Some studies in the infra-red region of the spectrum

William G. Wearmouth

How to cite:

Wearmouth, William G. (1933) Some studies in the infra-red region of the spectrum. Doctoral thesis, Durham University.

"SOME STUDIES in the INFRA-RED REGION of the SPECTRUM."

A THESIS

BEING AN ACCOUNT of RESEARCH WORK carried out under the Direction of Professor J. E. P. Wagstaff, D.Sc., at Durham University Science Laboratories during the period October, 1931 - October, 1933, and

submitted by

WILLIAM G. WEARMOUTH of University College, in Candidature for the degree of Doctor of Philosophy.

-- CONTENTS --

LIST of ILLUSTRATIONS.

Fig. 22 Graph showing inequality of transmission of the two Gas Observation tubes, and the effect of tilting one relative to the other. Region 2.5 μ - 4.0 μ .

Fig. 23 Graph showing inequality of Tube Transmission in the region 4.0 μ - 6.50 μ .

Fig. 24 Graph showing the ratio of the Transmission Powers of the Tubes when the Rock-Salt and end plates are removed.

Fig. 25 Graphs to show inequality of Transmission of the two gas tubes in the region 5.0 μ - 8.5μ.

Fig. 26 Absorption Band of Carbon Dioxide at 2.72μ, taken at different pressures.

Fig. 27. Absorption Band of Carbon Dioxide at 4.25μ.

Fig. 28 Absorption Band of Carbon Dioxide at 14.87μ.

Fig. 29 Absorption due to Carbon Dioxide in the region 1.0 μ - 2.0μ for different Gas Pressures.

Fig. 30 Absorption Band of Nitric Oxide at 5.30μ, observed at different Gas Pressures.

Fig. 31 Absorption Band of Nitric Oxide at 5.30μ.

Fig. 32 Absorption Band of Nitric Oxide at 2.68μ taken at different gas pressures. (1)

Fig. 33 Absorption Band of Nitric Oxide at 2.68μ (2)

Fig. 34 Absorption Band of Nitric Oxide at 2.68μ.(3)

Fig. 35 Absorption in the region 1.0μ - 2.0μ due to Nitric Oxide Gas.

::: ::: :::

Fig. 36 Absorption due to different thicknesses of water film in the region 1.0μ - 2.5μ.

Fig. 37 Absorption Bands of water in the region 1.0μ-2.5μ.

Fig. 38 Absorption Bands of water in the region 2.5μ-3.5μ.

Fig. 39 Absorption due to different thickness of films of water in the region 4.0μ - 5.0μ.

Fig. 40 Absorption due to water in the region 5.5μ-6.5μ.
(Different thicknesses of liquid film used).

CHAPTER 1.

INTRODUCTION and APPARATUS.

SOME STUDIES in the INFRA-RED REGION of the SPECTRUM.

Section 1.

INTRODUCTION.

1. The first experimental evidence of the existence of radiations beyond the red end of the visible spectrum was obtained by Herschel. He placed a thermometer in that region of the solar spectrum, now called the infra-red, and obtained variations in temperature. His son demonstrated the existence of emission bands in the same region by the discontinuities in evaporation from a surface moistened with alcohol. Later experimenters developed instruments of precision for work in this region; as for instance, Langley's bolometer; the radiometer of Crookes; the radiomicrometer of Boys; and the combination of thermopile and galvanometer, developed by Paschen and others. By the use of such instruments, they were able to measure accurately the small amounts of energy which are usually found in the region of the infra-red.

II. After this work it became necessary to find methods for the establishment of wavelengths in the infra-red. This pioneer work was done most successfully by Paschen[1], Langley[2], Reubens[3], and Trowbridge[4]. They measured the indices of refraction of quartz, fluorite, rock-salt and sylvine. These materials had been found to transmit infra-red radiations quite readily, and were most suitable for use in the manufacture of prisms for work in the infra-red. From the indices of refraction of these materials it was possible to calibrate the prism - deviation in terms of wave-length, and so a method of measuring wave-lengths in the infra-red was perfected. Prisms of quartz, fluorite, rock-salt and sylvine have since been in general use for experimental investigations in the near infra-red region, i.e., up to 22 μ.

