a large range of air-flows. Above about 220 cc. per minute the air passes through the solution too rapidly for the ozone to be extracted. Below about 140 cc/min. the current again falls off. This is because the ozone output of the rig is less.

Flow rates used on the ozonesonde vary between 160 and 220 cc/min.

Current vs.applied e.m.f.

In this test the airflow, and lamp and shutter settings are kept constant. The current is measured for various values of the opposing e.m.f. This is the ozone curve, (fig. 6(a)). To determine the zero-ozone curve (fig. 6(b)), the readings are repeated with the shutter closed, i.e., with ozone-free air passing into the bubbler. The explanation of these curves was given in chapter III.

It is seen that between .4 and .5V, both curves show constant current with changes in e.m.f. This is the

working range of e.m.f. A load line of 5kΩ is drawn through the chosen e.m.f. of .425V, and shows that the flat region of the curves is sufficient to allow the use of a telemetering system of this resistance.

The choice of e.m.f. is more restricted than is apparent from these curves, for the response time varies with e.m.f. and reduces the possible working range.

Response time vs. e.m.f.

The response time is determined by obtaining a constant ozone current from the bubbler, and then closing the shutter for 30 seconds. The minimum reading of the bubbler output and the original constant reading, enable the exponential response time to be calculated.

It is observed (fig. 6(c)) that the response time is good over a considerable range of e.m.f., but over only .05V of the working range of e.m.f. Thus the e.m.f. must lie between about .4V and .45V. The shape of the response time - e.m.f. curve has not been satisfactorily explained.

With the chosen e.m.f. of .425V, there is no current in the absence of ozone; the ozone curve is flat, and the response is an optimum.

Collection and Response vs. Depth of Solution in Bubbler.

These curves (fig. 7) help in determining the optimum design of the reaction cell in the bubbler. They show

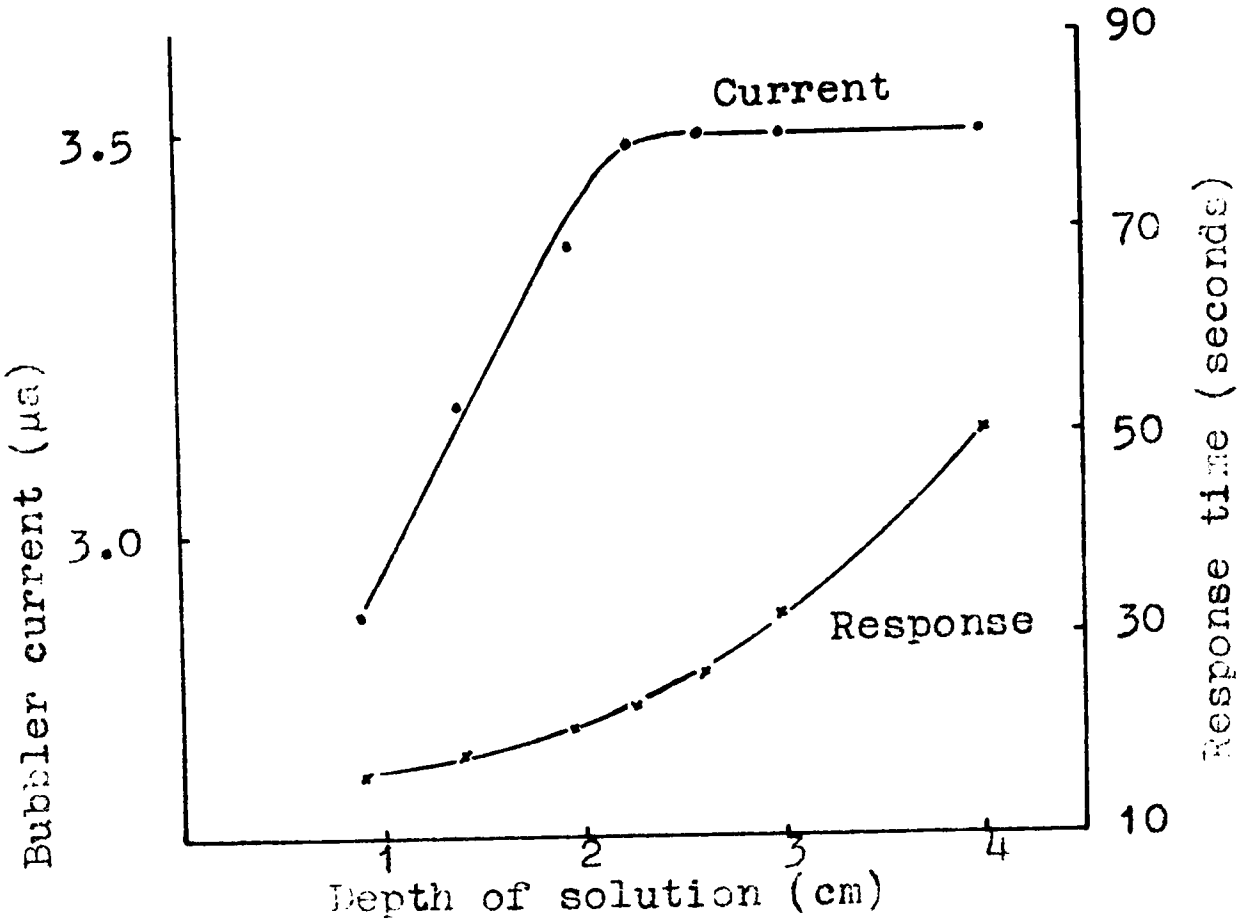


Figure 7. Variation of bubbler current and response time with depth of solution.

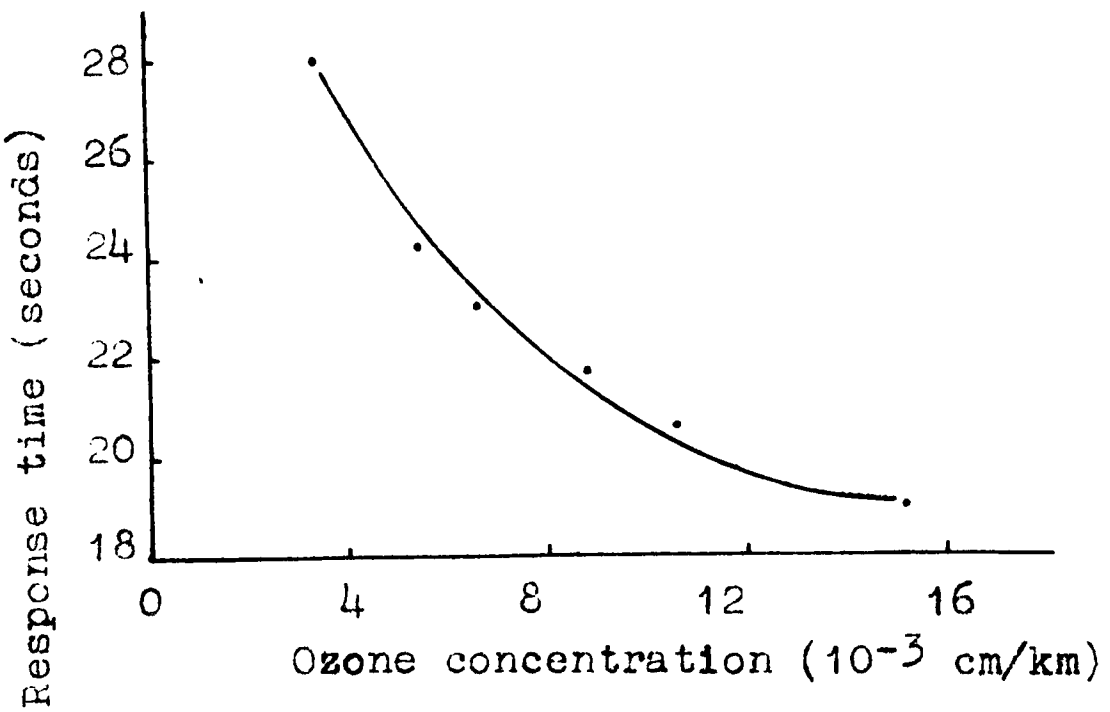


Figure 8. Variation of response time with ozone concentration.

that, below about 2.3 cm. depth of solution, the ozone is not completely extracted from the air, and that the response time increases as the depth of solution increases.

The design of the cell must be such that all the ozone is extracted, and the response time is as small as possible. These conditions are satisfied with 2 cc. of solution, corresponding to a depth of 2.4 cm.

At low pressures the ozone will be extracted more efficiently, due to the increase in rate of diffusion. This is discussed more fully in chap. IX.

Response Time vs. Ozone Concentration.

It was shown by experiment that the response time is dependent on the ozone concentrations. Fig. 8 shows that the response time is better at high ozone concentrations.

With tropospheric concentrations of ozone the response time is about 25 sec., while in the stratosphere, where maximum response is required, the increased ozone concentrations should result in a response time of less than 20 sec. In fact, the response worsens due to temperature effects which are discussed in chapter IX.

CHAPTER VI.

LOSSES IN THE BLOWING SYSTEM.

To obtain the coulometric equivalence of current and ozone entering the system (see page III.2), certain conditions must be fulfilled:

(1) Incoming ozone must not encounter any oxidizable material before it reaches the solution;

(2) All ozone must be extracted from the air as it passes through the solution;

(3) No iodine must be lost, before reaching the platinum cathode, by absorption in the material of the reaction cell, or by evaporation from the solution.

These conditions are important in any ozone-detecting system, and become even more significant in the blowing system, where the incoming ozone is taken through the pump. As a result much work was done to determine the most suitable materials and conditions to satisfy these demands. The results achieved were far better than could have been hoped.

Condition (2) is fulfilled by using more than a minimum depth of solution, as was shown in chapter V.

Evaporation of iodine from the solution (condition (3)) is reduced by using a large cathode area to remove the iodine quickly. No evidence has been found to show that iodine is lost by evaporation.

The remaining conditions may be divided into the prevention of ozone and iodine losses by absorption.

Ozone Losses.

Ozone losses by absorption occur (a) in the material of the pump, and the air-intake and inlet tubes connected to it, and (b) in the lubricating oil of the pump.

Tests for ozone absorption.

The ozone absorption by a material is tested as follows. The ozone test rig is adjusted to give a constant ozone output which is measured with a bubbler constructed in glass. Glass absorbs neither iodine nor ozone, and the glass bubbler has been shown to measure ozone correctly.

The inlet system to the bubbler is arranged so that the material can be easily and quickly put in the path of the incoming ozone. When this is done, the output of the bubbler falls, due to high initial ozone absorption by the material, and then slowly increases to a steady output lower than, or equal to that before the material was introduced.

By comparison of these changes for equal surface areas of absorbing materials, it is possible to determine the most suitable materials.

Pump Materials.

The pump is one of the moulded components in the ozone assembly, and so the choice of materials was limited. In

fact, the only thermoplastics suitable for withstanding the wear on the pump are nylon and cellulose acetate.

Both acetate and nylon were found to stop absorbing ozone after a lengthy exposure to ozone, but the acetate had a lower initial absorption, and the absorption stopped sooner than for nylon. Hence acetate is used to make the pump. This has the added advantage over nylon of being easier to work.

Tubes carrying ozone.

These tubes must be flexible and the choice was between polythene and P.V.C. (polyvinyl chloride) tubings.

Polythene was found to absorb considerably less ozone than P.V.C., but still absorbed a little even after two hours exposure to ozone.

Hence polythene tubing is used for the intake and inlet tubes, and is stored permanently in an ozone atmosphere to reduce these losses to a minimum.

Pump Lubricating Oil.

Oils were tested for ozone absorption by bubbling the ozone output through a small volume of oil, and measuring the residual ozone with a glass bubbler.

The pump needs a thin oil, and watch oil which had always been used on the pump, was found to absorb least ozone. Other oils tested included Apiezon A oil which was

second beat, and silicon oil which, in addition to rotting polythene tubing, proved to absorb more ozone than other oils tested. A promising oil was Florube, an I.C.I. product, supposedly resistant to ozidizing agents. However, it was found to absorb ozone more strongly than Apiezon A.

Hence watch oil is used for lubricating the pump. The supply of oil used is regularly ozonised.

Pump Piston.

It was thought that the hardened steel piston normally used in the pump might absorb ozone, so pistons of other materials were made and tested.

A glass piston gave no improvement over the steel one, thus suggesting that the pump-casing materials and oil were producing the loss.

A P.T.F.E. (polytetrafluoroethylene) piston was made in the hope of its being self-lubricating and not needing oil. However it flowed due to the intense heating after about two hours use, and had to be lubricated. Tests with this piston, with and without watch oil lubrication, suggested that ozone losses in the pump were due to absorption in the pump casing and base, and not in the watch oil.

Table 1.

ABSORPTION OF OZONE AND IODINE

The columns show the materials in order of suitability for use with the bubbler. The material absorbing least heads the column.

MATERIALS		OILS
OZONE	IODINE	OZONE
Glass	Glass	Watch oil
Acetate	Polystyrene	Apiezon A oil
Nylon	Acetate	Florube oil
Polythene	Polythene	Silicon oil
P.V.C.	Perspex	
	P.V.C.	
	Nylon.	

Iodine Losses.

Iodine losses by absorption occur almost entirely in the walls of the reaction cell, and partly in the small length of inlet tube in the solution.

Tests for iodine absorption.

The iodine absorption by a material was tested as follows. The glass bubbler measures the constant ozone output from the test rig. Small pieces of the material are dropped into the solution in the reaction cell. The bubbler output immediately falls due to high initial iodine absorption, and then increases as the material absorbs less. By comparison of these changes for equal surface areas of absorbing materials, the most suitable materials may be determined.

The results are summarised in table 1. Glass, as expected, is the most suitable material, absorbing no iodine at all - within the limits of the experiment. Glass is suitable for making a laboratory detector, but for the mass production required for ozonesonde work, moulding techniques must be used.

The most suitable plastic was found to be polystyrene, followed in order of suitability by acetate, polythene, perspex, P.V.C. and nylon.

Hence polystyrene is used for the construction of the reaction cell.

In addition to its better ozone absorbing properties, polythene is more suitable than P.V.C. for the inlet tube, from consideration of iodine absorption.

Reduction of Losses.

In the manufacture of the pump and bubbler, great care is taken to keep all the components clean, and certain treatments are carried out to reduce any losses.

Ozonisation.

The pumps and polythene tubing are stored in an ozone atmosphere. When the ozonesonde is assembled these components are further thoroughly ozonised by continuous pumping of ozone through them. The watch oil used for the pump is always well ozonised before use.

Iodisation.

The bubbler is filled with KI solution and ozone is bubbled through to produce iodine. This is not removed electrochemically, and the walls of the reaction cell are allowed to absorb iodine then, and not when the bubbler is in use, measuring atmospheric ozone.

Results Achieved.

These treatments have proved to be very effective. Sixteen bubblers and pumps were treated in this way, and stored on the bench in conditions similar to those at an ozonesonde station. Tests carried out for losses after

storage showed that:

1. No measurable loss occurred in the pumps;

2. Losses ranging from 0 to 7% occurred in the bubblers.

On the basis of these results it has been assumed that the total losses in a flight are 4% ± 4%. This total loss was shown to be a percentage loss rather than a constant loss.

CHAPTER VII.

THE OZONESONDE.

The bubbler has been incorporated into an ozonesonde using basically the same auxiliary equipment as that used with the transmogrifier on the Brewer-Milford ozonesonde. Some modifications have been made, and unexplained phenomena in the transmogrifier results have been resolved.

The ozonesonde consists of the ozone assembly and the Kew radiosonde transmitter, which has been described by Dymond (1947). The ozone assembly is designed so that it can replace any of the Kew plug-in elements without modification of the transmitter.

The Telemetering System.

In the Kew sonde, information is transmitted to the ground in terms of an audio frequency in the range 700-1000 c/s, which modulates the carrier frequency of about 28 Mc/s. The audio frequency is controlled by an inductance which changes by mechanical movement of a mumetal armature attached to the measuring element; in the ozonesonde the audio frequency is varied by a current-controlled inductance- the transductor. The ozone current from the bubbler is passed through a coil on the centre section of a mumetal core. This changes the incremental permeability of the core and hence the inductance of the oscillator coils on the outer limit of the core. The transductor is described in

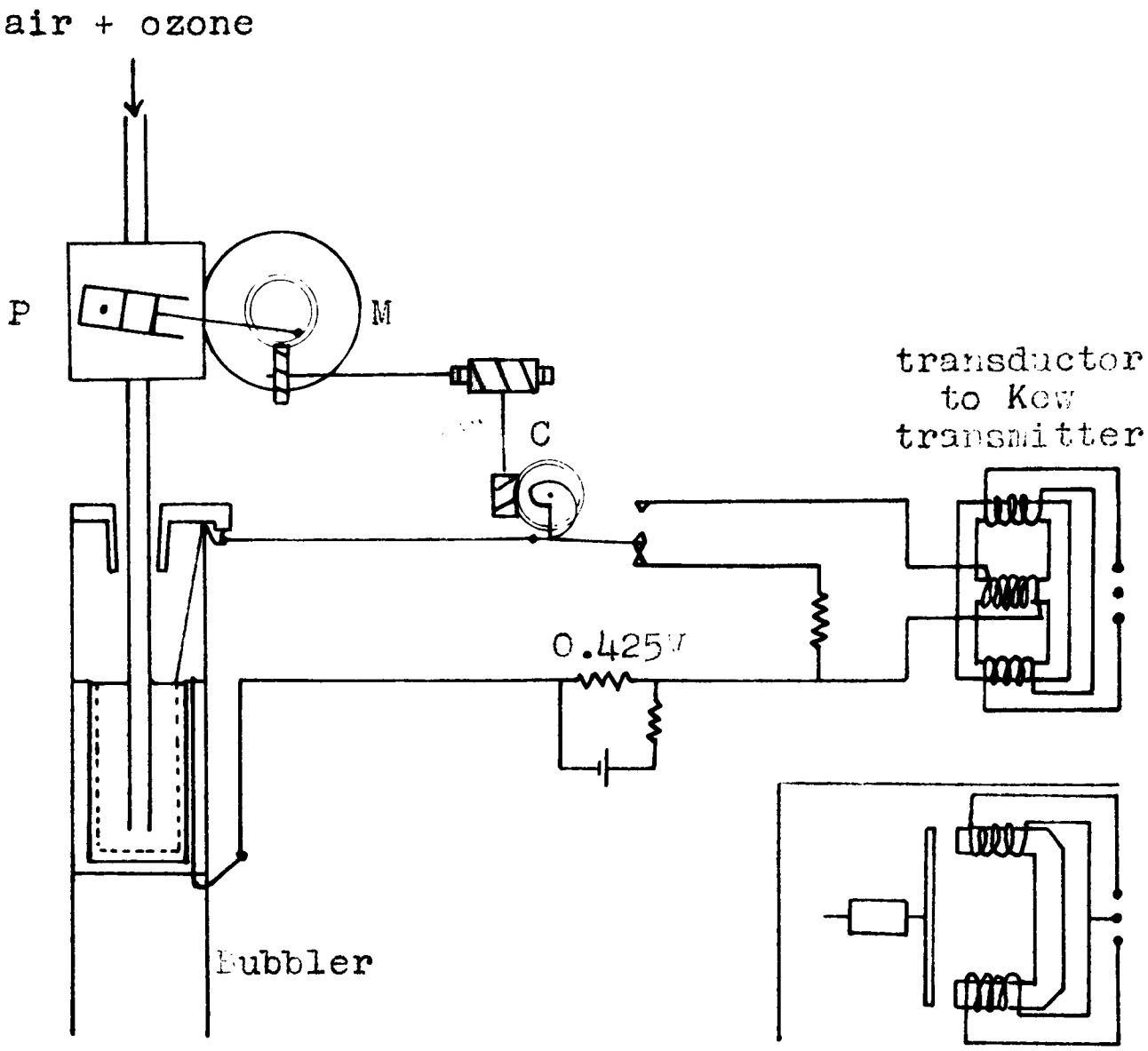


Figure 9. Diagramatic illustration of general arrangement of the bubbler ozonesonde. Air is blown (180 cc/min) through the bubbler, by a small positive displacement pump P. The electrical output is telemetered by the transductor. This replaces the standard Kew element which is shown inset for comparison. (M, motor 4000 rev/min; C, switch cam 1/2 rev/min).

detail in the next chapter.

The ozone assembly is shown diagrammatically in fig. 9. The complete assembly is contained in a 500 cc. Dewar flask to prevent any undue cooling during flight.

The Pump.

This is a small piston pump with a rocking cylinder to operate the necessary valves. The cylinder is a precision bore glass liner in a moulded acetate case, and the piston is of hardened steel. The bore is 3 mm. and the stroke is 6 mm., giving a capacity of about 40 cubic mm. The block on which the cylinder rocks is moulded in cellulose acetate, and is cemented on to the motor casing which is of the same material. This motor is an Ever Ready toy motor, which runs at 4,000 to 5,000 rev/min. with a 2.4V battery giving about 0.3 amp. The crank of the pump is provided by an eccentric steel pin in a moulded nylon (or polystyrene) fan attached to the spindle of the motor. This fan is essential for cooling of the motor, and circulates heat in the Dewar, so helping to prevent the temperature falling too quickly.

The pump should give a flow rate independent of pressure. This was shown to be true by measurements which are described in chapter IX.

Air-flow Measurement.

At the opposite end of the motor to the pump, there is

a three-stage worm and spur reduction gearing; each stage is 20:1, giving an overall reduction of 8000:1. Through this gearing, the rotation of the motor operates the microswitch shown diagrammatically in fig. 9, and for about 12 seconds at approximately one and a half minute intervals, the bubbler current is switched out of circuit, and the zero of the transductor is transmitted. Since the interval between these zero signals is the time for 8000 strokes of the pump, the mean airflow in this time interval is easily calculated from the preflight airflow calibration.

Motor Battery.

The 2.4V necessary to drive the motor are provided by a lead-acid-zinc cell. It has a capacity of about 1 ampere-hour and has good discharge characteristics. A feature of the motor battery is that it is of non-spill design, made specially for the ozonesonde by Harnard Batteries Ltd. The use of this battery results in most of the recovered assemblies being in very good condition, and needing little attention before being flown again.

General Construction.

The assembly is constructed on a framework above the cork of the Dewar. It is supported from the three-pin plug in the Kew transmitter by an L-shaped bracket of U-section mild steel; from the horizontal part of the bracket, two



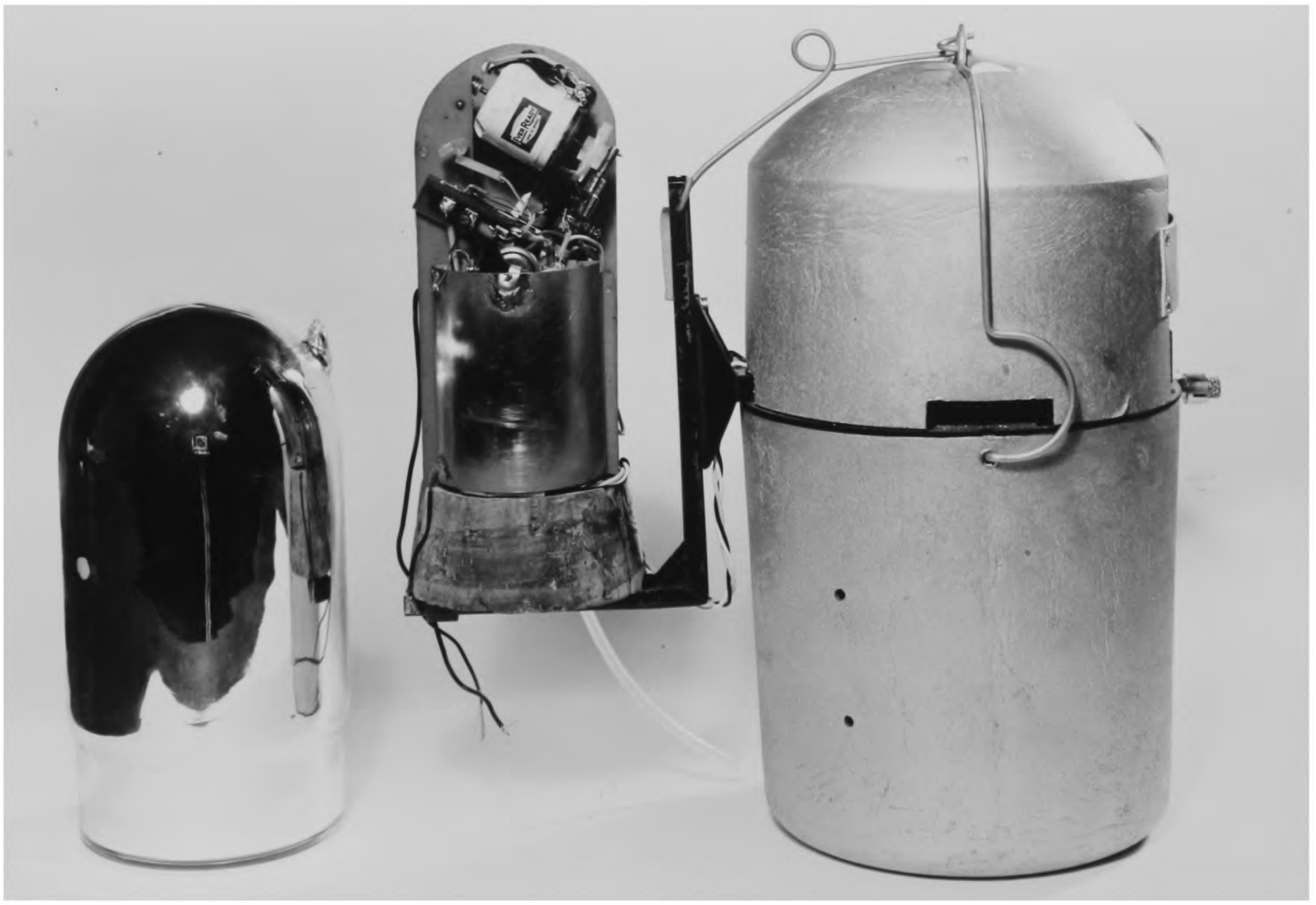


PLATE 2. OZONESONDE WITH NON-SPILL BATTERY AND CALIBRATOR UNIT.

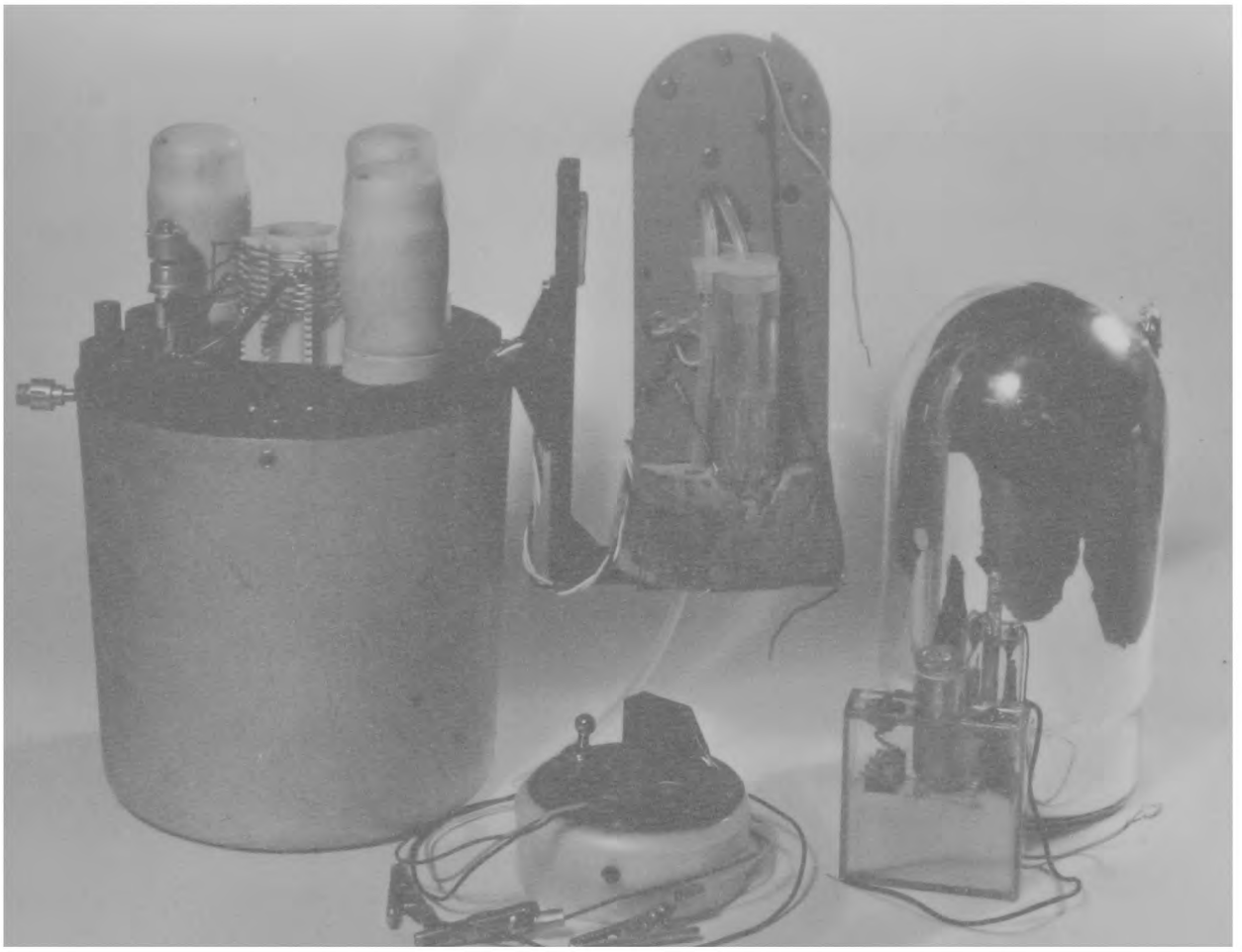
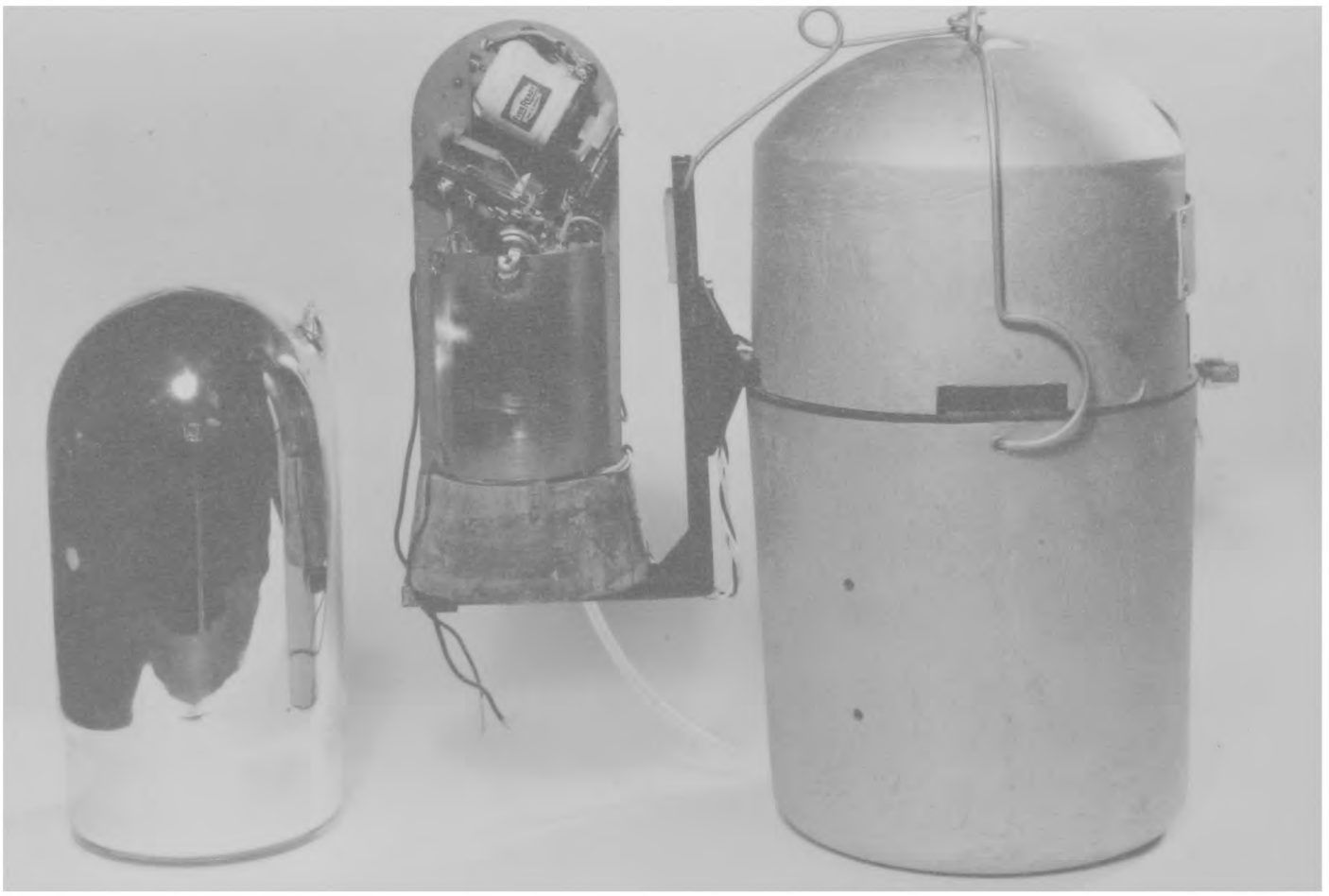


PLATE 3. OZONESONDE READY FOR LAUNCHING.



tufnol plates pass up through the cork. The plates are held apart by three spacers as well as the bracket, and divide the space into three compartments, one containing the transductor and switch, the central one the motor battery with the motor and pump above it, and the third containing the bubbler. General views of the ozonesonde are shown in plates 2 and 3.

The total weight of the assembly is 640 gm. This unbalances the Kew sonde and necessitates a lifting bracket through holes in the top of the L-bracket and the transmitter lifting bracket; this also takes some of the weight from the three-pin plug. In flight the assembly is enclosed in a cloth bag to contain the broken glass, should the Dewar break on landing. The polythene intake tubing projects through the cork and this bag, together with the negative leads of the motor and motor battery, so that the motor need only be switched on immediately before launch.

It is of interest to note that in 57 flights at Liverpool, 38 assemblies were recovered, and on these only 7 Dewars were broken.

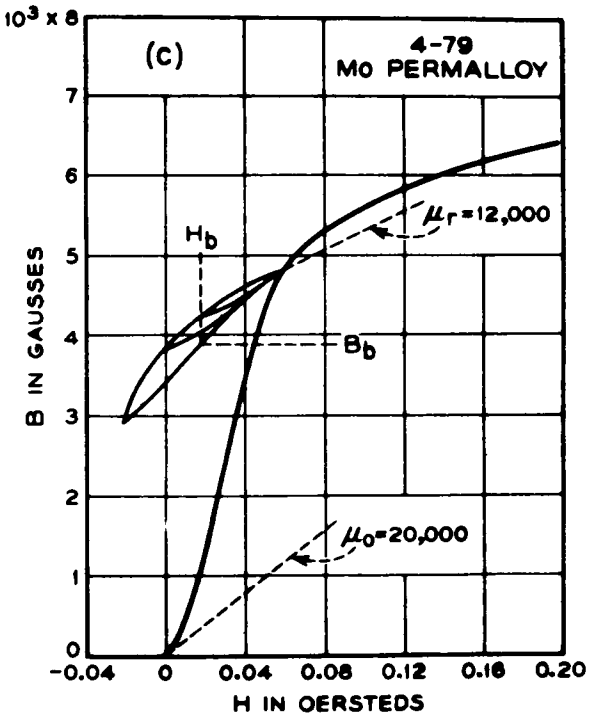


Figure 10. Normal magnetization curve with a small alternating field superimposed.

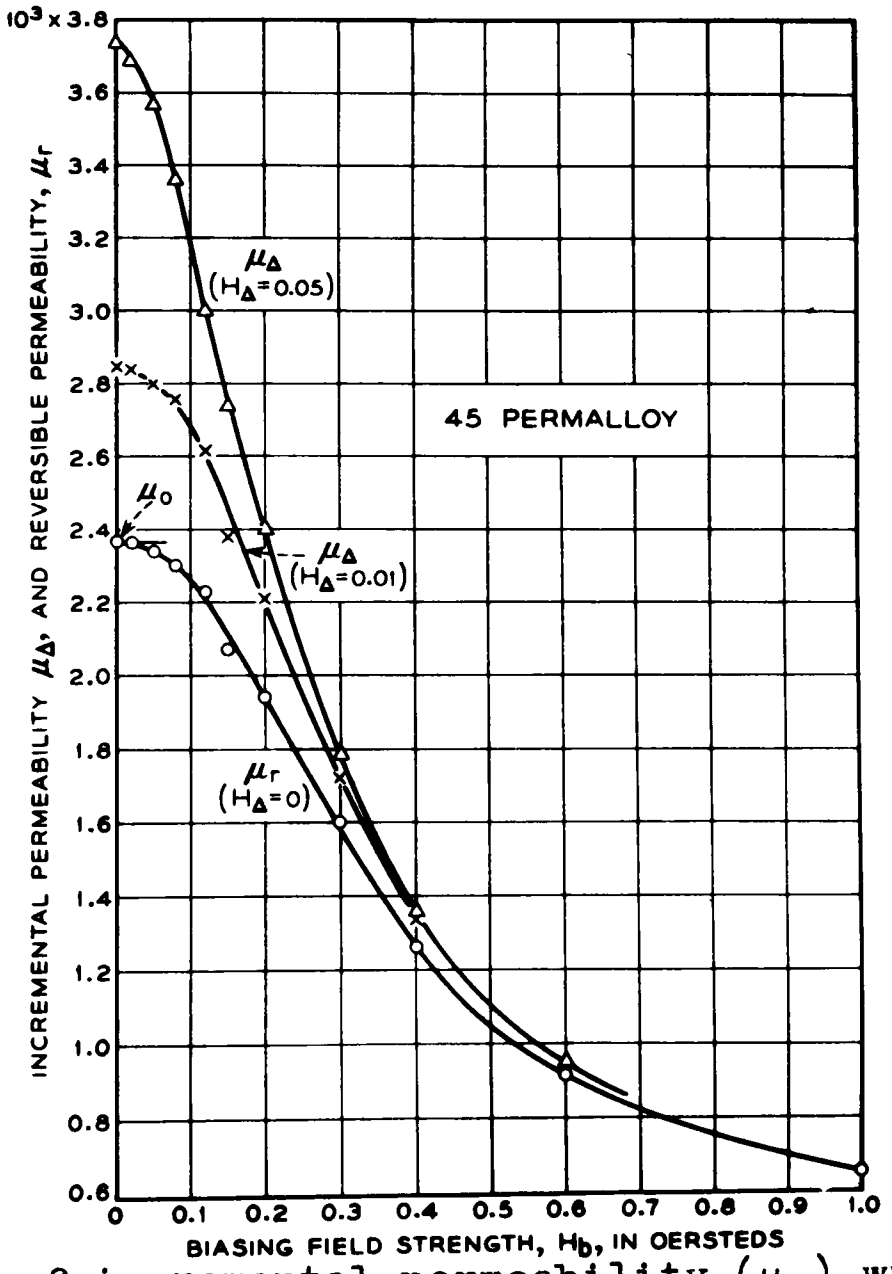


Figure 11. Variation of incremental permeability (μ_Δ) with biassing field (H_b) for different amplitudes of oscillations (H_Δ).

CHAPTER VIII.

THE TRANSDUCTOR.

The transductor is similar to that used with the transmogrifier, but has been modified and improved.

Transductor Principle.

The principle of the transductor depends on the properties of ferromagnetic materials. A typical magnetization curve (Bosorth 1951 p.539) is shown in fig. 10, in this case for 4-79 Mo Permalloy, which is very similar to mumetal used in the transductor. The heavy curve is the normal magnetisation curve, and the small loop shows the cycle which the metal undergoes when a small alternating magnetic field is superimposed on the steady field. The incremental permeability is the mean slope of such subsidiary cycles; it depends both on the amplitude of the cycle, and on the point of the magnetization curve about which it is taken. Fig. 11 shows curves of incremental permeability against the steady magnetic field for different amplitudes of the alternating field (Bosorth p.541).

In the transductor, the steady magnetic field is provided by the bubbler current passing through a coil. This controls the incremental permeability, and hence the inductance of the oscillator coils which plug into the Kew sonde. Thus, changes in the bubbler current are measured as changes in the audio frequency. In the transductor design

used, the frequency is directly proportional to the bubbler current in the range 700-1000 c/s.

Transductor Design.

The core of the transductor is made up of mumetal laminations 0.005 inches thick, pattern 188 from Magnetic and Electrical Alloys Ltd. A matching pair of a C and a T gives a section of outside dimensions 5 cm. × 2.95 cm. The core consists of five pairs of laminations, with C's and T's alternating, and two extra T's on each side. The laminations are held together by the surface tension of films of Apiezon oil between them, and are fixed relative to the coils with two or three polythene wedges.

The control coil is wound on the centre limb, and is made up of 15,000 turns of 44 S.W.G. enamelled copper, having a resistance of about 4.5 kΩ.

A biassing coil of 600 turns is wound beneath the control coil, and about 1ma. through it provides the biassing field that is necessary to work on the sensitive portion of the curve in fig. 11.

The oscillator coils are wound on an outer limb of the core as one centre-tapped coil of 40 S.W.G. with 1000 turns in each half.

Amplitude Limiter and Sensitivity.

The sensitivity of the transductor, defined as the change in audio frequency per microampere change in current

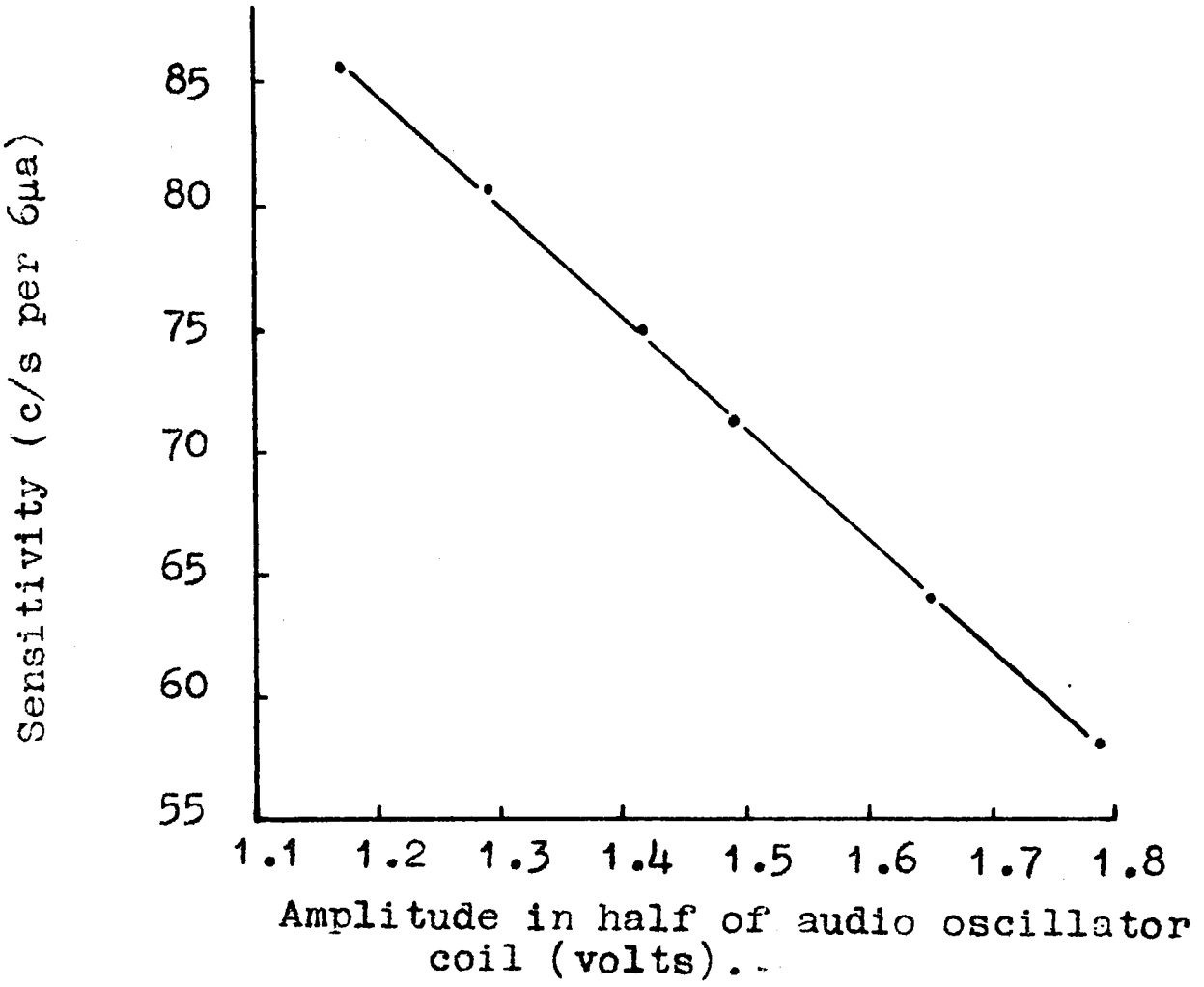


Figure 12. Variation of transductor sensitivity with amplitude of oscillations.

through the control coil, depends on the amplitude of the audio frequency oscillations (see fig. 12). This is due to the change in slope of the curve in fig. 11, as the amplitude of oscillations, H_o, changes.