III. With the advent of methods for the measurement of wave-lengths, it soon became evident, from the results of various investigators, that some relationship existed between the bands in the infra-red and the constituents of the molecule. The following examples illustrate this point :- Angstrom[5] investigated several organic liquids and found relationships existing between their bands and the occurrence of certain organic radicles. Again, AschKinass[6] and Paschen[7] investigated water vapour, and Ransohoff[8] the effect of the (OH) radicle. During the period 1905-1909, Coblentz[9] published several accounts of his researches and results on absorption, emission and reflexion in the infra-red. His results confirmed the point of view that certain bands are associated with various chemical groups, such as CH_2, OH, NH_2 etc.

IV. With some of the earlier prism experiments, it was found that when wave-length was plotted against absorption, definite bands or peaks occurred in certain regions. Later work on prisms showed that for the same region in the infra-red, some prisms have more favourable dispersion than others. By choosing the appropriate prism the bands or peaks mentioned above were resolved at the higher dispersion into groups of peaks; and later, by the use of gratings, and the combination of prism and grating, which afford far greater dispersion, it was possible to bring out the fine structure in a band.

In the very near infra-red region, i.e., up to 1.0 μ, some photographic work has been accomplished using specially sensitised plates. The results though interesting are somewhat lacking in definition, and the information obtained from them is not of much help in the elucidation of the molecular structure.

V. Since the publication of the results of Coblentz, a great deal of work has been carried out by other investigators, and several references to their work are made in this thesis. It would be impracticable, in a thesis of this nature, to give a full historical account of all results obtained and the many lines of attack used by previous investigators. Mention, however, is now made of a paper published by Sir R. Robertson[10] and his collaborators entitled, "Infra-Red Absorption Spectra of Ammonia, Phosphene, and Arsine." In this paper Sir R. Robertson gives a description of the necessary precautions which must be taken to ensure accurate results; and he stresses the difficulties which are encountered if these precautions are not taken. The precautions are :- the necessity for ensuring a constant source of radiation, the need for taking strict account of the temperature of the prism - since its refractive index changes with temperature - securing a highly sensitive thermopile and galvanometer, and the frequent calibration of the assembled instrument against standard lines in the spectrum.

VI. Drude[11] has attempted to give a theoretical interpretation to the formation of absorption bands in the infra-red. By working on the dispersion formula of various crystals, and the conception of vibrating charged particles, he has shown that when a band occurs in the ultra violet there must be a corresponding one in the infra-red. It is known that the bands in the ultra-violet are due to electrons, and from Drude's work one can say that the particles concerned in the infra-red must be either atoms or molecules. The results of modern work point to the fact that band spectra in the infra-red arise from atoms and molecules - the bands reflect transitions in the oscillations of the atoms of a molecule, and transitions in the rotation of the molecule itself.

VII. Several types of bands are found in the infra-red, but the types are most easily identified in the cases of gases. Those for Solids and liquids are found to be less sharply defined than those for gases which renders their identification far more difficult. In solids and liquids the nuclei of the molecules are more constrained and therefore their vibrations do not seem so orderly. Again, in the case of the absorption bands for gases the interpretation of the meaning of the bands is much less difficult. For gases there are three types of bands :-

(a) Oscillation Bands;
(b) Rotation Bands;
(c) Oscillation — Rotation Bands.

We will consider them in this order.

In the early work in the infra-red region, bands were found as maxima of emission or absorption. These bands were in the form of smooth peaks with a well-defined maximum, and the results showed that several of such bands are simple harmonics of some fundamental frequency. The most probable explanation of these harmonic bands is that the radiation falls on the molecules whose nuclei are vibrating to and from each other, and the radiation is absorbed in quanta depending upon the frequency of the vibrations. The nuclei are, comparatively speaking, quite close to each other, and this causes their vibrations to be controlled by a force which does not strictly obey an inverse square law, and the vibrations are therefore anharmonic, consisting of fundamentals and harmonics representing one, two or three quanta. Absorption of radiation according to this scheme gives rise to the so-called Oscillation Bands. Such bands are usually found in the near infra-red region.

In addition to Oscillation Bands we can have the Rotation Bands. These have been given a theoretical explanation by Sommerfield. He considered the case of a diatomic molecule of moment of inertia I rotating about an axis perpendicular to the line joining the atoms, with an angular velocity W. He quantized the moment of momentum, so that each quantum jump represents a change in the moment of momentum. If the moment of momentum be taken as a whole multiple of $\frac{h}{2\pi}$, then $I\omega = \frac{mh}{2\pi}$. The Kinetic energy is given by $E = \frac{h^2 m^2}{8\pi^2 I}$.

Following the ideas and work of Bohr :-

$$n\nu = E_1 - E_2 = \frac{h^2}{8\pi^2 I}(m_1^2 - m_2^2)$$

and by the selection principle m can change by either ±1 or 0.

$$\therefore \qquad \nu = \frac{h^2}{8\pi^2 I}(\pm 2m + 1).$$

The spacing difference is therefore $h/4\pi^2 I$ which is in accordance with facts.

Pure rotation bands for gases have been observed in the far infra-red and towards the end of the near infra-red, i.e., above $22.0\,\mu$.

In addition to the Oscillation and Rotation Bands, it has been found that in the near infra-red region, some of the bands show a fine structure. E. V. Bahr, in 1913, was probably one of the first investigators to demonstrate their fine structure. His results showed the resolution of a band of hydrochloric acid gas into a series of small bands, which were ascribed to the rotation of the molecule. Such bands are now called "Oscillation Rotation Bands."

They have been theoretically explained as follows :- Both oscillation and rotation are quantized in an oscillation rotation band. The quantum condition is :-

$$h\gamma = \gamma_0(n-n_1)h + h^2/_{8\pi^2 I}(\pm 2m+1)$$

provided there is only one moment of inertia.

It can be shewn that this formula indicates a fundamental with exact harmonics, and each band would have three "rotation" branches, those towards the higher and lower wave-lengths, the rotation fringes being $h/4\pi^2 I$ apart, and the third, which may be absent (if $m = o$), or removed from the centre by an amount equal to the constant term $h/8\pi^2 I$. The foregoing treatment only applies when there is one moment of inertia, but even so it does not quite explain all the known facts. One fact which has emerged from the results published by many investigators is :- The centres of the bands are not in harmonic ratio. Kratzer[12] has suggested that the nuclear vibrations are not of sufficient magnitude for the nuclei to be removed outside each others sphere of influence. The law of force governing the vibrations will not be strictly an inverse square law, and he has deduced that the vibrations will therefore be anharmonic. This deviation from the true harmonic is therefore due to the compounding of rotation and transverse vibrations.

The theoretical interpretation of the bands found in the case of liquids and solids is not so easy but a little work on this subject has been done by Kratzer.

VIII. It is of interest to record in this brief introduction that no bands have ever been found for the gases Hydrogen, Oxygen, Chlorine, Bromine and for Iodine in the infra-red. The atoms in these molecules are supposed to be absolutely identical, and it is assumed that there is no electric moment between them nor deformation, and consequently no absorption due to them is found in the infra-red.

IX. In the following pages an account is given of some work carried out in order to set up a Spectrometer arrangement for the accurate analysis of infra-red absorption bands of solids, liquids and gases. A fair account of the work must be divided in five sections :-

(a) Introduction and general description of apparatus;

(b) Investigation of possible errors in the spectrometer, and the study of solids;

(c) Observations on gases;

(d) Study of Liquids;

(e) Conclusions and bibliography.

X. The chapter dealing with the apparatus gives a full description of the spectrometer arrangement; the sources of infra-red radiation; the thermopile and recording apparatus. The types of absorption cell used for gases and for liquids are also amply described; and the apparatus used for preparing pure nitric oxide has been diagrammatically represented.

XI. A complete study was made of the possible errors in the calibration of the spectrometer, a detailed account being given in Chapter 11. The calibration and errors were checked experimentally, and the differences between the calculated and observed calibrations are illustrated by means of graphs. The calibration was checked against well-known absorption bands of calcite, the fundamental band of nitric oxide at 5.30μ, and the emission line at 1.014μ of the mercury vapour lamp. The effect of prism temperature variations on the calibration of the rock-salt prism soon became apparent, and the errors due to this were calculated and corrections applied to all observations.

XII. With the apparatus described, a full investigation of the absorption bands due to carbon dioxide at different pressures was made; also the whole absorption spectrum in the infra-red of Nitric Oxide. Previous workers had only been successful in showing the existence of the fundamental at 5.30μ; during the work about to be described the presence of a first harmonic at 2.68μ was recorded, but no absorption band was found corresponding to the second harmonic.