During a flight the amplitude of oscillations, and hence the sensitivity, changes at an unknown rate due to changes in the H.T. voltage of the Kew transmitter. To avoid this, the oscillations are limited by a voltage-biassed germanium diode connected across half the oscillator coil.

The Brewer-Milford sonde used an amplitude of about 1.0 volts amplitude in the half-coil. This small amplitude caused receiving difficulties on occasions, and so the diode at present is biassed with .425V, giving about 1.4V amplitude in the half coil.

This increased amplitude reduces the sensitivity, but this has been brought back to its original value by cutting 2mm. from the C laminations in the transductor core instead of 1mm. (Jones et al, 1959), and by taking great care in assembly of the laminations.

The overall result is that the received signal is stronger, while the sensitivity is not impaired.

The sensitivity was found to be temperature dependent. This is discussed fully in the next chapter.

Negative Readings.

A serious and unexplained trouble which occured on some flights of the Brewer-Milford sonde was the appearance of signals corresponding to negative ozone amounts. A negative reading definitely appeared in 10 out of 50 flights examined, and may have caused a reduction in measured ozone amounts on the other flights. This same effect was apparent on 10 of the 16 flights with the prototype bubbler. It was thought to be due to reducing agents in the bubbler, although this should not be possible in the transmogrifier. However, closer examination revealed that the negative reading was really a positive shift of the zero signal, and as the result of transmitting with and without aerials, it seemed that radio frequency effects were responsible for this zero shift.

The observed effects on the flights were reproduced exactly in the laboratory, by artificially introducing into the transductor, some 27 Mc. pickup from the transmitter. The effect could be produced only when the pickup was injected across the bubbler leads, and it varied with the position of the pickup leads. It was apparent from the laboratory tests carried out that the presence of the diode is essential for this effect to occur, and that the r.f. pickup must be directly across the diode.

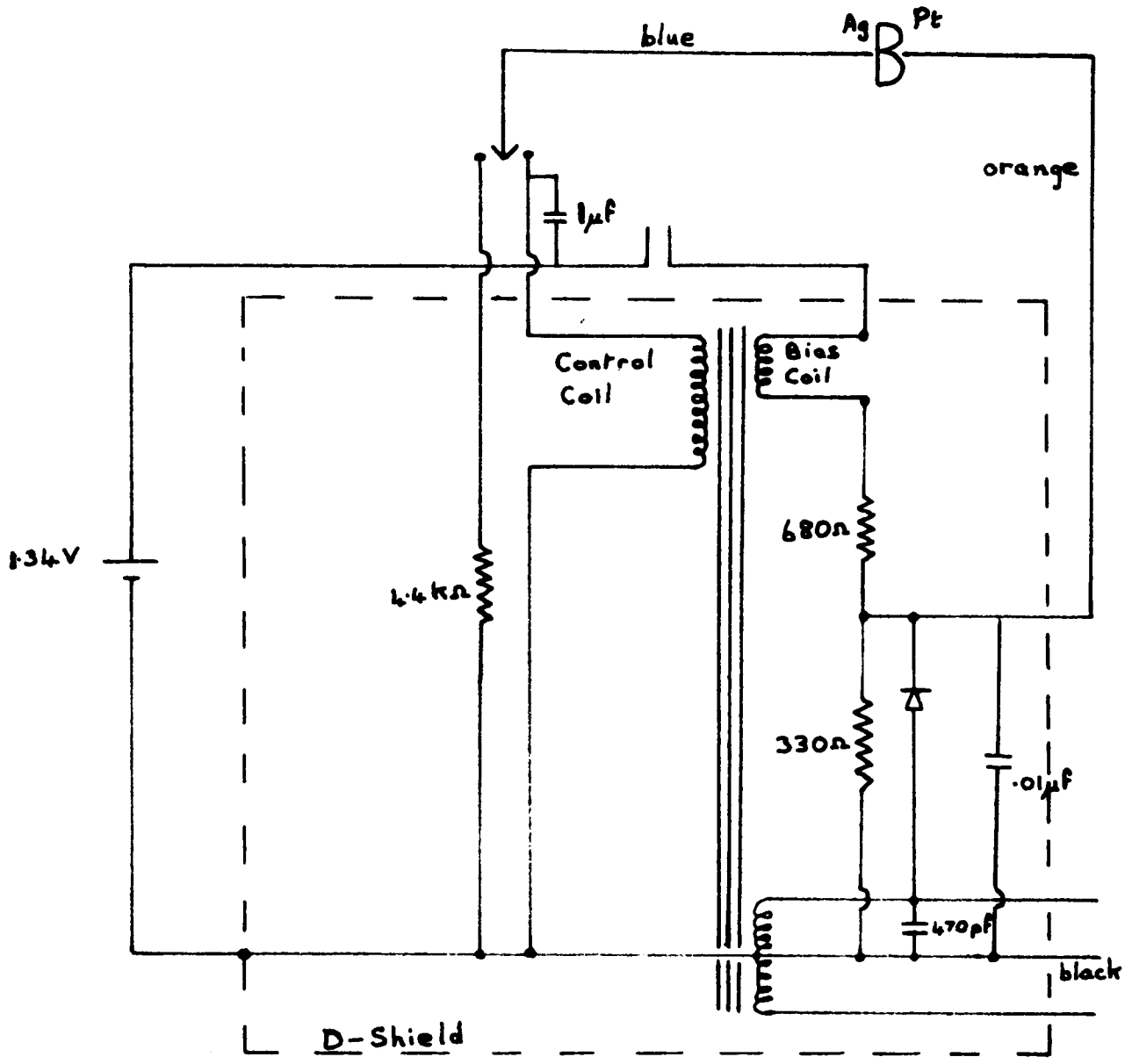


Figure 13. Bubbler ozonesonde circuit diagram.

In the present arrangement (fig. 13), the lead from the bubbler cathode connects directly to the top of the positive side of the diode, while in the transmogrifier the lead was connected indirectly to the diode. This difference explains why this zero shift was more prevalent in the early bubbler ozonesonde flights. The fact that this zero shift was different each time it occurred, was no doubt due to differences in the positions of the detector leads in the assembly, and to different transmitter power outputs.

These effects have not been explained, but can easily be avoided; simply by connecting a 0.01μF paper condenser between the positive side of the diode and the centre tapping of the oscillator coil.

E.M.F. Applied to bubbler.

This e.m.f. is obtained from a voltage divider formed by two carbon resistors in the circuit providing the current in the bias coil. The exact e.m.f. of 0.425V is obtained by connecting the 680Ω and 330Ω Lab-pack resistors in circuit, and filing away part of one or the other to increase its resistance, until the required e.m.f. is obtained.

Zero checks.

The current through the bias coil is provided by a Mallory cell RM.625, which has a 250 mah. capacity. The magnitude of this current controls the zero frequency of the

transductor.

The zero frequency becomes lower during a flight due to temperature effects, and must be checked regularly. This is carried out by the snap-action microswitch mentioned earlier. It takes the control coil out of the bubbler circuit, and replaces it by a matched resistor, which acts as a dummy load on the bubbler. Thus for about 12 seconds every one and a half minutes, the zero frequency is transmitted; this is sufficient time for a reading to be made.

When the ozone assembly shares a transmitter with pressure and temperature elements, a different cam is used, so that the control coil is switched out for about 30 seconds. This ensures that a zero signal is transmitted during the P,T, ozone cycle which usually takes about 30 seconds.

Auxiliaries.

A 1μF tantalum electrolytic condenser is connected permanently across the control coil, to present a short circuit to any a.c.(audio) induced from the oscillator coil.

The complete transductor assembly is put inside a mumetal "D" shield to reduce effects due to the earth's magnetic field.

Calibration.

The transductor has to be calibrated before flight, and a "calibrator" unit is supplied to the ozonesonde stations. This is connected by three crocodile-clips to the orange, blue and black wires of fig. 12, and currents of 0, 2, 4, 6 μa. are passed through the control coil in the forward and reverse directions, giving seven readings in all. The current is derived from a 1.34V Mallory cell in series with resistors inside the calibrator. Another calibrator switch position puts a resistance across the bubbler terminals. This resistance is chosen so that if the circuit for the bias current and bubbler e.m.f. is in order, then the frequency in this position approximates to that of the -6μa. position in the calibration.

CHAPTER IX.

TEMPERATURE AND PRESSURE EFFECTS ON THE OZONESONDE.

The environment of the ozonesonde during a flight cannot be reproduced exactly in the laboratory, and so the exact behaviour of the ozonesonde cannot be described. However, as a result of extensive tests at different temperatures and pressures, the general behaviour of the ozonesonde in flight is thought to be understood.

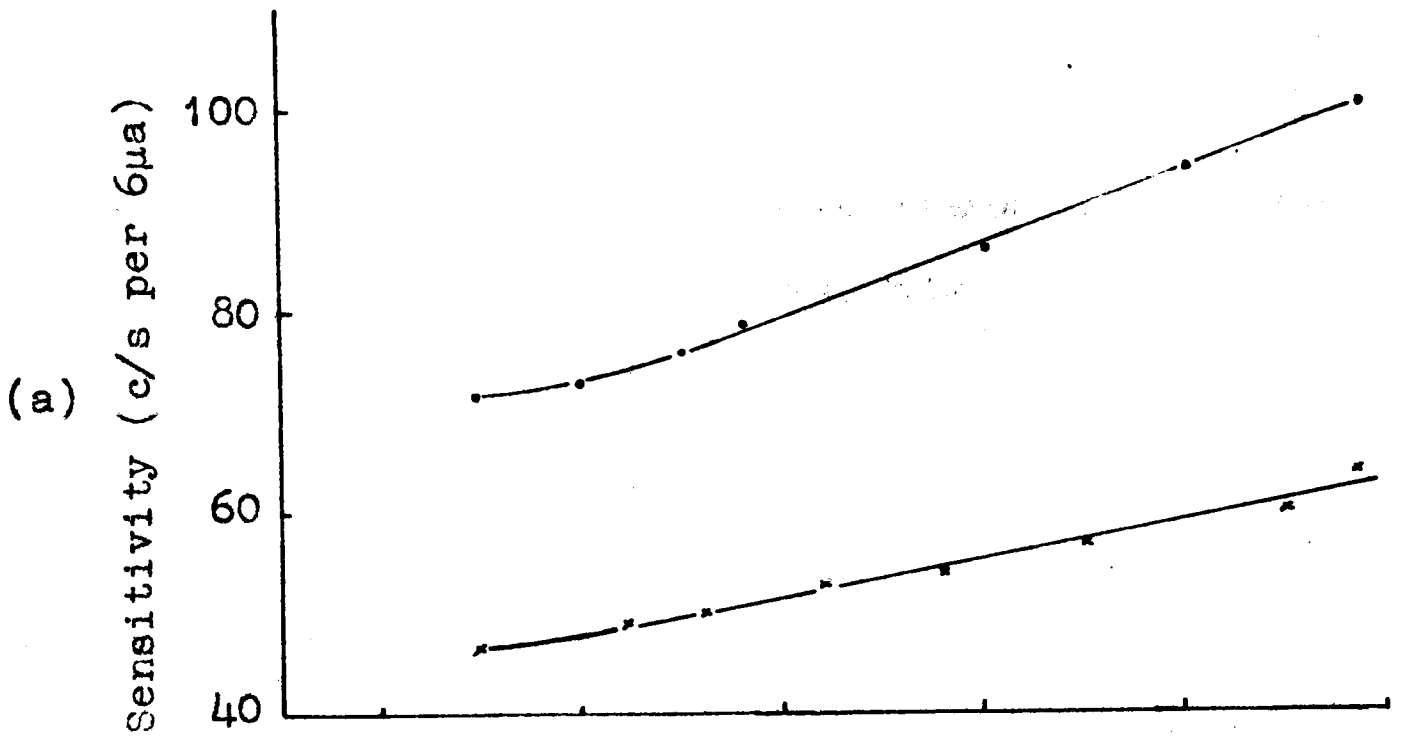
These investigations have led to more accurate interpretation of the data obtained, and have explained some discrepancies in the results of Brewer and Milford (1960).

Temperature Effects

During a flight the temperature inside the Dewar will fall, due mainly to leakage through the Dewar and cork, which exceeds the heat su plied by the pump motor. This fall in temperature effects both the transductor and the bubbler.

The Transductor.

During flight, as the temperature of the transductor falls, the zero frequency of the ozone signal gradually falls. At the same time, however, the sensitivity of the transductor falls. This was not realised by Brewer and Milford, and their absolute and profile errors are larger



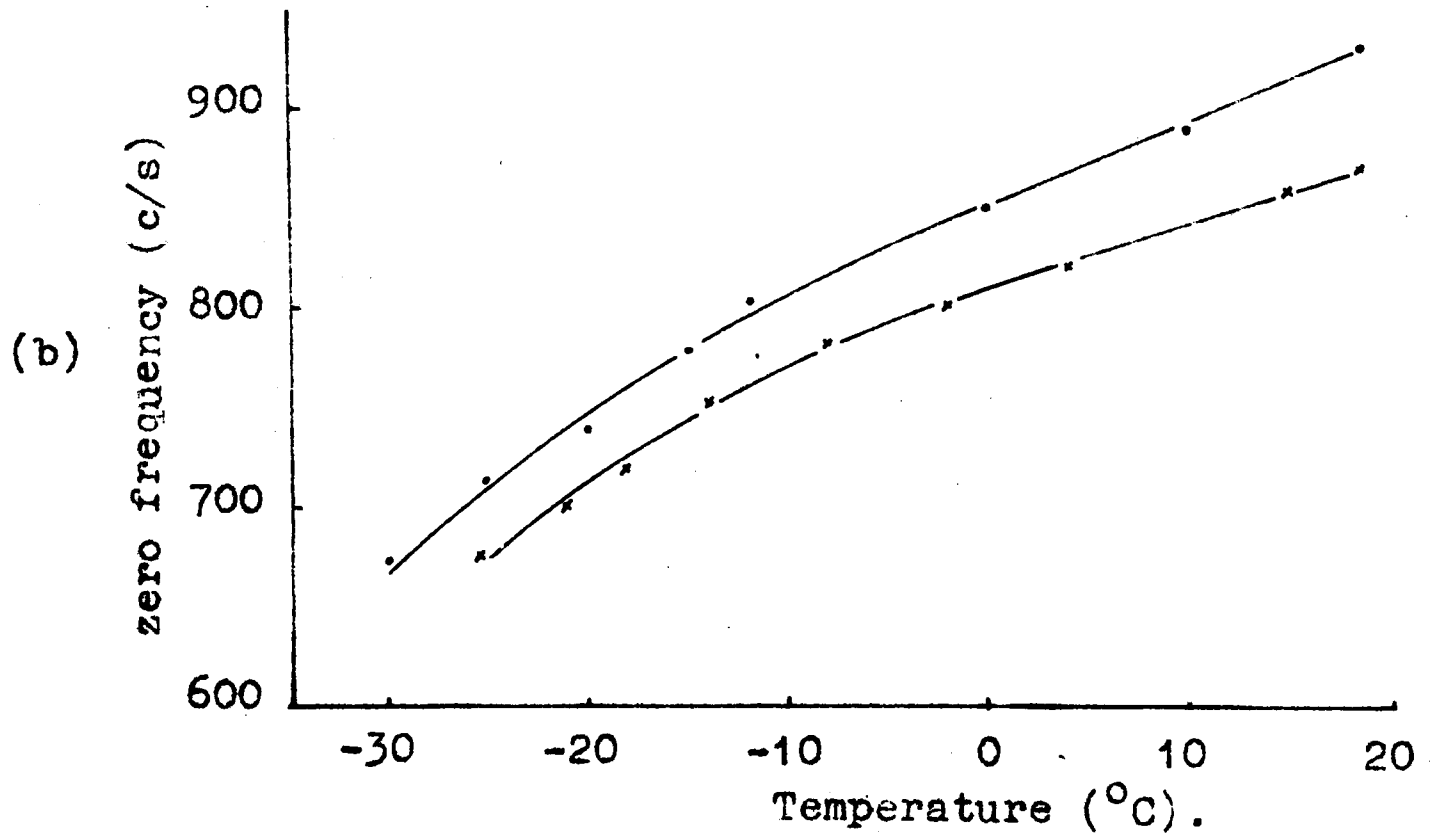


Figure 14. Variation of (a) sensitivity (b) zero frequency of transductor with temperature. Curves for two transductors are shown.

than those published. The change of zero frequency and sensitivity are shown for two typical transductors in fig. 14 (a) (b).

As a result of measuring these temperature changes for several transductors, the zero drift from +20°C to -10°C was found always to be between 3 and 5 c/s per °C, while a 1% change in sensitivity always corresponded to between 3 and 5 c/s zero drift. Thus for all flights it has been assumed that 4 c/s change in the zero frequency means 1°C change in temperature of the transductor, and 1% change in sensitivity. Typical flights show a 8°C fall in temperature and a 8% drop in sensitivity between launch and burst.

To locate the source of these temperature changes all the components in the transductor assembly were tested separately. It was found that the resistors and capacitors have no significant temperature effects; it is assumed that any effects on the coils are negligible; and so the observed changes must be due to the characteristics of the Mallory cell, the diode and the mumetal laminations, being temperature dependent.

The effects of these co ponents may be separated by cooling firstly only the Mallory cell, then the diode only, and finally the complete transductor assembly.

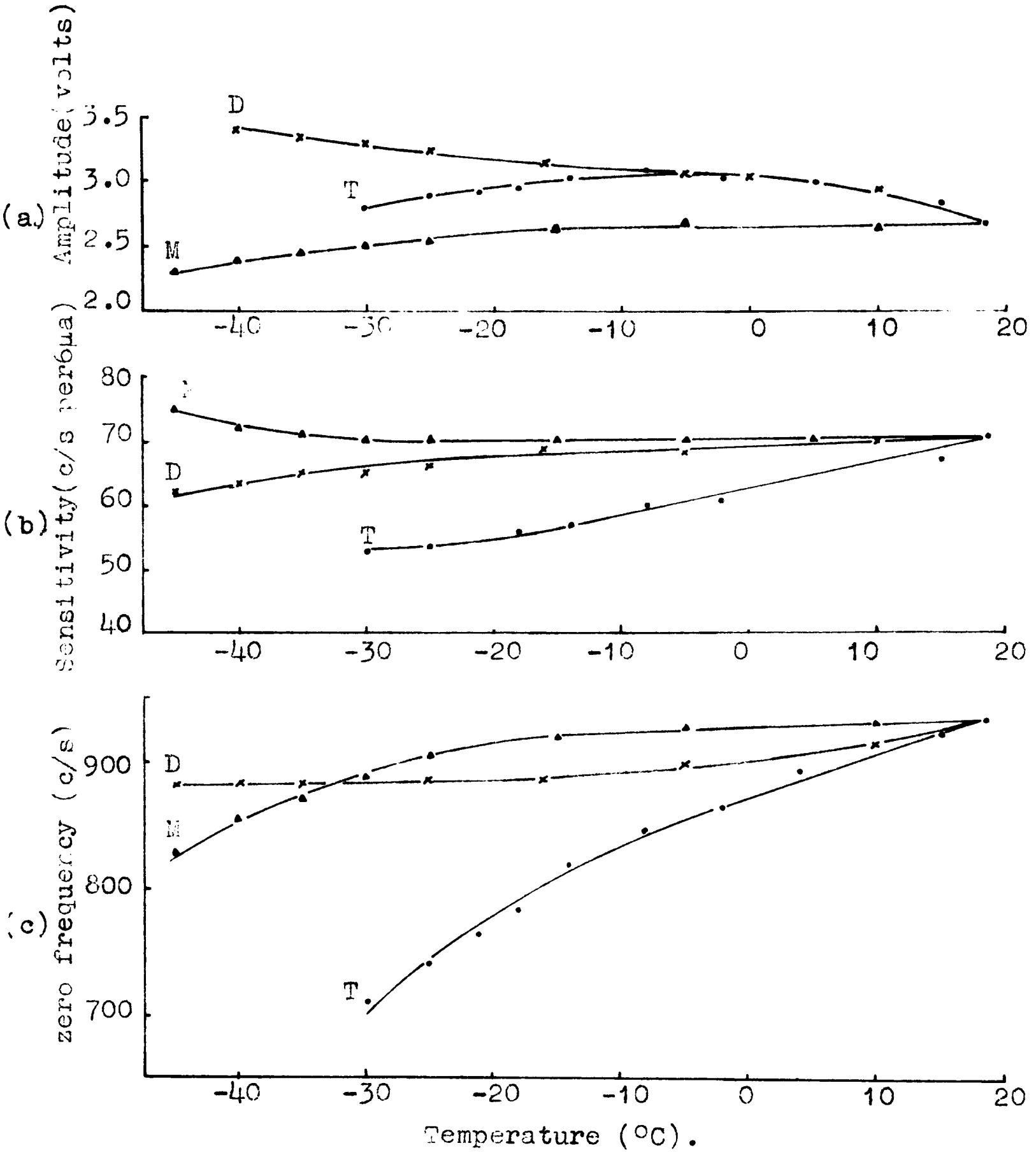


Figure 15. Temperature effects on (a) amplitude, (b) sensitivity, (c) zero frequency.
T: complete transductor; D: diode only;
M: Mallory cell only.

Fig. 15 shows how the zero frequency and sensitivity depends on the temperature of these components. Also shown is the variation of the amplitude of audio oscillations. It is seen that the changes of sensitivity and zero frequency with temperature are almost linear between room temperature and -10°C. From the zero drifts observed on flights the temperature of the transductor has probably never fallen below 0°C, and the discussion of these curves is limited to this range of 20°C to -10°C.

Zero Frequency Drift

The Mallory Cell.

As the Mallory cell is cooled, its e.m.f. decreases, (0.02V between 20°C and -10°C), and the bias current falls. This reduces the biassing field H_b, and, from fig. 11, chap. VIII, the incremental permeability, μ_Δ, increases; the inductance of the oscillator coils increases, and so the frequency decreases. From the curves, the Mallory cell provides 10% of the overall temperature effect on the transductor.

The Diode.

As the diode cools, its forward impedance increases and the amplitude of the audio oscillations increases. This increases the incremental permeability (see fig. 11), and

the frequency decreases. The diode is responsible for 45% of the total effect.

The Laminations.

As the temperature decreases, the permeability of mumetal decreases, and so the biassing induction decreases, with the result that the frequency decreases. The laminations contribute the remaining 45% of the total effect.

Sensitivity Changes

In the temperature range considered, it is seen that the Mallory cell and diode have little effect on the sensitivity, the laminations accounting for most of the changes.

The Mallory Cell.

Between +20°C and -10°C, the e.m.f. of the Mallory cell changes by less than 2%. The resulting small change in the voltage applied to the diode does not produce a measurable change in the amplitude of oscillations, and the sensitivity does not change. Below -30°C the e.m.f. of the Mallory cell decreases rapidly, and the sensitivity increases.

The Diode.

As the diode cools, its forward impedance increases and the amplitude of oscillations increases. This decreases the sensitivity, the contribution being 13% of the total sensitivity changes.

The Laminations.

Bozorth (1951, p.714) states that the permeability of iron decreases with temperature more slowly in low fields than in high fields. If a similar relation is assumed for the incremental permeability, and is applied to mumetal, it follows that the slope of the μ_Δ - H_b curve in fig. 11 becomes steeper at lower temperatures. Since frequency is related inversely to μ_Δ, and the control coil current directly to the biassing induction, a steep slope of the μ_Δ - H_b curve corresponds to a poor transductor sensitivity. Therefore, as the temperature of the laminations decreases, so the sensitivity decreases. The laminations are responsible for 87% of the total temperature changes in the range +20°C to -10°C.

Temperature Effects on the Bubbler

In all the ascents with the bubbler, there has been no indication that the solution has frozen. Indeed, calculations which are outlined below suggest that the temperature of the solution reaches only about 5°C. This is lower than the transductor temperature obtained from the observed zero frequency drifts, and the difference is due to cooling by evaporation of the solution.

Cooling by Evaporation.

If the wet-bulb temperature of the air passing through

the solution is calculated, it is apparent that the solution is cooling by evaporation throughout the flight. Whipple's formula (Brunt 1939) is

$$e'-e = (p-e')\frac{Cp}{L'\epsilon}(T-T')$$

where T, T' are the dry and wet-bulb absolute temperatures respectively; e, e' the vapour pressures of normal air and saturated air at T'; p the total pressure; L' the latent heat of water vapour at T'; Cp the specific heat of dry air, and ϵ the ratio of densities of water vapour and dry air at the same temperature and pressure.

For the low water content of the upper air, e is negligible compared with e', and the formula reduces to

$$(T-T') = \frac{e'}{p-e'} \cdot 1650 \text{ approximately.}$$

From this the wet bulb temperatures are found approximately to be as follows:

200 mb $-5^{\circ}C$

100 mb $-15^{\circ}C$

30 mb $-24^{\circ}C$

These values are based on $T = 300^{\circ}A$.

Thus the solution temperature is always above the wet-bulb temperature, and so the solution must always cool by evaporation.

Assuming that the air is saturated when it leaves the solution, then at 1000 mb, and an airflow of 200 cc/min. through the solution at 20°C, about 2 cal/min. are needed to saturate the air.

It was found from laboratory measurements that the temperature of the air in the pump is 300±9°A, and is independent of the air's temperature before entering the pump. Thus this air is always warmer than the solution, and provides some of the heat necessary for evaporation. The net result is that the solution must supply about 1.5 cal/min., and the solution temperature falls by about 0.4 °C/min.

Warming by Conduction.

The solution temperature immediately falls below the temperature of the bubbler surroundings, as indicated by the transductor zero drift, and so heat is conducted into the solution through the walls of the bubbler. This inflow of heat increases as the difference of temperature between the solution and surroundings increases, and so the solution cools less rapidly as its temperature falls.

Solution Temperature.

Precise calculation for the solution temperature at any instant is not possible due to continuously changing conditions, but an approximate calculation showed that the

solution temperature is about 10°C after 40 minutes of the flight, ie., at about 100 mb., for normal rates of ascent, and about 7°C at 30 mb. It is estimated that the solution would reach 0°C only after more than 130 minutes, and would take considerably longer to freeze. A flight, ascent and descent, normally lasts less than 100 minutes.

The solution would, of course, freeze by boiling at about 6 mb., but this pressure has never been reached on the many bubbler ascents.

Boiling.

From the calculated solution temperatures at the different pressure levels, it is apparent that the solution has probably never boiled. In any case, there is no reason why the bubbler should not work correctly if the solution should boil.

Current vs. e.m.f.

It is to be expected from equation (4) chapter III that the spontaneous e.m.f. of the bubbler will change with temperature. The change in fact, is very small in the temperature range considered, and no measurable effect on the current vs. e.m.f. curves has been found.

Response Time vs. Temperature.

It was observed by laboratory measurements that the response time of the bubbler worsens as the temperature of

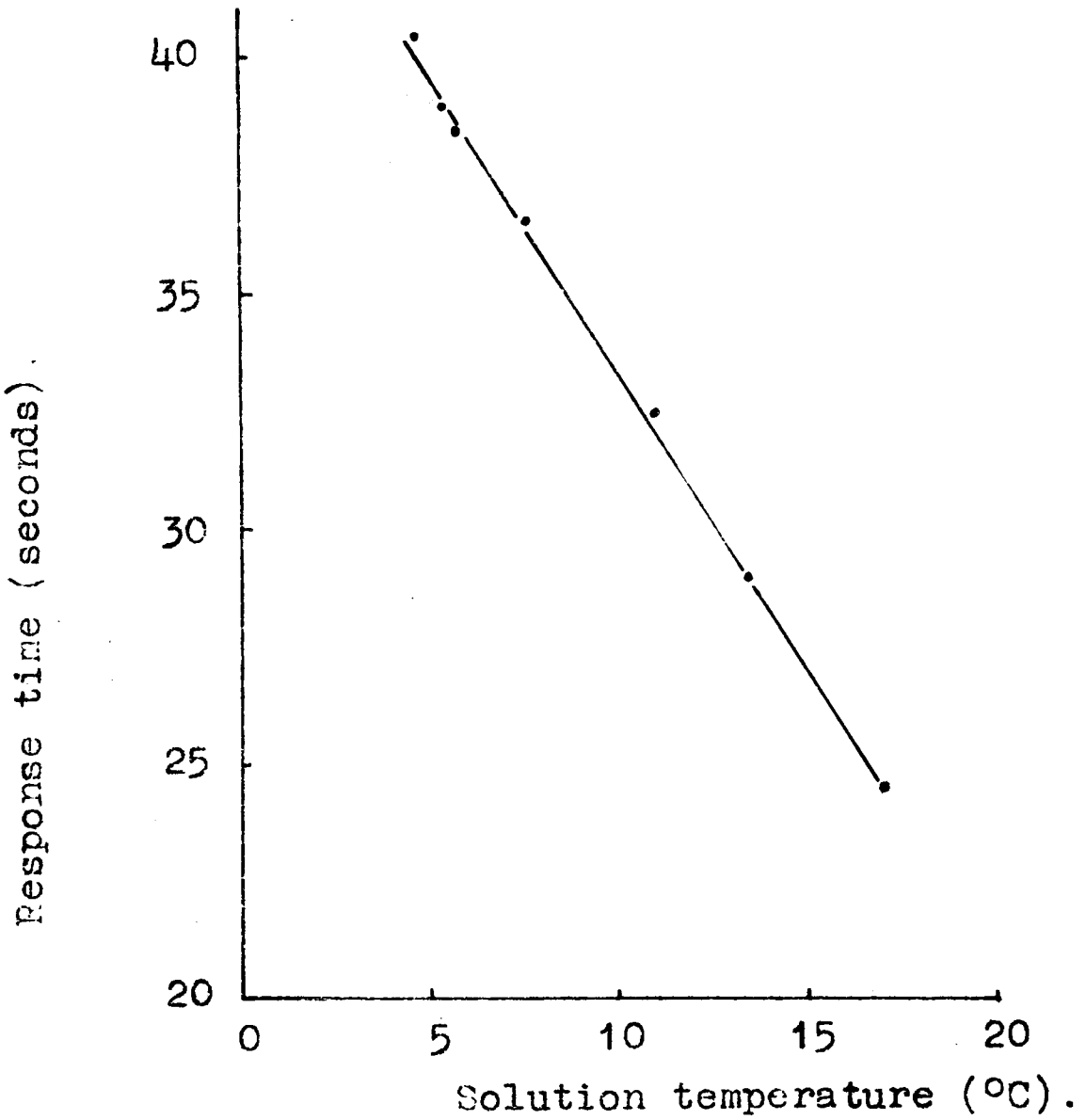


Figure 16. Variation of response time with temperature of solution.

the solution is decreased. The relationship obtained is given in fig. 16, and shows a 5% change in response time per °C in the range 17°C to 5°C. According to Mingane (1953, p.191), the diffusion coefficient changes by about 2% per °C. Thus from consideration of the relation $T = \frac{V\delta}{FA}$ (p.IV.5), the remaining 3% is probably accounted for by the temperature variation of δ, the diffusion layer thickness, which depends on the viscosity of the solution, although there is possibly some temperature effect on the ratio $\frac{I_2}{I_3}$ (p.III.7).

Thus, in a typical flight, in which the solution temperature changes from 20°C to 7°C, the response time becomes worse by about 65%. However, the response time in the stratosphere is about 30% better than the response in the troposphere, due to the increased ozone concentrations (see p.V.5), and so the net change in response time is about 35% between launch and burst. This deterioration in response is lessened by evaporation as described in the next section.

Pressure Effects.

Changes in pressure affect only the solution in the bubbler, and the efficiency of the pump. No tests were carried out on the bubbler with regard to its ozone-detecting properties, due to the practical problems of

producing reasonable ozone concentrations at reduced pressures in the laboratory. There is no reason to expect the properties of the bubbler to be affected by pressure changes, except for an improvement in the rate of extraction of ozone from the air as it bubbles through the solution.

Ozone Collection and Response Time.

The gaseous diffusion coefficient is inversely related to pressure, and so the depth of solution required for complete ozone extraction at low pressures will be less than that used in the bubbler (p.V.4). Thus the volume of solution in the bubbler could be reduced to improve the response time, and still obtain complete ozone collection in the stratosphere. This would result in low collection in the troposphere, and has not been done in the present series of ascents. In fact, the response time does improve automatically during a flight, in exactly the manner proposed, due to evaporation. It is estimated that about 0.2cc. of the solution evaporates, and, from fig. 7 chapter V, this reduction in volume should result in about an 8% improvement in response time.

This improvement, together with the temperature and ozone concentration effects on the response time, means that a response time of 24 seconds in the troposphere will deteriorate to about 3[illegible] seconds at the burst. At normal

rates of ascent the balloon rises about 150m. in 30 seconds, and this resolution is adequate for large-scale studies.

The Pump Flow-rate.

The flow-rate of the pump was measured at different pressures down to 25mb. in the laboratory. It was found that the flow-rate was independent of pressure, within the limits of the measurements.

To measure the flow-rate, a gas jar was filled with Apiezon oil and inverted over a trough of the oil. The time to displace all the oil in the gas jar, with air blown in by the pump, enabled the flow-rate to be simply calculated.

Pump Efficiency.

The efficiency of the pump was observed at room temperature at reduced pressures. The pump worked efficiently down to about 13mb. when the bubbling action began to show signs of irregularity. This became progressively worse, and at the lowest pressure reached (8mb), the bubbles appeared about three at a time, every five seconds.

The limiting pressure at which the pump will work efficiently depends on the dead volume of the pumping system. The smaller the dead volume, the less time it will take to build up the necessary pressure to overcome the back pressure of the bubbler. Thus, reduction in the dead volume

would result in the pump working efficiently to lower pressures.

The dead volume in the pumping system will vary slightly between assemblies, and so the limiting pressure will vary. On the two highest ascents, which reached 9mb., this limiting pressure was not reached, as the ozone signal showed no signs of irregularity which occurs with intermittent bubbling.

The sucking bubbler system was tested alongside the blowing pump for comparison. It was much less efficient, and showed intermittent bubble formation at 32mb. When the solution boiled at 26mb., it quickly failed completely, by the solution syphoning itself out through the air intake tube.

These tests demonstrate clearly that the sucking pump becomes inefficient when the pressure is comparable with the vapour pressure of the solution, while the blowing pump continues to work efficiently after the solution boils, and is limited only by the dead volume. The pump design has recently been improved, and the pumping efficiency should now be limited only by freezing of the solution.

CHAPTER X.

ACCURACY OF RESULTS

The results of the bubbler ozonesonde depend on many things, in addition to the efficiency of the bubbler. These introduce more possible errors into the results than the actual measurement of ozone by the bubbler.

Evaluation of Data.

From the coulometric equivalence of ozone and current shown in chapter III, it is found that $1\mu a = \frac{695}{F_m}$ units of ozone (10^{-3} cm/km). F_m, the mean air-flow, in cc/min., through the bubbler is found from $F_m = F_c \times \frac{t_c}{t_s} \times \frac{T_s}{T_p}$.

F_c = preflight air-flow, in cc/min., measured for a cam-revolution time of t_c seconds. t_s = cam revolution time in seconds at any instant during the flight. T_s = ambient air temperature (^oA) of the ozonesonde. T_p is the temperature of the air in the pump.

If, from the preflight transductor calibration, 1c/s = $A\mu a$, then the ozone measured at any instant during the flight is given by

$$O = 695\ L.\frac{NA}{F_c}.\frac{t_s}{t_c}.\frac{T_s}{T_p}\quad 10^{-3}\ \text{cm/km} \qquad ...(7)$$

where L is a correction factor for ozone losses in the system, and is taken as 1.04 (see chap. VI). N = number of cycles between the ozone signal and zero signal, plotted on

the radiosonde 10-minute frequency/time graphs.

The total errors introduced by the various quantities in the above relation, may be conveniently estimated in terms of an absolute accuracy and a profile accuracy. The profile accuracy, ie., the accuracy to which ozone changes during a flight are significant, is better than the absolute accuracy. However, analysis of the series of ascents described in a later chapter has shown that the absolute ozone measurements are much better than the estimated possible errors suggest.

Absolute Accuracy

Bubbler Readings

The bubbler is an absolute instrument, but a correction factor, L, has to be applied to the bubbler output to account for losses in the system, which were discussed earlier. It was shown that a correction factor of 1.04 is correct to 4%, and is probably even better after the preflight ozonizing.

Airflow.

The preflight airflow calibration entails measuring the time (about 100 seconds) for 8000 pump strokes, i.e., one complete cam revolution (t_c), and simultaneously finding the mean airflow (F_c) from a capillary flow-meter with a water manometer. It is the product of these quantities

which is significant in the calculation of the ozone amount, and generally repeats within 2", even if the motor speed changes.

A temperature correction is applied to the airflow during flight; it is simply the ratio of the ambient ozonesonde temperature, to the temperature of the air in the pump, in °A. The ambient temperature T_s is measured by the Kew radiosonde flown in tandem with the ozonesonde, and is known very accurately, but the method of evaluating the flight data probably introduces about 1% error. The value of T_p was shown earlier to be 300° ± 9°A, and so the error in this airflow correction is about 4%.

Transductor.

The preflight transductor calibration should give the sensitivity, A, correct to 1%, but the drop in sensitivity, due to the temperature of the transductor decreasing during the flight, and its rate of change are not known accurately. For all the flights it has been assumed that a 1% change in sensitivity corresponds to 4c/s drift of the zero frequency. As was shown earlier, a 1% change may correspond to anything between 3 and 5c/s drift, thus introducing an error of 0% at the surface increasing to about 3% at the burst.

Evaluation from plotted data.

To evaluate plotted data for a flight, the zero signals

are first joined with straight lines: the zero drift is generally quite steady, and often, one or two continuous straight lines only, cover the complete flight, with each zero signal within 1c/s of the line. The ozone signals are also joined by the best straight lines, so that the actual recorded frequency is always within 1c/s of a line. It is clear that this method is to some extent subjective, but not sufficiently to influence the main results.

The next step is to break up the flight into sections in which the ambient temperature lapse rate is approximately constant. For each section the mean value of t_s, the cam revolution time, is measured from the interval between zero signals. This together with the value of T_s at each end of the section, enables the ratio t_s/T_s to be determined throughout the section, and this multiplied by other terms in equation (7), gives the ozone concentration per c/s at any point.

The mean value of t_s for each section of the flight can be determined to within 1%, although individual values of t_s within the section may differ from the mean by about 3%.

Ozone Amount.

The ozone reading, Nc/s, may have an error of up to 2c/s at any point in the flight, due to the method of evaluation of the plotted data. This corresponds to about

1×10^{-3} cm/km. of ozone. However, in assessing the integral amount of ozone in an ascent these errors should be averaged out.

Overall Absolute Accuracy.

When the errors for the different factors involved in calculating the ozone amount are added together, it is found that the absolute error in the ozone amount is about 20%, or 1×10^{-3} cm/km., whichever is larger.

Ascent and Descent Profiles.

Whenever possible, the ozone profile has been measured on the descent as well as the ascent, in order to determine the consistency of the ozonesonde. Above 100mb. the descent profile is sketchy, as the drag on the parachute is small and descent rapid, often more than 1000 m/min., compared with 300 m/min. ascent. The rate of descent is generally greater than the ascent rate at all levels, and this increases the separation of the profiles. This is further enhanced by the difference in response times due to the cooling of the solution.

This temperature effect would explain the increased separation at lower levels found by Brewer and Milford. At lower levels, the difference in solution temperature, and hence the response times, between ascent and descent will increase, since the solution is cooling throughout the

flight, and the separation of the profiles increases. On the bubbler flights this difference of separation has not been obvious. In general, the opposite effect, of larger separations at higher levels, has been more apparent, and this is attributed to the faster rate of fall at the higher levels.

Ascent and descent data have been obtained on the majority of flights at Liverpool, and the profiles show very good agreement, except on two flights in the present series, where the profiles disagree at the tropopause. On BL5 and BL56, the ascent did not show much ozone until well above the tropopause, and then as a sharp increase, whereas the descent showed normal ozone changes down to the tropopause. The reason on each occasion was probably that reducing agents were present either in the intake tube or solution, causing the reading to be low until the reducing agent had been completely oxidized, when the ozone reading increased sharply. Indeed, it was confirmed that before flight BL56, the pump was switched on indoors by mistake, and so "dirty" room air was passed through the inlet system and solution.

This reducing agent effect definitely occurred on another Liverpool flight W1; and probably occurred on a Nairobi flight, N4, although there was no descent data to confirm it.

Improvement in Accuracy.

The accuracy could be improved by checking the losses in the system immediately before flight. This was attempted at Liverpool. A variable ozone source and a glass bubbler with its auxiliary equipment were sent to Liverpool. Measurements of the ozone output from the source were made with the glass bubbler and the ozonesonde before flight, and the difference gave the losses in the ozonesonde. The results were not satisfactory due to many possible sources of error in storing the glass bubbler, and using it only once a week; and since it doubled the time of preflight preparations, from 10 minutes to 20 minutes, this attempt to improve the accuracy was abandoned after a few flights.

This problem would be overcome if a simple standard ozone source could be made.

Accuracy Achieved.

It is difficult to assess the accuracy achieved with the bubbler, but when the ascents are analysed in terms of ozone amounts in layers of the atmosphere, it is seen that the accuracy is better than that estimated. This is best shown by the annual variation of ozone above 25 mb. during the Liverpool series of flights (see next chapter). This curve shows the expected photochemical variation very

well, and since the amplitude of the variation is of the same order as the estimated error, then either the curve obtained is pure chance, or, more likely, the results are more accurate than estimated.

CHAPTER XI.

THE FLIGHTS.

Most of the flights with the bubbler ozonesonde were made at Aughton, near Liverpool, in a regular weekly series for more than a year. Some interesting flights were made at irregular intervals at Nairobi, and, more regularly, at Malta.

All the flights shown in appendix B are with the blowing bubbler.

Flights at Liverpool (53°N).

After more than a dozen flights with the prototype sucking bubbler, and a few flights with the blowing bubbler before the problem of zero shifts was overcome, a series of weekly ascents was started at Liverpool.

The ascents took place at noon, and over a period of more than a year (November 3rd 1959 - December 15th 1960), only two weeks passed without an ascent. The first time was due to staff problems over Christmas 1959, and the second occurred when apparatus went astray in the post in October 1960.

In fifty-seven flights at Liverpool there were only five occasions when no useful information was obtained, and two of these were due to failure of the Kew transmitter. There were four other flights for which the absolute accuracy was obviously poor, but nevertheless provided useful profile

information.

The flight procedure at Liverpool was to fly the ozonesonde, transmitting ozone data continuously, in tandem with the routine radiosonde at noon.

At the end of the weekly series of ascents at Liverpool, three other flights were made (#1, T1, T2). T1 and T2 were made with a transistorized bubbler ozonesonde (mentioned later); and #1 was with the ozonesonde described in this work.

#1 was the first of a short series of daily ascents which was planned to take place during the sudden stratospheric warming which generally occurs early in the year. The McGill University Arctic Research Section was attempting to forecast the arrival of the stratospheric warming over the U.K., and flight #1 was made on the basis of their forecast. However, the warming did not reach the U.K. and the series was halted.

A minor warming over the U.K. occurred in late January (1961), but no flights were made as a more spectacular warming was anticipated. However, the total ozone showed the sharp increase previously associated with major warmings. As a result of missing this increase in total ozone, and owing to difficulties of carrying out daily ascents at a later date, the stratospheric warming programme was abandoned.

Flights at Nairobi (1°S).

Flights at Nairobi started in March 1960, and for a short time after a period of personal instruction, some useful flights were made. However, the radiosonde station was beset by staff problems, and the flights became very intermittent, and only eight ascents, including two failures, have been made during the past year. The results obtained however, are of considerable interest.

Flights at Malta (37°N).

From June until December 1960, a flight was made at Malta every fortnight on Thursdays to coincide with the Liverpool ascent.

In thirteen flights there were four failures; two of these happened because the ozone assembly had been damaged in transit and should not have been flown.

The usual flight procedure at Malta was to launch the ozonesonde alone, immediately after completing the routine ascent. This was necessary due to high winds making a tandem launching difficult.

Heights Attained.

The heights reached during the series at Liverpool were very disappointing. Out of fifty-three successful flights, only eighteen reached 25mb., and thirteen did not reach even 50 mb.

Both Malta and Nairobi flights in general reached greater heights than at Liverpool. This may be due to the higher storage temperature of the balloons (1250 gm.) in the lower latitude stations.

Flight Failures.

The main source of trouble has been the switch gearing. The most likely switch fault occurs when the gears fail to mesh correctly, and the motor cannot turn the cam against the force of the microswitch. his occurred on three flights (BL11,20,24) when the switch stuck on the ozone signal soon after the launch. By drawing in a zero line so that the ascent and descent agreed reasonably well, useful information was obtained. On another occasion the switch stuck on the zero signal, and no ozone signal was transmitted.