XIII. An investigation was made of the absorption due to an aqueous solution of carbon dioxide. No marked absorption by this mixture, other than that due to water, was found in the near infra-red region; and it was impracticable to carry out an investigation at higher wavelengths, owing to the great opacity of even thin films of water in this region. A complete experimental study of the absorption due to ethyl alcohol, water, and an aqueous solution of potassium permanganate was made. The results differ in many ways from those of previous workers, and the differences are given.

A band due to potassium permanganate has been observed in the region near 5.60μ.

XIV. A bibliography is supplied together with an appendix giving a number of references to previous work in the infra-red region of the spectrum.

Section II

APPARATUS.

I. The apparatus was arranged in two different ways. The first arrangement, which was used for the greater part of the work, was based on the work done by Bailey and Angus[13] by their monochromatic method. In this arrangement a very intense beam of almost pure monochromatic radiation traverses the specimen under investigation. The radiation from a source N, rich in infra-red rays, is focussed on to the slit S of the spectrometer by means of concave mirrors. The converging beam so formed is collimated by the spectrometer mirror, passes through the rock salt prism, P, is reflected at the Wadsworth Mirror W[14] to another concave mirror, and is then brought to a focus on the exit slit S_2 of the spectrometer. From this slit an almost pure monochromatic beam of radiation emerges; by means of a second system of mirrors this beam is made to traverse a space in which may be placed the specimen under investigation; finally, it is focussed on the thermopile mounted in a special air-tight container, T. This system of mirrors enables the rays to be reversed and the distortion of the final image due to spherical aberration is greatly reduced. The errors introduced by reflection at the first two mirrors are reversed at the second pair of mirrors and almost complete compensation results. The thermopile is connected in series with a "Super Paschen Galvanometer" by means of ordinary twin lighting flex fixed inside a length of glass tubing. No disturbance in the galvanometer readings were noticed when this system of leads was in operation. The galvanometer is mounted on top of a brick pillar sunk well into the floor of the building. This method of supporting the galvanometer was found most reliable, the galvanometer "Zero spot" on the recording scale showing only very minute disturbances; the galvanometer was employed normally at a sensitivity of 10^{-10} amps per mm. deflection, at a scale distance of one metre.

II. The spectrometer used was a large-scale model "Infra Red Spectrometer" fitted with a rock-salt prism and Wadsworth Mirror device[4]; a specially calibrated wavelength drum was also fitted. The thermopile was removed from its housing immediately behind the exit slit S_2 and placed in the special container at T.

III. Later an experimental arrangement No. 2 was used; it was based on the original method of Bailey and Angus[13]. From Fig. 2 it will be seen that the spectrometer position has been altered; the radiation from the source N was passed through the observation cell to the entrance slit of the spectrometer by means of mirrors, and after passing through the spectrometer it fell immediately on the thermopile placed in a holder (No. 2) behind the exit slit S_2. In this arrangement there were fewer mirrors than for arrangement No.1, and therefore the total loss of energy was greatly reduced. This gain was noticed in the increased galvanometer deflections for arrangement No. 2. Where this arrangement was fully tested, the results obtained confirmed those previously derived by method 1.

IV. The whole apparatus, with the exception of the galvanometer, was set up on a stout table; plywood cases, lined with asbestos, were built round the Nernst filament, the spectrometer, the observation cells and thermopile. The positions of these covers are marked out with dotted lines on the diagram of the apparatus (Figs. 1 and 2). The openings in the cases, through which the radiations passed from one section to another, were as small as possible to eliminate any stray radiation; a small pulley and belt arrangement was fixed up for rotating the wave-length drum and prism table, the drum graduations being read by means of a telescope. Through the top of the spectrometer case a thermometer was fixed, so that the prism temperature could be measured at intervals during the experiments. By means of two small heating lamps, the temperature of the cases was maintained slightly higher than that of the room, in order to prevent any deposit of water forming on the surfaces of the rock-salt prism and end plates of the observation cells. A small shutter arrangement was placed in the opening in front of the collimator slit of the spectrometer. By raising or lowering this shutter the radiation could be cut off from the thermopile when desired.

V. All the focussing mirrors external to the spectrometer were of the silver-on-glass type, and were mounted on heavy lead cones fitted with adjusting devices. They were so chosen that the image of the filament just covered the entrance slit of the spectrometer, and the collimator mirror was fully covered with radiation. Under these conditions the maximum amount of energy fell on the exit slit of the spectrometer. Chromium-plated brass mirrors were tried, but these proved most unsatisfactory.