Another possible cause of trouble is that the pump may work loose, and not seat properly on its base. If this occurs the pumping rate decreases and becomes irregular. This is probably the explanation of the unsatisfactory flight, BL14.

On other occasions (BL11,17,20), it was clear, by comparison with the total ozone, that the results were low. The profiles were good, and showed none of the symptoms of pump trouble; the low results were probably due to dirt in the inlet system or bubbler. These flights still provide

useful information on the profile of the vertical distribution.

Two other failures at Liverpool were due to the Kew transmitter not working after the launch.

The reasons for other flight failures are not obvious, and are probably due to dry joints in the transductor circuitry, although there has been cause to suspect the motor battery on one or two occasions at Malta.

Improvements.

It is hoped that some of these troubles have been overcome in the recent redesign of the bubbler ozonesonde by Dr. A.W. Brewer and Dr. E.L. Simmons. The pump and gearing has been redesigned, and the microswitch replaced by a rotary wafer switch. Also the bubbler has its own transistor transmitter included in the Dewar, thus being a complete ozonesonde unit within the 500cc. Dewar. It is hoped to add pressure and temperature elements to the unit, so that the vertical ozone distribution may be obtained independent of radiosonde measurements.

The results of two trial flights (T1,2) are shown in the appendix.

Presentation of Results.

In order to show the many individual flights compactly, and in a form which makes intercomparison fairly easy, the

TABLE 2.

Units of Ozone Measurement

	Local Density ($\mu g/m^3$)	Mass Mixing Ratio ($\mu g/kg$)	Volume Mixing Ratio (pphm)	Local Equivalent Thickness $(cm/km)\tau$
1 $\mu g/m^3$ =	1	$1/\Delta$	$0.06/\Delta$	4.67×10^{-5}
1 $\mu g/kg$ =	Δ	1	0.06	$4.67 \times 10^{-5} \times \Delta$
1 pphm =	$16.5 \times \Delta$	16.5	1	$7.81 \times 10^{-4} \times \Delta$
1 cm/km =	2.14×10^4	$2.14/\Delta \times 10^4$	$1.28/\Delta \times 10^3$	1

where Δ is the air density (in kg/m^3)

$$\text{Total ozone} = \int_0^\infty \tau \, dh$$

flights have been presented on a reduced scale, approximately two-fifths the original size. Most flights are displaced 20 units to the right of the previous one in the sequence. A few have been displaced 40 units to avoid overlapping of the data.

This method precludes the drawing of the corresponding temperature distribution, but the temperature at major changes in lapse rate are written in at the appropriate level. The tropopause level is indicated with an arrow.

Where known, the total ozone, measured at Oxford, is entered above each flight in the Liverpool series. No totals were available for Malta and Nairobi.

Co-ordinates.

The co-ordinates in the presented results are t ose directly measured during a flight, i.e., absolute concentration (10^{-3} cm/km) of ozone against pressure in millibars.

Figures for converting the ozone concentration into other units which may appear in other published results, are given in table 2.

CHAPTER XII.

GENERAL DISCUSSION OF THE FLIGHTS

Variations in individual ascents at Liverpool.

The series of ascents at Liverpool shows clearly the contrast between the stratification in the stratosphere and the thorough mixing in the troposphere. It is clear, however, by the differences between ascents, that there is considerable activity in the stratosphere.

In the first half of the year there is nearly always a sharp increase in the ozone concentration at the tropopause, while in the second half the increase is generally slower. It is also apparent that there is much ozone and much variation in the lower stratosphere early in the year, the ascents shewing large differences from week to week, whereas in the Autumn, the ascents show little change in their general distribution.

100mb. minimum.

A striking feature of the ascents is the persistent appearance of a minimum in the ozone distribution near 100mb. Its appearance is quite irregular except that it is not obvious in the period July to October inclusive. It seems to have no connection with the total ozone, appearing for both low and high ozone totals (e.g., BL1, BL13). This feature can be found in the work of other authors, and is probably due to the general circulation in

the stratosphere rather than chance.

The only other available results which show detailed structure as in the present work, are those obtained by Milford (1958) with the transmogrifier at Liverpool, 1957-58. Examination of these reveal that this same minimum appears on many flights and is absent in the same period.

Other published results are spectroscopic, and are probably not sensitive enough to show this minimum on every occasion. However, Dutsch (1959) gives data for Umkehr observations on 24 days during 1956-57 at Arosa. On seven of these occasions, it is found that there was a minimum ozone content in the layer 125 to 62.5mb. None of these was in the period of July to October; unfortunately only one observation was made in that period.

Ramanathan and Kulkarni (1960) have also published Umkehr data for many latitudes and for many times of year. They comment on the occasional appearance of a minimum in the 12-18km. layer and associate it with large total ozone, and the occurrence of a double tropopause in Winter and Spring. In the 63 observations, this minimum was apparent only four times, these being in December and February at Srinagar (34^{o}N).

Paetzold (1959) gives results obtained at Weissenau

(48°N) with his spectroscopic ozonesonde. He finds a minimum at about 17km. quite frequently in Spring and Summer and considers it to be caused by the advection of ozone-rich polar air into the stratosphere below 17km.

Thus the results obtained with the bubbler at Liverpool, and the few results of other authors indicate that this minimum at about 100mb. occurs mainly in the Winter, Spring and Summer and in temperate latitudes.

This 100mb. minimum does not appear in a mean vertical distribution, but this may be due to its variation in magnitude and in height. The above discussion, however, suggests that the minimum may be due to the general circulation, and that detailed investigation is desirable.

<u>High level minimum.</u>

Another unusual minimum was observed (at about 25km) on a few of the occasions that the balloons reached high levels. This minimum occurs in or above the levels of maximum ozone and appears clearly in BL27, 28, 29, 46, and possibly in BL43. The first three were in May and the others in August. It is interesting to note that Mateer and Godson (1960) observed a similar minimum at about 30km. at Resolute in the Autumn. It is unfortunate that the bubbler ascents did not reach these high levels often

enough to see if this minimum is a regular feature of the vertical ozone distribution.

The late winter stratospheric warming.

During the autumn months the middle stratosphere at high latitudes becomes steadily colder, and the general circulation in the Winter months is characterised by a circumpolar vortex around this cold core. Towards the end of the Winter a rapid warming sets in and the vortex gradually dies out. Associated with this warming is a sharp increase in the total ozone (Godson, 1960).

From the bubbler ascents it is clear that this warming occurred over the U.K. in January 1960. Within the month, the stratospheric temperatures had increased by up to 15°C and the total ozone had almost doubled. Most of the ozone increase was accounted for by changes in the lower stratosphere content.

Detailed analysis of ascents during this period might have provided useful information about the mechanism causing the rapid increase in ozone. Unfortunately, there were three ozonesonde failures in this period, and even when the ozonesonde worked well, results were not obtained at high levels due to poor balloon performance.

In 1961, the rapid warming associated with the break-down of the polar vortex did not extend over the U.K., and

was completed over the Canadian Arctic by the beginning of March.

Nairobi Ascents.

Although only a few ascents have been made, they have shown that there is little ozone near the equatorial tropopause. The characteristic increase at the tropopause of high latitudes is missing, the ozone concentration generally increasing very slowly from just above the tropopause. The vertical distribution does not show much variation with time of year, suggesting that there is little activity in the equatorial stratosphere. These ascents are discussed again in a later chapter.

Malta Ascents.

Nearly all of the Malta ascents made with the bubbler were in the second half of 1960. Most of these show the type of distribution obtained at Nairobi, although the December and early June flights show the familiar distributions of higher latitudes.

Ascents at Malta should be useful in determining the flow of air between the stratosphere and troposphere at the break of the tropopause. Malta is at 37°N where both the equatorial and temperate tropopauses frequently overlap. This was clearly the case on the flights MB1 and MB2, while MB7, 8, 11, 12 definitely show the temperate tropopause,

and possible the equatorial tropopause. On flights MB3 and MB5, only the equatorial tropopause was apparent.

It is of interest to compare MB2, with the Liverpool ascent BL32. Both ascents took place at mid-day, June 16th 1960, and each distribution has a layer of ozone-rich air at about 150mb. Both ascents show a temperate tropopause at about 200mb, and an equatorial one at about 90mb. Study of occasions like this should yield some useful information about air movements.

CHAPTER XIII.

ANALYSIS OF THE VERTICAL DISTRIBUTION OF OZONE IN LAYERS

For studying the systematic trends, and for comparing the results of the many flights, the ozone amounts have been measured in layers of the atmosphere for each flight. The layers are investigated for an annual variation, and to take into account any day-to-day variations, the layer totals are plotted against total ozone.

Choice of layers.

The atmosphere has been divided into five layers as listed below. The pressure levels were chosen so that the thickness of the layers approximated to those given in published spectroscopic measurements, and hence direct comparison may be made with them.

Layer.	ICAN thickness of layer
1. Surface to tropopause	10.8 km.
2. Tropopause to 120 mb.	4.2 km.
3. 120 mb. to 50 mb.	5.6 km.
4. 50 mb. to 25 mb.	4.4 km.
5. Above 25 mb.	-

The layer totals were measured on the original flight results with a planimeter. The amount in layer 5 is obtained by subtracting the amount below 25 mb. from the total ozone measured spectrophotometrically.

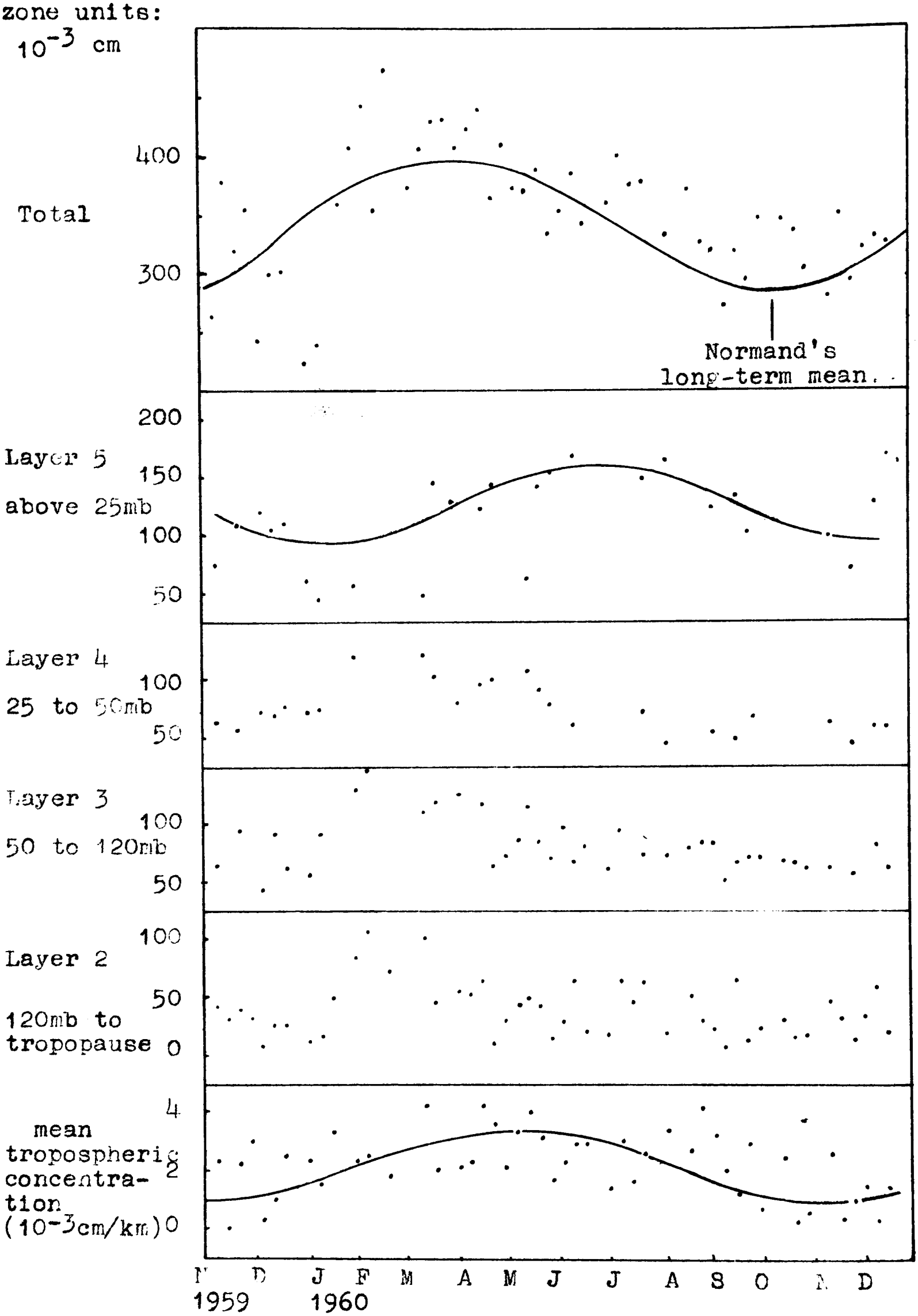


Figure 17. Annual variation of total ozone (at Oxford) and total in layers (at Liverpool).

The amount of ozone in layers 1 and 2 is dependent on the height of the tropopause which forms the boundary between them - in fact, the results show a very good negative correlation between the amount in layer 2 and the tropopause height. To eliminate this dependence, the mean concentration in each of these layers has been determined. All the data are tabulated in appendix C.

Annual Variation of Layer Totals.

The annual variations for the total ozone and the ozone in layers at Liverpool are shown in fig. 17. The total ozone shows much fluctuation about its mean curve which differs considerably from Normand's long-term mean. The form of this curve during 1959-60 is quite unusual, and it was not possible to find another with such a sharp increase in January in past records. It is observed that there is a secondary maximum in July. This occurs at many places in late Summer or Autumn, as is pointed out by Craig (1950).

Layers 2 (tropopause-120 mb), 3 (120 mb -50 mb), 4 (50 mb - 25mb)

It is not obvious that the ozone in these layers is following the variation of the total. Indeed, the mean in each layer shows little variation after the Spring, although they all followed the sharp increase in the total ozone in January. Paetzold (1959) found a clear variation

in similar layers with his optical sonde. This may be because his flights were spread over a few years. His total ozone variation was close to the long term mean.

The relation of the ozone in these layers to variations of the total are obscured in the annual variation by the day-to-day changes. It is shown later (fig. 18) that the layer totals are more closely related to the total ozone than is apparent from fig. 17.

Above 25 mb.

The results of the layer totals are shown to be basically correct by the variation of the ozone above 25 mb. This curve shows a variation which might be expected from photochemical theory, and is perhaps the best evidence that the absolute accuracy of the ozonesonde is better than indicated by the estimated possible error. The estimated error in this layer is comparable with the amplitude of the variation, and yet, with the exception of a few ascents, the mean variation is followed closely throughout the year. This consistency indicates, at least in the mean, that the region controlled by photochemical processes extends down to about 25 mb, which is perhaps lower than is generally accepted, but confirms the findings of Dutsch (1959) from Umkehr measurements. It is unfortunate that there are only three results - and

two of these are extrapolated values - during the period December to February which covers the minimum in this layer. If these points are used, the photochemical variation is not symmetrical about its mean, suggesting that these results are too low. The ascents were good, and the most likely reason is that the total ozone at Liverpool was different from that at Oxford. The Daily Weather Reports for these days do not reveal any marked variation in the synoptic situation which could provide a difference in the totals. However, the ozone totals at Eskdalemuir and Oxford (Liverpool lies roughly midway between these places) often differ although the synoptic situation is similar at both places. Observations at Eskdalemuir were made on only one of the three dates concerned and showed 0.312 cm. compared with 0.240 cm. at Oxford on January 7th 1960. The total at Liverpool probably lies somewhere between these, thus increasing the amount above 25 mb. to a value nearer to that expected from the symmetrical annual mean variation shown.

It may be mentioned that if the Eskdalemuir total is taken into consideration for the rest of the year, the scatter of points about the mean is not significantly different from that shown.

From the symmetrical variation shown, the mean amount

of ozone above 25 mb. at Liverpool (53°N) is about 0.125 cm with a peak-to-peak amplitude of about 0.060 cm. These figures compare well with spectroscopic results which should be most accurate at these high levels. Paetzold (1959) gives results obtained with his optical ozonesonde at Weissenau (48°N). The mean is about 0.130 cm. with a peak-to-peak amplitude of about 0.040 cm. Dutsch (1959) does not give sufficient Summer Umkehr observations at Arosa (47°N) to follow the high level variation, but the mean appears to be about 0.130 cm. and he quotes a 30% or less, seasonal variation above the region of the ozone maximum, i.e., above about 25 km.

Tropospheric ozone.

The annual variation of tropospheric ozone has a maximum in early Summer (see fig. 17), and does not follow the variation of total ozone. It is seen in fig. 18 however, that there is a tendency towards a positive correlation between the ozone in the troposphere and the total ozone.

The range of mean tropospheric concentrations is small, (0 to 4.2×10^{-3} cm/km) and the error in the values may be as much as 1×10^{-3} cm/km (see p. X.5), but the Summer maximum shown by the mean curve is probably real, and a possible explanation is presented below.

Tropospheric ozone may arise by several methods: (a) ozone produced in the troposphere by dissociation of molecular oxygen as in the upper stratosphere, (b) ozone produced by photochemical reactions involving the oxides of nitrogen, (c) electrical discharge in the troposphere, (d) transfer of ozone from the stratosphere.

The first source requires radiation of wavelengths less than 2400Å, and the intensity of these wavelengths is greatly reduced by absorption in the ozone in the stratosphere. The second source requires radiation of wavelengths less than 3660Å and may be significant in producing ozone in the troposphere. The amount formed by electrical discharge is probably small, particularly in temperate latitudes where thunderstorms are infrequent. The last method of ozone transfer is undoubtedly a significant contributor, as will be seen below.

Examination of the Liverpool series of ascents shows that the ozone increases below, rather than at or above it, i.e., the tropopause is not acting as a barrier to the ozone, on about a third of the ascents. This is not a seasonal or regular effect, except that it was not observed in February or March, although this may be due to the chance sampling of the weekly ascents. It is probably significant that eleven of the twenty-one points

above the mean curve in fig. 17 corresponded to ascents with ozone increasing below the tropopause, whereas only four of twenty-three points below the line did. Thus ascents not showing this cross-tropopause transfer generally show less-than-average tropospheric ozone content.

It is suggested then, that the main source of the tropospheric ozone may be transport through the tropopause from the stratosphere. However, the fact that there is a maximum in the Summer, whereas the cross-tropopause transfer seems to occur just as frequently at other times of the year, requires further explanation.

It may be that the cross-tropopause transfer, when it occurs, is greater in the Summer months. When there is outflow of ozone, it is dispersed by turbulent motions in the troposphere and further outflow from the stratosphere will replace it. This rate of outflow might be expected to be most rapid in the Summer when the turbulent motions are greatest, thus producing a maximum in the annual variation of the tropospheric ozone content.

However, two other possibilities exist. Firstly the photochemical reactions involving the oxides of nitrogen would be expected to have a maximum in the Summer, although later than the observed maximum. Secondly, the subtropical

jet, and hence the break in the tropopause, is nearer to England in the Summer than in the Winter, when it is farther South. So, if there is outflow of stratospheric ozone into the troposphere at the tropopause break, as is generally thought, then a maximum tropospheric concentration might be expected in the Summer.

A combination of either or both of the above mechanisms with the cross-tropopause transfer could account for the observed annual variation of tropospheric ozone.

The mechanism which transports stratospheric ozone into the troposphere is probably the same as that which brings nuclear explosion debris into the troposphere, and so investigation of the deposition of the fission products should yield an annual variation similar to that of ozone. Crooks et al (1960) give results obtained for the deposition by rain of strontium 90, for several years, but not, unfortunately, for all of 1960.

The results show a maximum deposition at about the same time as the maximum of the tropospheric ozone content, thus suggesting that air motions, rather than photochemical processes, are producing the ozone variations in the troposphere.

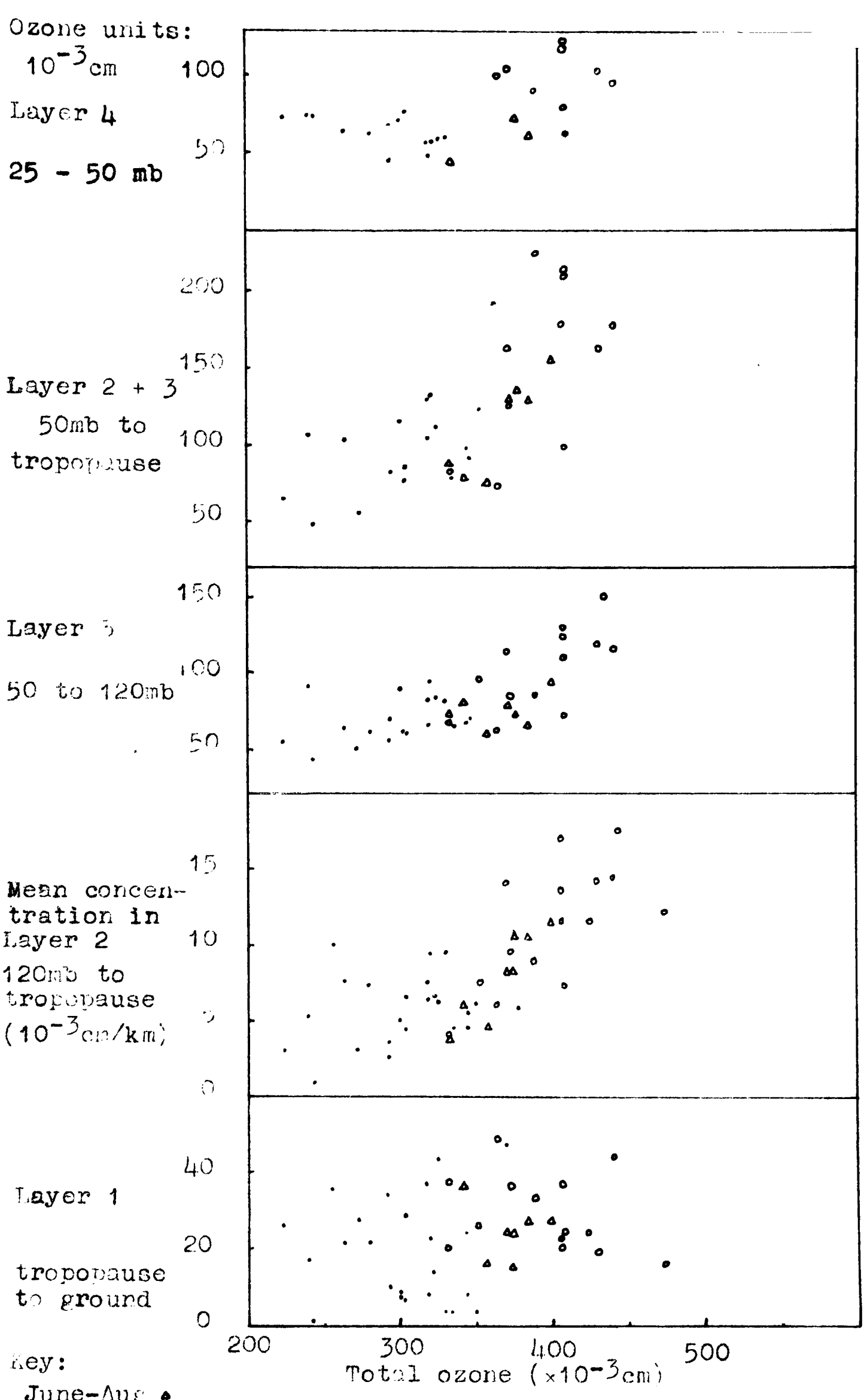


Figure 18. Variation of layer totals with total ozone. Liverpool flights, Nov.1959-Dec.1960.

Variation of Ozone in Layers with Total Ozone

The variation of the ozone amounts in the different layers is shown in the scatter diagrams of fig. 18. The variation above 25 mb., layer 5, is not shown as it was seen in fig. 17 to be independent of the total ozone.

From these diagrams it is clear that there is a relation between the layer ozone amounts and the total, except in the troposphere as was to be expected from the annual variation in fig. 17. Closer examination of these diagrams reveals that the correlation, and the line of regression, vary with time of year in all the layers.

The division of the ascents into time of year was determined by the variation of the total ozone rather than by the calendar seasons. The variation of the total may be considered in four phases as follows: from early January to the end of February covering the sharp increase; March to the end of May covering the period between the main maximum and the secondary maximum in June-July; June to mid-August which includes this secondary maximum, and finally the period from mid-August to the minimum in January. Unfortunately, there are insufficient data for the first period, and the two or three readings obtained are included with the next period, so there are only three periods in the ascents to be

TABLE 3.

Coefficients of correlation between ozone amounts in layers and the total ozone.

Layer.	Correlation Coefficient		
	Autumn	Spring	June - Aug.
2 Trop.-120mb	0.35	0.70	0.90
2. (mean concentration)	0.24	0.67	0.97
3. 120-50mb.	0.37	0.70	0.35
(2+3) Trop.-50mb.	0.46	0.75	0.89
4. 50-25mb.	-0.37	-	-

considered.

The correlation coefficients for the scatter diagrams are shown in table 3, for different times of the year. There are probably too few points (8) in the June-August period, and the year has been divided finally into two, August to January, and January to August, which may be considered as Autumn and Spring respectively, and will be referred to as such in subsequent discussions.

Layer 1.

There is no clear evidence of a relation between tropospheric ozone and the total ozone. The mean amount of ozone in the troposphere is about 7% of the total in Autumn and about 8.5% in the Spring. These figures may be compared with those obtained by other methods. Mateer and Godson (1960) who found a similar annual variation of tropospheric ozone, give 14% as a mean figure for all seasons. Paetzold (1959) shows the tropospheric amount with an annual variation similar to that of the total, and from his data, the mean amount appears to be about 4.5% in the Autumn and 9% in the Spring.

The bubbler results should be better in the troposphere than those of the spectroscopic methods, which are unreliable at these low levels.

Layer 2. (tropopause-120mb).

Fig. 18 shows that the mean concentration of ozone

in this layer has a good correlation with the total in the Spring, but a very poor one in Autumn. If only the 8 ascents between June and August are considered, the correlation is remarkably high (see table 3). When the layer total is plotted, much the same seasonal variation is found. By drawing in the approximate regression lines it is clear that this layer accounts for more of the change in total ozone in Spring than in Autumn.

Layer 3. (120mb-50mb).

This layer shows much the same variations as layer 2, except that the difference between Spring and Autumn is not so marked. Also, for the period June to August, there is little variation in the layer total, and the correlation coefficient is very low, whereas the correlations for the other periods are almost the same as for layer 2.

Layer 4. (50mb-25mb).

The variation in this layer is very interesting. Its behaviour is a complete reversal of that of layers 2 and 3.

The amount in Autumn shows a good, but negative correlation, while all other layers have shown a poor positive correlation. Also, it is striking that the Spring variations bear no obvious relation to the total,

whereas the correlations in the other layers were best at this time of year. Although more points are desirable in this layer, there are probably enough for these relations to be significant.

Discussion of Layer Variations

It is difficult to reach any definite conclusions about these layer variations since there are comparatively few results, particularly in the most interesting layer 4, due to the many low-level bursts in the series of ascents. Also, the ascents are at weekly intervals, and the layer variations could be due to chance sampling.

Therefore the following discussion of the results, and the conclusions reached, must be regarded as tentative.

Further investigations on the same lines would best be carried out with a series of daily ascents rather than at weekly intervals.

The mechanisms of ozone changes.

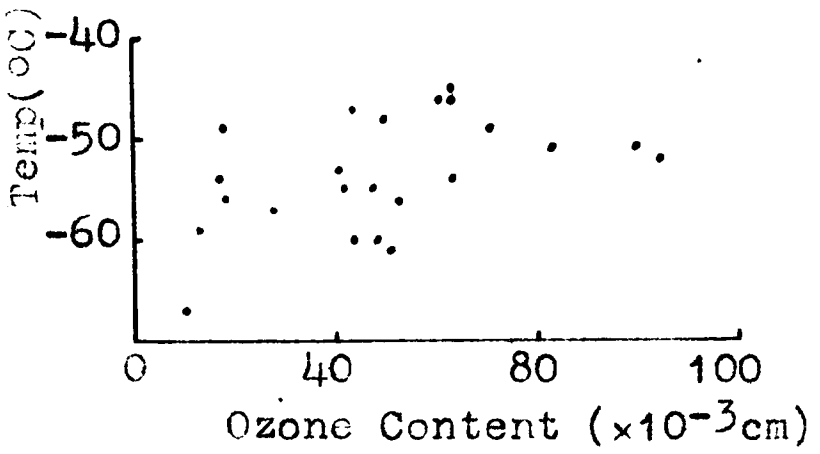
It is clear from fig. 18 that the mechanism of ozone changes between 50 and 25mb. is different from that in the stratospheric layers below. The mechanisms involved are dynamic and advective. It should be possible to distinguish between these by consideration of the temperature changes associated with the ozone changes.

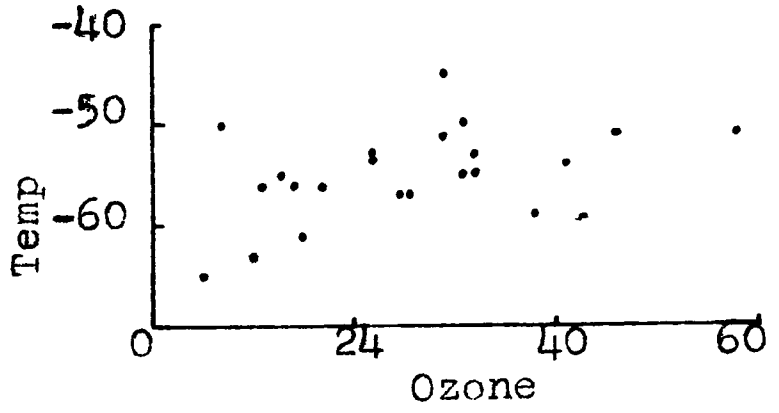
If the mean vertical distribution of ozone is

SPRING.

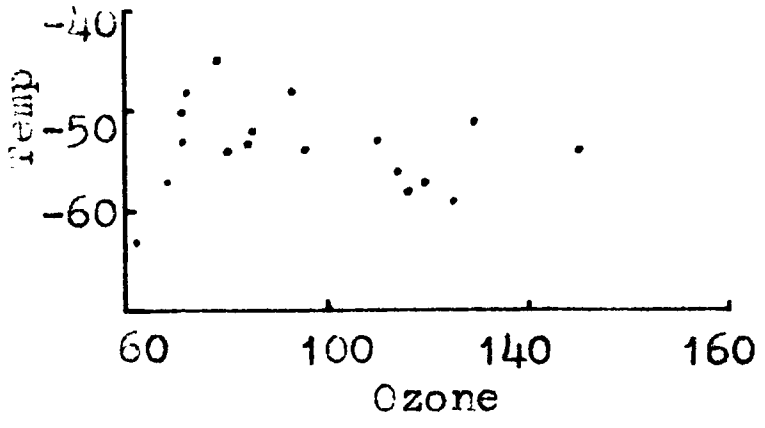
AUTUMN.

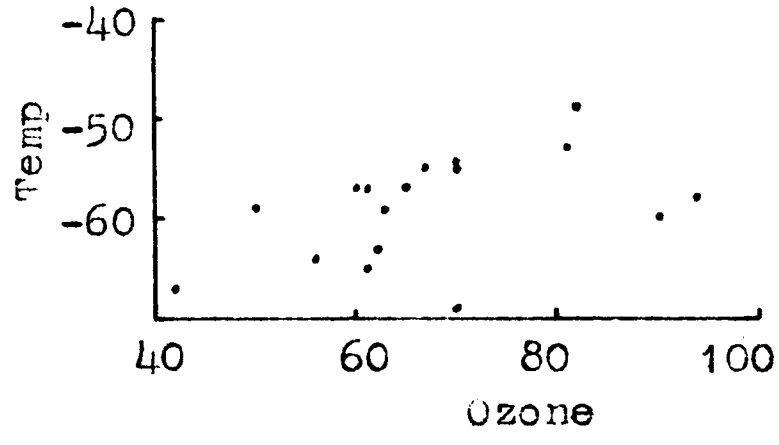
Layer 2 (tropopause - 120mb)



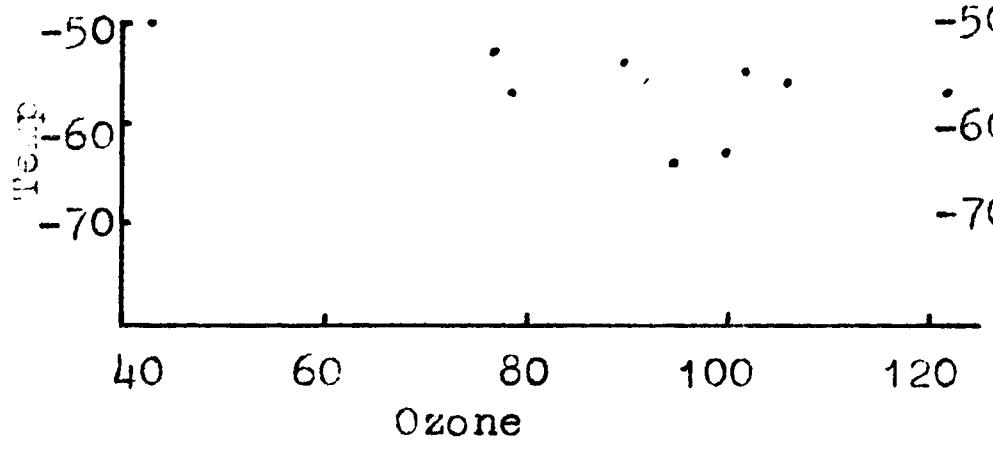


Layer 3 (120mb - 50 mb)





Layer 4 (50mb - 25mb)



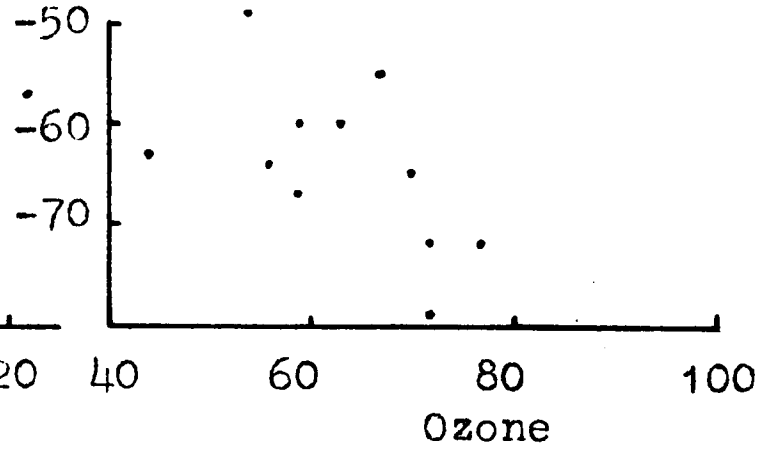


Figure 19. Variations of layer ozone content with mean temperature of layer.

determined for the present series of ascents it is found that the ozone/air mixing ratio is increasing with height up to at least 10mb., both in Spring and Autumn. Hence, if vertical movement is the dominating mechanism of ozone changes in any layer, then there should be a positive correlation between the ozone and mean temperature in that layer. If advection is the main cause of ozone changes, then the ozone-temperature relation will be dependent upon the history of the air mass, and may not be clear since temperature will not be conserved like ozone.

The variation of the mean temperature with the ozone content in the layer is shown in fig. 19 for layers 2, 3 and 4 in Autumn and in Spring.

Autumn.

In this period, August to January, it is seen that in layers 2 and 3 there is a positive correlation between temperature and ozone, suggesting that vertical movement is the main reason for the ozone changes in these lower levels. To consider the possibility of advection causing these changes, we must examine the latitudinal gradients of ozone and temperature at these levels.

There is little latitudinal variation of total ozone in this period, although there is presumably a gradient in the photochemical equilibrium layer, with high ozone to

the South and low to the North. To maintain the observed distribution of total ozone, there is probably a reverse gradient in the lower stratosphere, i.e., high to the North and low to the South. In the same period there is a warm pool of air in this layer, with colder air towards both the pole and equator (see e.g., Ramanathan and Kulkarni (1960)). Thus, both high and low ozone content could be associated with cold air, and if advection were the cause of changes in layer 3, we should not expect such a clear-cut ozone-temperature relation.

Hence, advection is rejected, and vertical movement must be the main cause of changes of the ozone content in layer 3.

In layer 4, although there are less data, it seems clear that there is a negative correlation between the ozone and temperature. So, just as the layer ozone - total ozone reversed its behaviour in this layer, so does the ozone - temperature relation. This reversed relation between temperature and ozone cannot be explained by vertical movement since the ozone/air mixing ratio is increasing upwards at these levels.

Advection must then be the main cause of the ozone changes in layer 4. This is seen to be reasonable by consideration of the stratospheric temperature distribution.

This layer is just above the pool of warm air, and the temperature decreases towards the Pole, with little change towards the Equator. Thus high ozone would be associated with cold air as seen in fig. 19.

These temperature-layer ozone-total ozone relations for Autumn require that when the total increases, the change is brought about mainly by subsidence between the tropopause and 50 mb., and advection between 50 and 25 mb. of warmer air with lower ozone content from the South. When the total decreases, this is brought about mainly by ascent in the lower levels and advection of colder air with more ozone from the North.

Thus when the layer 3 total increases, the total in layer 4 should decrease, and vice-versa. This was found to be true with the exception of four ascents.

Spring.

In the period January to August the situation is not quite so clear. None of the layers shows a definite positive or negative correlation between ozone and temperature, although layer 2 shows a tendency towards a positive correlation. This will be seen to be real in the next chapter when the ozone-temperature relations at individual levels within this layer are considered.

These relations suggest that vertical movement is

not the main mechanism for ozone changes in the Spring, particularly in layers 3 and 4, although it may be playing a greater part in layer 2. Thus advection must be the main cause of ozone changes in the Spring, in the stratosphere below the photochemical equilibrium region.

It is found that when the ozone in layer 3 changes, then in general, the ozone in layers 2 and 4 changes in the same sense. This demonstrates that although the layer 4 total does not show a correlation with the total ozone as do layers 2 and 3 (fig. 18), it is probably the same mechanism producing the changes in all the layers.

CHAPTER XIV.

OZONE AND VORTICITY.

In the stable stratosphere, vertical movements should be largely suppressed, and the vertical component of the absolute vorticity of a parcel of air should be a fairly conservative property. Since the long-term mean value of relative vorticity at any latitude is near to zero, then on the average, the absolute vorticity increases steadily from the equator to the pole. These properties are similar to those of the ozone/air mixing ratio in the lower stratosphere, and investigation of these two conservative properties of the lower stratosphere should yield useful information about the movements of the air.

Let us consider the relationship to be expected between ozone and vorticity. If the air is advected, then high ozone/air mixing ratio should be associated with high absolute vorticity, and vice-versa. The same might be expected with vertical motion, since it is more correct to speak of circulation (=vorticity×area), and not of vorticity, being conserved. Thus, if an air column is stretched downwards from above, i.e., the cross-sectional area of the column is decreased, then both the ozone mixing ratio and vorticity should increase. It is also possible for the air column to decrease its area by stretching upwards

from below, but then the ozone mixing ratio would decrease while vorticity increased. However, in the former case vorticity and temperature should show a positive correlation, whereas in the latter, they would be inversely related, so consideration of temperature should distinguish between the two types of vertical motion.

Calculation of vorticity.

The method used to compute the normal component of the relative vorticity is that described by Graham (1953). This enables the vorticity to be calculated from the wind observations at the vertices of a triangle formed by radiosonde stations. The equation for the vorticity around a triangle ABC may be shown to be:

$$\text{Vorticity} = \frac{V_A}{h_A} + \frac{V_B}{h_B} + \frac{V_C}{h_C}$$

where V_A etc. are the components of the wind velocity parallel to the opposite side of the triangle, and h_A etc. are the perpendicular distances from the vertices A etc. to the opposite sides BC etc.

Five triangles are chosen for the present calculations. These are formed by the radiosonde stations at Liverpool, Hembay, Crawley, Camborne, Aldergrove and Shanwell. Liverpool lies inside the pentagon formed by the other stations and is common to each triangle. The vorticity

around each triangle is calculated, and the weighted mean of these values (weighted by the area of the triangles) is taken to represent the relative vorticity at Liverpool. To obtain the absolute vorticity, the Coriolis parameter at Liverpool is added.

The vorticity is calculated for seven pressure levels: 300mb, 200mb, 150mb, 100mb, 70mb, 50mb and 30mb. These are the only stratospheric levels for which wind data are given in the Daily Aerological Record. It would be preferable to use isentropic levels rather than isobaric, but this would require more complete wind data than is readily available.

The calculation of the vorticity for seven levels for each ozone ascent by hand is very tedious and time consuming. The labour was greatly reduced by use of the Ferranti Mercury Electronic Computor at the Oxford University Computing Laboratory. The programme for the calculation was kindly provided by The Meteorological Office.

<u>Results of the vorticity calculations</u>.

The mean values of the relative vorticity, and their standard deviations, at Liverpool for the different pressure levels are given in Appendix D. There are only a few values above 100mb. as there were generally insufficient

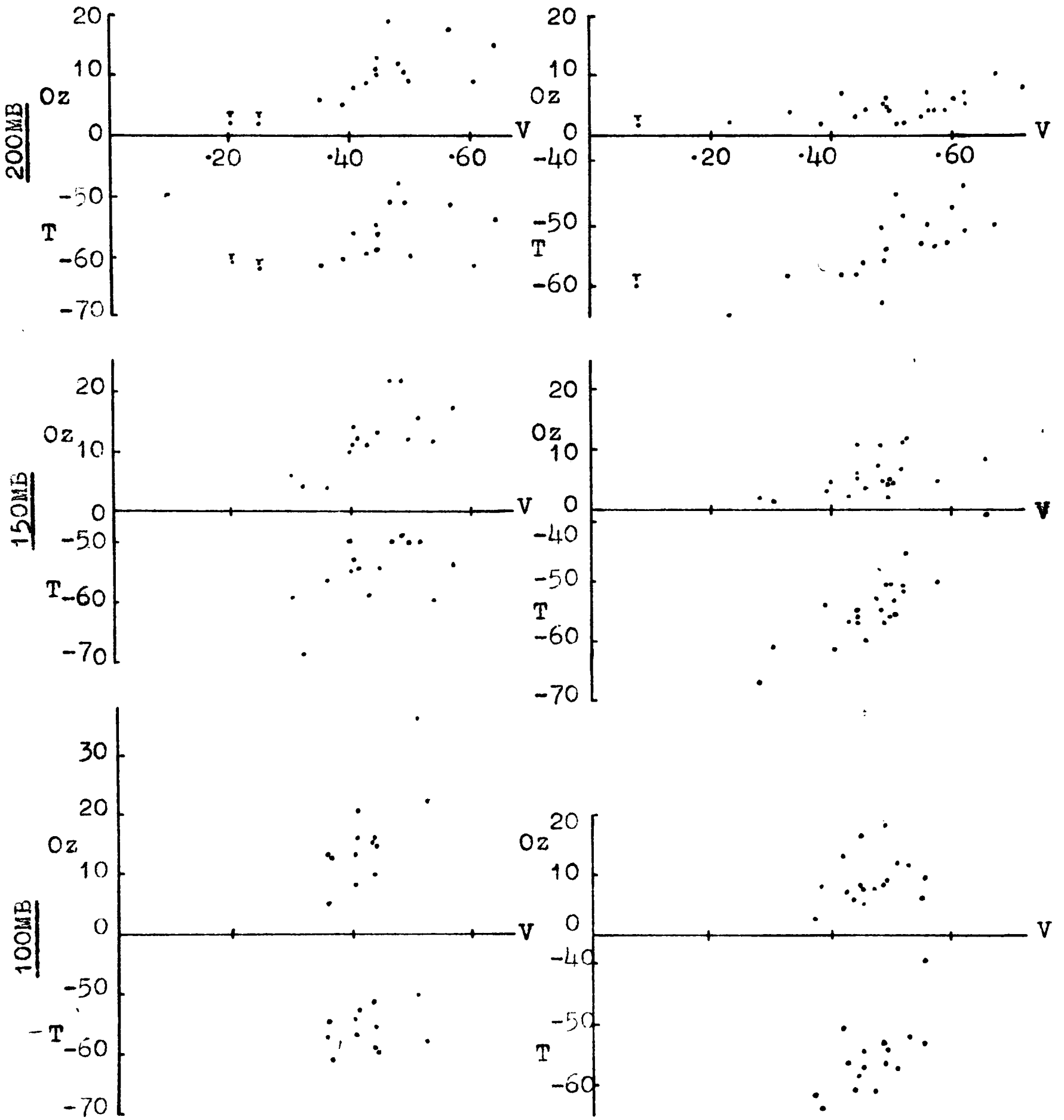


Figure 20. Variation of ozone concentration ($Oz \times 10^{-3}$ cm/km) and temperature ($T^{o}C$) with absolute vorticity ($V\ hr^{-1}$) at three stratospheric pressure levels.

wind data at these levels. The mean value has not been used if it was obtained from less than three triangles.

It is difficult to estimate the error in the vorticity as calculated, but by consideration of the differences in the values for each triangle, the absolute vorticity is probably correct to 25%, in so far as the vorticity can be estimated for a small parcel of air.

It is noticed that the spread of the vorticity values at each level decreases upwards, and at the 70mb, 50mb and 30mb. levels, there is little variation, the values being close to zero relative vorticity.

The Observed Vorticity-Ozone and Vorticity-Temperature Relations.

The ozone concentration and temperature as determined on the bubbler ascents are plotted against the corresponding value of vorticity for the stratospheric levels (200mb, 150mb. and 100mb), and are shown in fig. 20. On three ascents the 200mb. level was in the troposphere and these points are marked with a "T" in the scatter diagrams. The 300mb. level in the troposphere is not given as there is little variation of the ozone concentration. The 70mb, 50mb. and 30mb. levels are not shown as there are too few results, and too littl variation in vorticity, to be useful.

TABLE 4.

Coefficients of correlation (r) between ozone (o), vorticity (v), and temperature (t), for three stratospheric levels.

	Level	$r_{o/v}$	$r_{v/t}$	$r_{o/t}$
Spring	200mb.	.75	.48	.74
	150mb.	.73	.50	.63
	100mb.	.75	.28	.35
Autumn	200mb.	.60	.70	.40
	150mb.	.42	.85	.32
	100mb.	.24	.59	.33

The ozone-vorticity relation has different regression lines for the different times of year, and the year has been divided into the same three periods as in the earlier discussion of the layer variations, i.e., January to June, June to August and August to January. In this chapter however, the June to August period, for which there are insufficient results for a separate discussion, shows a regression line different from the other periods, and is not added to the January to June period. Thus January to June will be referred to as Spring, and August to January as Autumn.

The correlation coefficients of the scatter diagrams of fig. 20 are shown in table 4, along with the correlation coefficients between ozone and temperature. These are based on only a few observations and reference will be made to the diagrams rather than to the correlation coefficients in the discussion.

An explanation of these relations is given below in terms of advection and vertical movement, but, as in the discussion of the layer variations in the previous chapter, the conclusions must be regarded as only tentative, since the results are few, and are spread over a long period.

Discussion of results.

It is clear from fig. 20 that the relations between ozone and vorticity are in general as anticipated, i.e., high (low) ozone is associated with high (low) absolute vorticity. Although the correlation coefficients for the Autumn period are smaller than for Spring, the relation is still quite definite. The lower correlation is probably accounted for by the small variation in the ozone concentrations at these levels in the Autumn. As was shown earlier, this positive correlation is expected for both advection and vertical movement of the air. To distinguish between these two mechanisms another parameter, the temperature of the air, must be considered.

It was shown that for vertical movement, the vorticity would show a positive correlation with temperature if the air column is considered to move relative to a "base" above, and a negative correlation if the air moves relative to a lower "base". If advection is causing the ozone changes, then no special relation between vorticity and temperature should be anticipated since temperature is not a conservative property of the air like vorticity.

Spring.

On the basis of the above argument, it follows that in this period, January to June, the main cause of the

ozone changes must be advection, since temperature does not show a significant correlation with vorticity. This is the same conclusion as reached in the discussion of the layer variations in the previous chapter.

Autumn.

The changes in this period, August to January, must be due mainly to vertical movement, as was concluded in the previous chapter. This is indicated by the good positive correlation between temperature and vorticity, which shows also that the movement is relative to a "base" above the air column.

It is observed that in the Autumn there is a larger spread of vorticity values, particularly in the two lower levels. According to Kuo (1950), the latitudinal variation of absolute vorticity is much the same throughout the year. Thus the observed results suggest that vertical movement in the lower levels of the stratosphere produces larger day-to-day variations in vorticity than advection does.

Relations between ozone and temperature.

As was explained in the previous chapter, high (low) ozone should be associated with high (low) temperature in vertical movements, whereas no special relation is expected for advection of air.

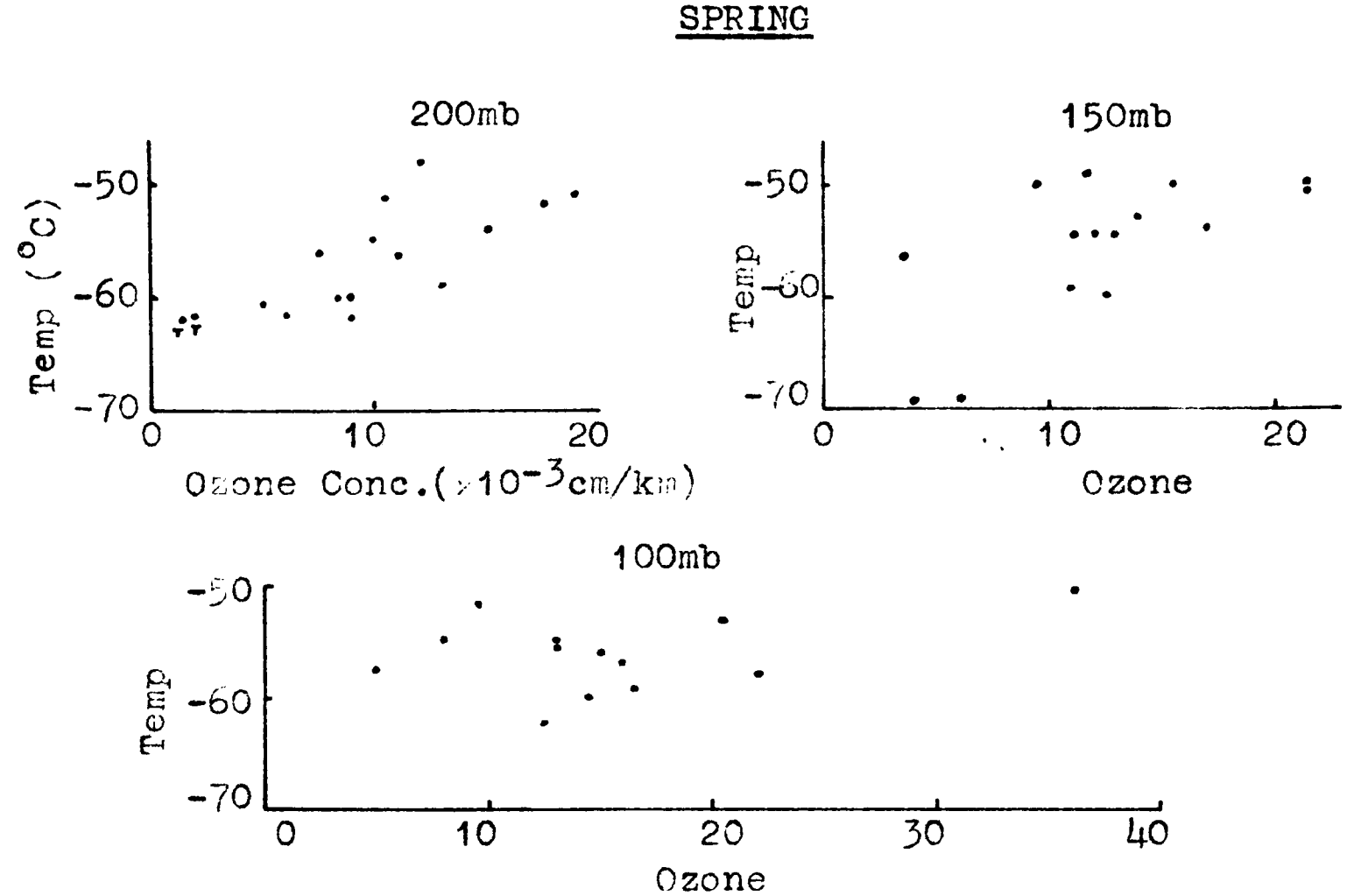


Figure 21. Variation of temperature with ozone concentration at three stratospheric pressure levels.

The ozone-temperature relations for the different levels during Spring and Autumn are given in fig. 21. These scatter diagrams do not show such clear relations as the layer total - mean temperature diagrams (fig. 19) in the previous chapter, but the same general picture emerges.

Autumn.

In the Autumn there is a positive correlation at each level, although the correlation coefficients are low owing to the small spread of ozone values. This is clearly the reason at 200mb. and 100mb., but is perhaps not the cause at 150mb. These confirm the previous deductions that vertical motion is the main cause of ozone changes in the Autumn.

Spring.

In this period, January to June, there is little relation between ozone and temperature at 100mb. and 150mb. The scatter diagrams indicate clearly that the correlation coefficients have no significance. At 200mb, however, the diagram shows that the high correlation is probably significant. It was seen in the previous chapter that the layer, tropopause to 120mb, showed a tendency towards a positive correlation. It now seems that this is due mainly to a good correlation in the lower levels of the layer.

Thus, the ozone-temperature relations at the different pressure levels in Spring indicate that advection is the main cause of the ozone changes at 150mb, but that vertical movement plays a greater part as we progress downwards in the stratosphere. Indeed, the good ozone-temperature correlation at 200mb. may mean that vertical motion is playing the major role at this level.

Conclusions.

It is unfortunate that the discussion has been based on so few results, and only three stratospheric levels, although measurements above 100mb. probably would not be very profitable owing to the small variation of vorticity in the higher levels. However, the results have confirmed the deductions made for the lower stratosphere on the basis of the layer variations, discussed in the previous chapter, and have illustrated perhaps more clearly that, in Spring, while advection is probably the dominating cause of ozone changes in the stratosphere below the photochemical equilibrium region, vertical movement may be playing a larger part, if not the more important part in the lowest levels.

CHAPTER XV.

THE GENERAL CIRCULATION.

The annual variation of the global ozone distribution cannot be explained by the photochemical theory, and must be due to the general circulation. It is thought by some that although the main features of the circulation are zonal, the mechanism causing the ozone cycle is a meridional circulation.

Many theories of this circulation have been proposed, based on existing information. It is hoped that eventually an ozonesonde programme will be initiated to obtain regular meridional cross-sections of the hemispherical ozone distributions. These should enable a meridional circulation to be determined more precisely than has been possible to date.

The present work has not provided sufficient data for a global analysis of the meridional circulation, but ascents have been made at Nairobi, near the equator.

These are the first results to show the detailed ozone structure at the equatorial tropopause, and are able to discriminate between the proposed circulations at the equator.

Meridional circulation at the equatorial tropopause.

The few ascents made at Nairobi between March and August 1960, have all, except N4, shown a steady increase

in the ozone concentration beginning 1 km. or more above the tropopause. Ascent N4, is very striking, and may not be correct. The sharp increase suggests that there was some reducing agent in the bubbler, as discussed in chapter X.

This lack of ozone in the vicinity of the equatorial tropopause rules out the possibility of downward movement towards or through the tropopause. Thus, the theories proposed by Ramanthan (1954) and Staley (1957) must be reconsidered.

However, the situation is still not clear, for while upward movement through the tropopause explains the ozone distribution, it does not immediately explain the observed temperature distribution. On each Nairobi ascent there is a sharp increase of temperature for several kilometres. This increase can be as much as 1.5°C/100m. for the first kilometre (e.g., N5), but the average over the first five kilometres, above which the temperature sometimes decreases, is about 0.5°C/100m.

Thus, there must be some radiative heating effect above the equatorial tropopause; this cannot be due to ozone, since the main concentration is at higher levels.

On the basis of the observed temperature and ozone distributions it is possible to make an estimate of the

rate of vertical movement, neglecting effects of advection. The air rising through the tropopause will probably be dry, any water vapour having condensed in the cold temperatures of the troposphere, and will cool adiabatically at approximately $1^{\circ}C/100m$. If the rate of ascent is N m/day it will cool at $\frac{N}{100}$ $^{\circ}C$/day. To maintain the observed temperature distribution, then heating by radiation must occur at the rate of $(0.5\frac{N}{100} + \frac{N}{100})$ $^{\circ}C$/day, i.e., $.015N^{\circ}C$/day.

There is little accurate information about the radiation effects at the equatorial tropopause. Ohring (1958), using an ozone distribution similar to that observed near the tropopause, calculates that there should be radiative heating between 17km. and 22km. He shows $2^{\circ}C$/day at 17km. decreasing to $0^{\circ}C$/day at 22km. Hence, the mean rate is about $1^{\circ}C$/day for the first few kilometres above the tropopause.

Thus, the rate of ascent of air through the equatorial tropopause would be about 60m/day, if Ohring's results are correct. This may be compared with the rate of descent in high latitudes calculated by Brewer (1949) to be about 50m/day.

APPENDIX A.

THE SURFACE BUBBLER.

In addition to the ozonesonde bubbler, a glass bubbler for continuous measurement of ozone has been used for surface and aircraft work. The use of the bubbler for long periods of time presents problems different from those of the ozonesonde. These problems and some results are discussed briefly.

Long Period Use of the Bubbler.

The bubbler, shown in the frontispiece, is of the same general design as the ozonesonde bubbler, but is constructed in glass, and the air is sucked through the solution. Thus there should be no ozone losses in the system. However, there is a possibility of losses in long period usage due to creeping of KI solution up the inside of the inlet tube, thus reducing the ozone before it reaches the solution in the cell. This is successfully prevented by siliconing the inlet tube to make it hydrophobic.

The reaction cell is larger than that of the ozonesonde bubbler and contains more solution, as loss of solution by evaporation is considerable over long periods. This increased volume of solution results in longer response times of about one minute. The reaction cell is kept in the dark as daylight produces a negative

reading (see Chap. III).

To obtain the correct ozone reading when the bubbler is used continuously it is essential to rinse the reaction cell with distilled water, and refill with fresh KI solution at least every 24 hours. This is necessary as the solution accumulates reducing agents (see Chap. III).

After a considerable time (several weeks) of continuous ozone measurements, a thick deposit of silver iodide will accumulate on the silver anode. This has a large electrical resistance, which shifts the bubbler characteristics (Fig. 6) and produces an increase in response time. This deposit may be removed by increasing the external voltage of the bubbler to one volt to pass a large reverse current until the silver iodide has been reduced to silver and iodine. The bubbler must then be thoroughly rinsed several times, and refilled with KI solution. If this is not done correctly, then a large zero current appears. A better method is to replace the anode with a new silver wire when the silver iodide layer becomes too thick.

Results.

Surface Measurements.

Surface measurements have been made mainly to determine the behaviour of the bubbler over long periods,

and a complete record of the surface ozone at Oxford has not been maintained.

Aircraft measurements.

The Meteorological Research Flight at Farnborough has been using the bubbler for ozone measurements up to about 15 km., and has obtained results in the vicinity of Liverpool on many of the balloon ascents. In general these show good agreement with the ozonesonde results. Their results were particularly useful in substantiating the abnormally high ozone values measured on flights BL12, 13, 15.

Measurements in aircraft.

It is proposed in the future to have high-flying aircraft which will reach about 60,000 ft. This brings them into the levels of high ozone concentration, and in addition to the effect of the ozone on the plastics and rubber on the aircraft, there is the possibility of effects on the passengers and crew since the air in the pressurised aircraft is drawn from the outside air. It is thus essential to know how much ozone is getting into the aircraft. A bubbler was loaned to B.O.A.C. to measure the ozone inside the present aircraft.

The air brought into the pressurised aircraft is tapped off from the engine, with the result that the air has been heated. It is cooled before entering the

aircraft. The heating of the air in the engine should assist in reducing the concentration of the ozone, since it dissociates at high temperatures, and is completely destroyed at about 300°C. This was shown to be effective by comparison of the results obtained in the Comet 4 and the Boeing 707. In the Comet 4, the air supply is raised to about 240°C, while in the Boeing 707, it reaches about 150°C.

Measurements were made on several flights, at about 37,000 ft., across the Atlantic. The ozone concentration in the Comet 4 (maximum 5 pphm) was lower than in the Boeing 707 (maximum 7 pphm) even though the Comet 4 measurements were made in the Spring when the ozone concentrations outside the aircraft were higher than in the Autumn, when the Boeing 707 results were obtained.

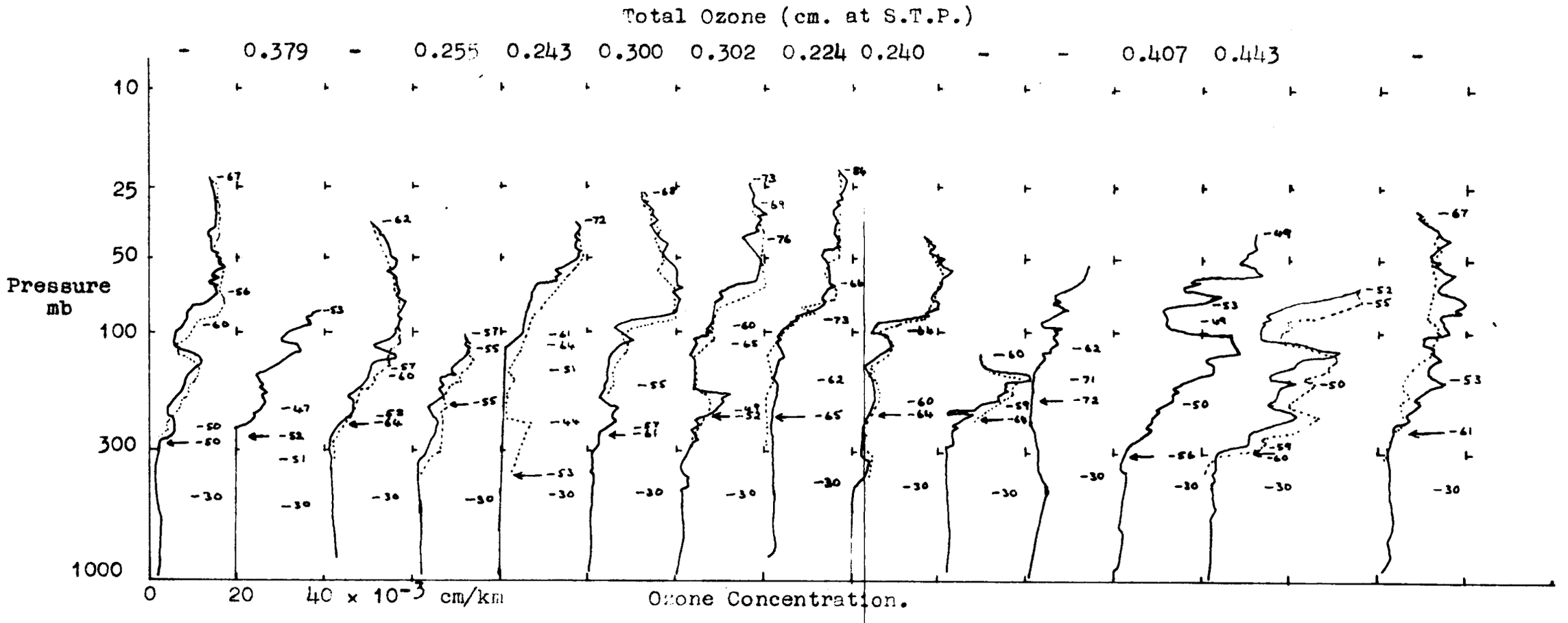
From the results obtained on different days, and at different times of the flights, the ozone concentration inside the aircraft seems to be independent of the outside ozone amounts, but more measurements will have to be made with higher outside ozone concentrations. Also the physical effects of prolonged exposure of the crew to these ozone amounts which are higher than the average surface concentration, must be investigated.

APPENDIX B.

Bubbler Ozonesonde Flights.

BL1 - BL14.

BUBBLER OZONESONDE FLIGHTS LIVERPOOL, November 1959 - February 1960.



Flight	BL1	BL2	BL3	BL4	BL5	BL6	BL7	BL8	BL9	BL10	BL11	BL12	BL13	BL14
Date	3/11 1959	11/11	19/11	26/11	3/12	10/12	17/12	31/12	7/1 1960	14/1	21/1	28/1	4/2	11/2

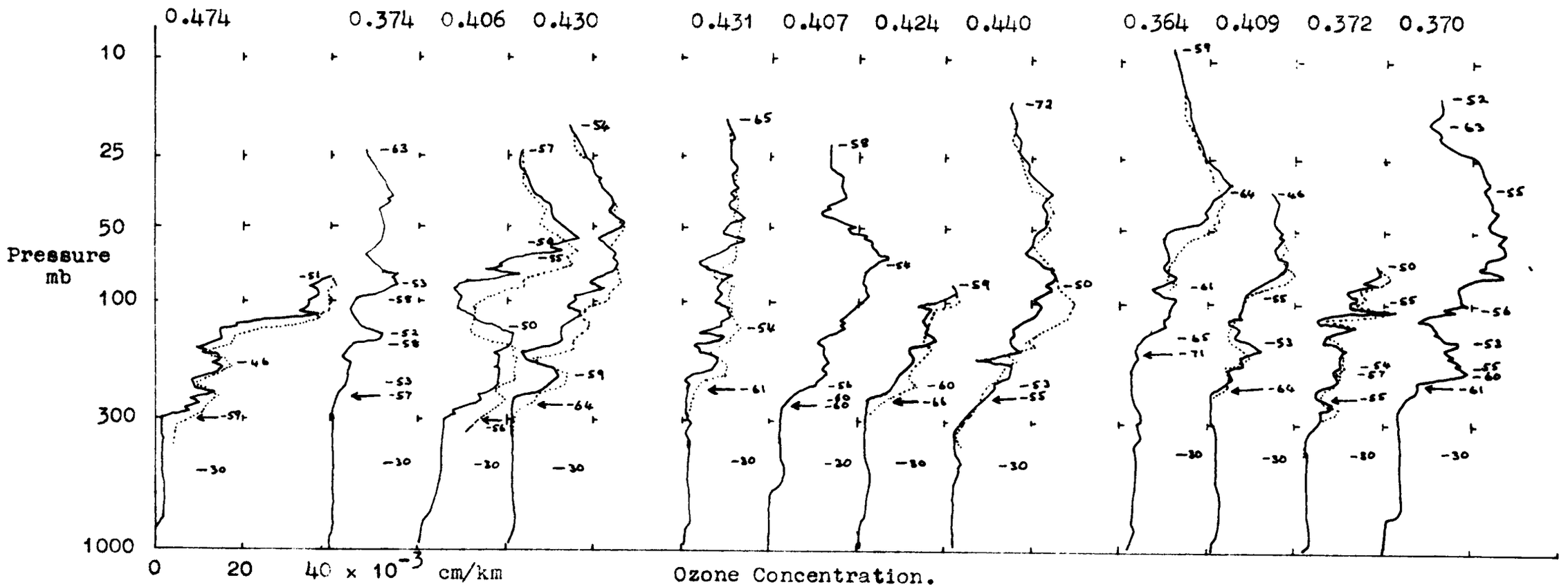
Note: The figures are temperatures in °C at major changes in lapse rate.

LEGEND: —— Ascent
..... Descent
⟵ Tropopause Level

BL15 - BL27.

BUBBLER OZONESONDE FLIGHTS LIVERPOOL, February 1960 - May 1960.

Total Ozone (cm. at S.T.P.)



Flight	BL15	BL17	BL18	BL19	BL20	BL21	BL22	BL23	BL24	BL25	BL26	BL27
Date	18/2 1960	3/3	10/3	17/3	24/3	31/3	7/4	14/4	21/4	28/4	5/5	12/5

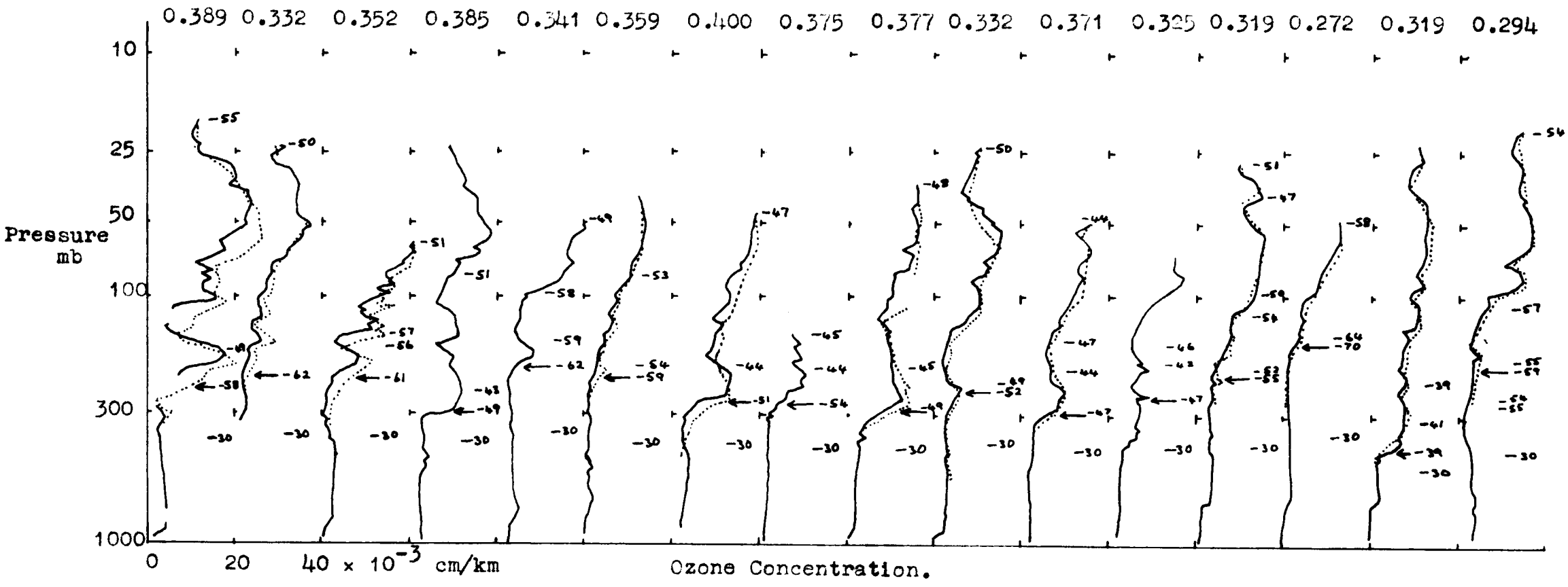
Note: The figures are temperatures in °C at major changes in lapse rate.

LEGENT: —— Ascent
..... Descent
←— Tropopause Level.

BL28 - BL46.

BUBBLER OZONESONDE FLIGHTS LIVERPOOL, May 1960 - September 1960

Total Ozone (cm. at S.T.P.)



Flight	BL28	BL29	BL30	BL31	BL32	BL34	BL35	BL36	BL37	BL39	BL41	BL42	BL43	BL44	BL45	BL46
Date	19/5 1960	26/5	2/6	9/6	16/6	30/6	7/7	14/7	21/7	4/8	18/8	25/8	1/9	8/9	15/9	22/9

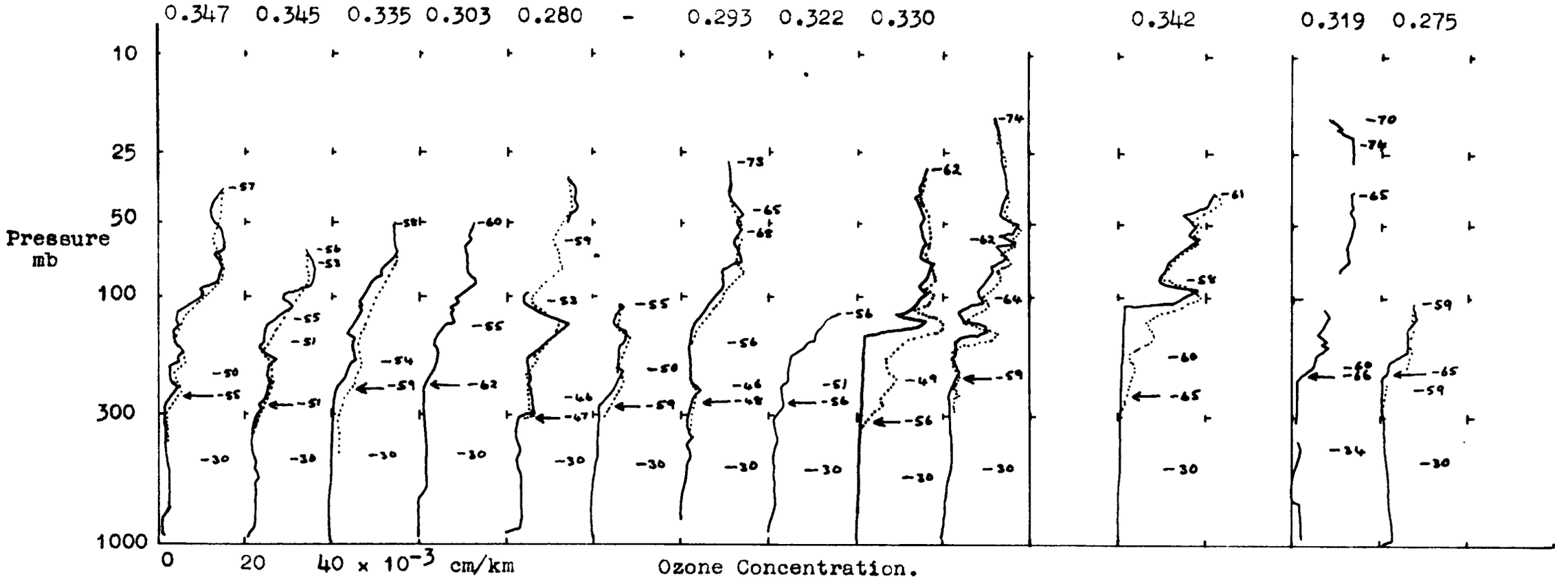
Note: The figures are temperatures in °C at major changes in lapse rate.

LEGEND:
—— Ascent
..... Descent
⟵ Tropopause Level

BL47 - BL57
and
W1, T1, T2.

BUBBLER OZONESONDE FLIGHTS LIVERPOOL, September 1960 - January 1961.

Total Ozone (cm. at S.T.P.)



Flight	BL47	BL48	BL49	BL50	BL52	BL53	BL54	BL55	BL56	BL57	W1	T1	T2
Date	29/9 1960	13/10	20/10	27/10	10/11	17/11	24/11	1/12	8/12	15/12	15/1 1961	28/11 1960	13/1 1961

Note: The figures are temperatures in ^{o}C at major changes in lapse rate.

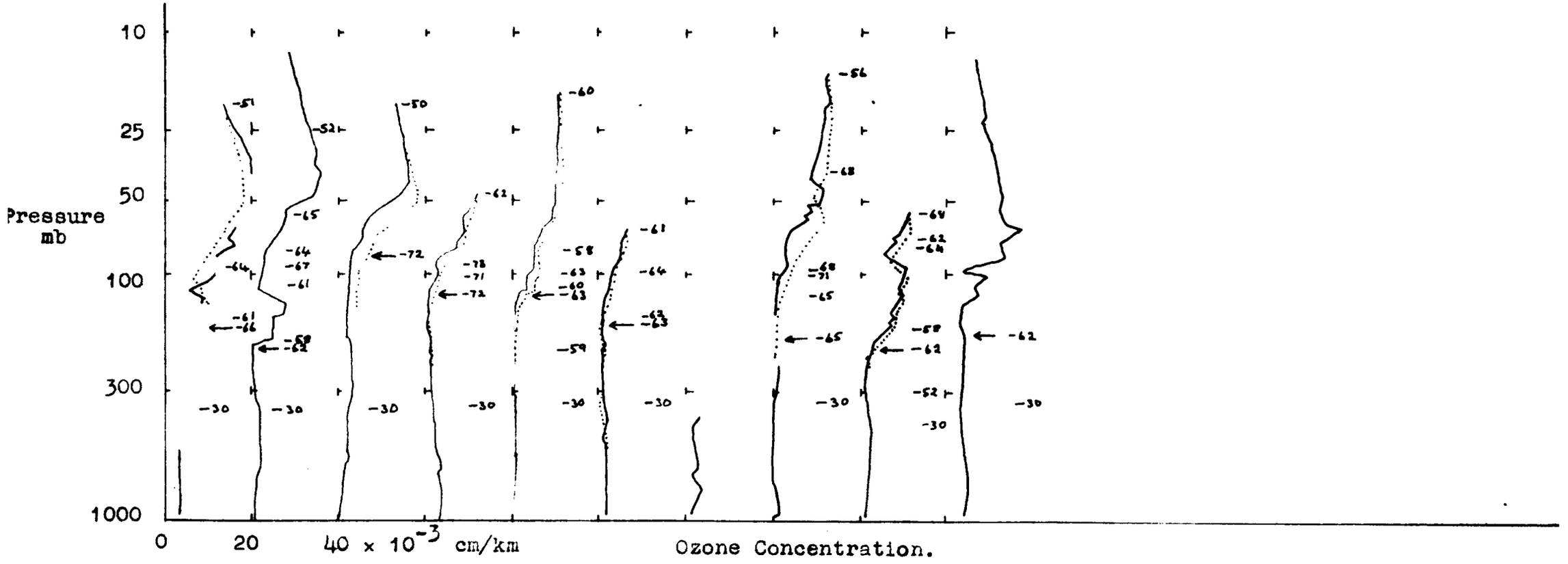
LEGEND: —— Ascent
..... Descent
←— Tropopause Level

MB1 - MB13.

BUBBLER OZONESONDE FLIGHTS

MALTA, June 1960 - December 1960

No Total Ozone Data



Flight	MB1	MB2	MB3	MB5	MB7	MB8	MB9	MB11	MB12	MB13
Date	2/6 1960	16/6	30/6	26/8	22/9	6/10	20/10	17/11	1/12	15/12

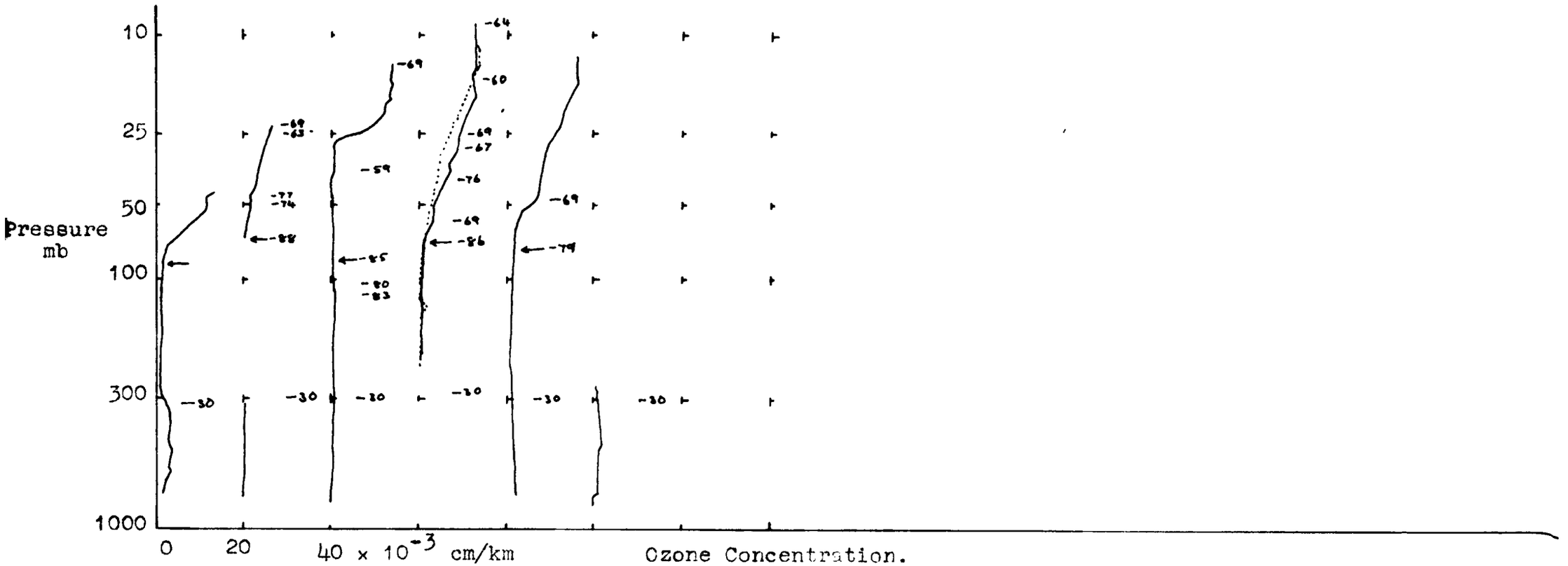
Note: The figures are temperatures in ^{o}C at major changes in lapse rate.

LEGEND: —— Ascent
····· Descent
⟵ Tropopause Level.

N2 - N7.

BUBBLE OZONESONDE FLIGHTS NAIROBI, March 1960 - August 1960.

No Total Ozone Data.



Flight	N2	N3	N4	N5	N6	N7
Date	11/3 1960	24/3	7/4	27/5	28/7	25/8

Note: The figures are temperatures in °C at major changes in lapse rate.

LEGEND: ——Ascent
……Descent
←—Tropopause Level.

APPENDIX C.

Flight BL.	Date 1959	Mean Conc. Layer 1	Mean Conc. Layer 2	Layer Totals Layer 1	Layer Totals Layer 2	Layer Totals Layer 3	Layer Totals Layer 4	Layer Totals Layer 5	Oxford Total
1	3/11	2.3	7.6	22	41	63	63	73	(264)
2	11/11	0	5.8	0	31	-	-	-	379
3	19/11	2.2	9.3	23	38	94	(56)	(109)	(320)
4	26/11	3.0	10	35	31	-	-	-	255
5	3/12	0.3	0.9	2	7	42	(72)	(120)	243
6	10/12	1.0	5	9	25	90	70	106	300
7	17/12	2.5	6.5	29	25	61	77	110	302
8	31/12	2.3	3	26	10	55	72	61	224
9	7/1/60	1.5	5.2	17	15	91	(74)	(43)	240
10	14/1	3.3	13	36	49	-	-	-	-
12	28/1	2.3	13.8	20	83	129	(120)	(55)	407
13	4/2	2.5	17.5	22	105	150	-	-	443
15	18/2	1.8	12	16	71	-	-	-	474
18	10/3	4.2	17	37	100	110	122	48	407
19	17/3	2.0	9.1	19	44	119	102	146	430
21	31/3	2.1	11.5	22	53	125	79	128	407
22	7/4	2.3	11.5	24	51	-	-	-	424
23	14/4	4.2	14.5	44	63	116	95	122	440
24	21/4	3.6	6	49	10	62	100	143	364
25	28/4	2.1	7.2	24	28	71	(82)	(224)	409
26	5/5	3.3	9.5	36	42	85	-	-	372
27	12/5	4.0	14	47	48	114	106	55	370
28	19/5	3.1	9	33	41	84	90	141	389
29	26/5	(1.7)	4	(20)	13	68	77	154	332
30	2/6	2.3	7.5	26	28	(96)	-	-	352
31	9/6	2.9	10.5	27	63	66	60	169	385
32	16/6	2.9	6	36	18	80	-	-	341
34	30/6	1.4	4.5	16	17	60	-	-	359
35	7/7	3.0	11.5	29	63	93	-	-	400
36	14/7	1.6	8.2	15	(44)	-	-	-	375
37	21/7	2.6	10.6	24	61	72	(72)	(148)	377
39	4/8	3.4	4	37	18	71	43	163	332
41	18/8	2.7	8.1	24	50	78	-	-	371
42	25/8	4.2	6.2	43	29	(83)	-	-	325
43	1/9	3.2	6.3	37	22	82	(54)	124	319
44	8/9	2.0	3.0	27	5	50	-	-	272
45	15/9	1.2	7.5	8	64	66	48	133	319
46	22/9	2.9	3.5	34	11	70	67	102	294
47	29/9	0.7	4.5	8	22	70	-	-	347
48	13/10	2.5	5.3	24	29	(67)	-	-	345
49	20/10	0.3	4.3	3	14	65	-	-	335

Appendix C. contd.

50	27/10	0.6	4.3	7	17	60	-	-	303
52	10/11	2.6	7.3	22	46	61	(62)	(99)	280
53	17/11	0.4	6.0	4	32	-	-	-	(350)
54	24/11	1.0	2.6	10	13	56	(44)	(70)	293
55	1/12	1.5	6.5	14	32	-	-	-	322
56	8/12	0.3	9.5	3	58	81	(59)	(129)	(330)
57	15/12	1.4	5.3	16	19	62	59	(170)	(326)

Note: ( ) Some extrapolation or interpolation involved.

APPENDIX D.

Mean relative Vorticity (hr^{-1}) and the Standard Deviation at different pressure levels for the Liverpool Ascents.

Ascent BL	300 mb r.v.	300 mb s.d.	200 mb r.v.	200 mb s.d.	150 mb r.v.	150 mb s.d.	100 mb r.v.	100 mb s.d.	70 mb r.v.	70 mb s.d.	50 mb r.v.	50 mb s.d.	30 mb r.v.	30 mb s.d.
1	.15	.32	.17	.06	.09	.06	.13	.04	-	-	-	-	-	-
2	.19	.08	.18	.04	.16	.02	.10	.04	-	-	-	-	-	-
3	-.15	.22	.00	.06	.02	.07	.04	.01	-	-	-	-	-	-
4	.31	.14	.15	.03	.06	.14	.09	.04	-	-	-	-	-	-
5	.08	.03	.09	.06	.08	.05	.02	.04	-	-	-	-	-	-
6	-.06	.11	.07	.07	.02	.02	.02	.04	-	-	-	-	-	-
7	.25	.19	.26	.10	.07	.02	-	-	-	-	-	-	-	-
8	-.15	.11	-.19	.18	-.11	.05	-	-	-	-	-	-	-	-
9	.12	.09	.07	.05	-.02	.02	-.04	.02	-	-	-	-	-	-
10	.03	.05	.19	.05	-	-	-	-	-	-	-	-	-	-
12	.09	.09	.07	.02	.07	.03	-	-	-	-	-	-	-	-
13	.11	.14	.14	.03	.10	.01	-	-	-	-	-	-	-	-
15	.04	.06	.06	.03	.08	.01	.09	.03	-	-	-	-	-	-
18	.16	.14	.04	.04	.05	.03	.01	.05	.01	.02	-	-	-	-
19	.07	.17	.03	.04	.00	.02	.01	.00	-.03	.01	-	-	-	-
21	.02	.08	.03	.03	.03	.03	-.01	.03	-.02	.02	-	-	-	-
22	.08	.13	.08	.04	.12	.11	.02	.04	-	-	-	-	-	-
23	.24	.15	.22	.52	.15	.07	.10	.08	.00	.11	.01	.01	-	-
24	-.13	.08	-.22	.11	-.10	.08	-.06	.03	-.06	.04	-.03	.02	-.04	.02

25	-.18	.07	-.07	.03	-.12	.03	-.02	.02	-.02	.02	.02	.03	-	-
26	.11	.14	.02	.03	-.02	.02	-.02	.01	-	-	-	-	-	-
27	-.15	.11	.01	.08	-.02	.05	.01	.05	.03	.03	.04	.04	-	-
28	-.04	.20	-.01	.02	-.03	.02	-.01	.02	-.01	.02	-.01	.02	.03	.01
29	-.20	.02	-.17	.04	-.12	.06	-.16	.03	-.04	.03	.00	.05	-	-
30	-.12	.09	-.03	.03	-.06	.02	-.06	.02	.01	.01	-	-	-	-
31	.21	.12	.18	.02	.11	.02	.06	.03	.04	.02	-.01	.07	-	-
32	-.31	.07	-.23	.03	-.05	.06	-.06	.06	.00	.03	-.02	.06	-	-
34	-.01	.18	.08	.10	.08	.04	.02	.02	.02	.01	.01	.02	-	-
35	.19	.30	.14	.09	.09	.03	.09	.03	.07	.02	.05	.00	-	-
37	.34	.13	.15	.03	.09	.02	.04	.03	.03	.01	-	-	-	-
39	-.02	.09	.04	.03	.02	.11	.01	.01	-.01	.03	-	-	-	-
41	.21	.24	.17	.02	.11	.06	.06	.04	.02	.01	-	-	-	-
42	.26	.28	.20	.06	.10	.06	-	-	-	-	-	-	-	-
43	.06	.14	.08	.10	.06	.07	-.00	.02	.01	.01	-	-	-	-
44	-.22	.02	-.34	.04	-.14	.07	-.05	.02	.01	.05	-	-	-	-
45	.41	.27	.30	.03	.24	.02	.13	.02	-	-	-	-	-	-
46	-.19	.06	-.09	.11	-.04	.04	.01	.02	-.01	.01	-	-	-	-
47	.16	.23	.13	.02	.08	.18	.04	.03	.01	.03	-	-	-	-
48	.16	.23	.07	.11	.08	.05	.07	.07	-	-	-	-	-	-
49	-.07	.18	.04	.04	.02	.03	.03	.02	.02	.01	-	-	-	-

50	.04	.15	.02	.05	.08	.03	-	-	-	-	-	-	-	-
52	.28	.08	.20	.05	.10	.27	.03	.06	-	-	-	-	-	-
54	.22	.09	.10	.08	.01	.01	-	-	-	-	-	-	-	-
56	.23	.15	.14	.03	.10	.05	.06	.02	.00	.04	-	-	-	-
57	.34	.38	.14	.12	.04	.04	-	-	-	-	-	-	-	-

Note: To obtain the absolute vorticity, the Coriolis parameter, f, for Liverpool must be added to the above relative vorticities.

$f = .42\ hr^{-1}$.

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