VI. Two sources of Infra-red radiation were tried:

(a) Nernst filaments supplied by A. Hilger, Ltd.;

(b) Globar elements made from fused bars of carborundum.

The Nernst filaments were found to be very satisfactory; they were operated from the D. C. supply of 150 volts and had a current consumption of approximately 0.5 amps. The main laboratory batteries were used for this supply, and the majority of the work had to be done after all the other users of the battery had left the building. Even so, slight fluctuations in the filament current were noticed during a series of observations, so the potentiometer device (P), mentioned by Sir R. Robertson[15], was installed, a a very fine control over the filament current being thus ensured. A diagram of this potentiometer device is given in Fig. 11. The Nernst filament was mounted on a lead cone fitted with adjustment devices all fully described by Sir R. Robertson in his paper. The periods during which the filaments were operated were measured, the average life of a filament according to these observations being about 200 hours. In general, however, the filaments were replaced before these latter stages were reached, as it proved very difficult to control the filament current during the final period. The Globar elements gave a fair emission up to 10.0 μ, but they required a very high current, of the order of 10.0 amps, and the heat given off by them caused the temperature of the room to vary considerably. The Nernst filaments were more economical, had none of these disadvantages, and were much more convenient to operate.

VII. (a) The energy passing through the systems 1 and 2 finally fell on the thermopile; the disturbances noticed by many previous workers in this region (R. Robertson[15]; Bailey[13]; Taylor[16]; and others) and shewn to be due to air currents, proved very troublesome. An air-tight container for the thermopile was designed and constructed, and when used in method 1, a very steady galvanometer zero reading was obtained. Later, another holder was designed for use in method 2 and diagrams illustrating the two holders are given in Figs. 3 and 5.

(b) No. 1 holder, which was made first, consisted of a hollow cylindrical brass chamber closed at one end by a welded-on brass cap; two windows were fitted in the sides of the chamber at opposite ends of a diameter. A rock-salt window was fixed in at R, and at W was a thin glass observation window. At the centre of another circular brass plate, clamped on to cover the other end of the container, the thermopile T was fixed so that when the container was completely sealed up, the thermopile centre came directly in line with the centres of R and W. The thermopile was placed in such a position with respect to R, that the effective "aperture" was equal to the "aperture" of the spectrometer. A side tube (not shown in the diagrams) was also fitted, and through this the vessel could be evacuated; for most work, however, a pressure equal to atmospheric was maintained inside the case. The container was fixed by an ebonite rod to an adjustable metal carriage; by means of this carriage the position of the thermopile could be altered at will. To ensure further freedom from galvanometer "zero drift", the thermopile container was completely surrounded with asbestos and cotton wool lagging together with highly polished metal shields.

(c) Holder No. 2 was designed to be of much smaller dimensions. It had a lower thermal capacity than No. 1 and was arranged so that it could be fixed to the spectrometer immediately behind the thermopile slit, in place of the open type container provided by the makers of the spectrometer. The holder was used in this manner in the experimental arrangement No. 2. A diagram of the holder (not drawn to scale) is shown in Fig. 5. The rock-salt window R was waxed in position and a glass observation window was situated at W. A projection was left on the brass container and threaded as shown, so that the eyepiece and "screw on" brass cover, originally supplied by the makers for the old type of container, could be screwed into position. The thermopile was slipped into position, and the container sealed off by a rubber washer and brass plate arrangement. A little vacuum wax was applied to parts where leaks appeared. Better thermal shielding was possible with this type of holder, the decrease in galvanometer zero drift being very noticeable.

VIII. For the work on gases two types of absorption cell were used :-

(a) Brass tubes fitted with side tubes for evacuation purposes;

(b) "All glass" tubes, also fitted with glass side tubes.

(a) Fig. 7 shows the brass tubes; they were modelled on the same lines as given by Sir R. Robertson[15] in his paper. They were 40.2 cms. long, outer diameter 3.2 cms. and made of brass; the ends of the tubes were ground parallel to each other, and rock-salt end plates of 3.5 cms. diameter, thickness 0.5 cms., were fitted. A little vacuum grease was smeared over the brass surface which came into contact with the rock-salt plate, and the end plates were kept in position by means of "screwed on" end-caps. Where leaks developed near the plates, a little shellac varnish was painted over and in all cases this overcame the trouble. The tubes were connected to each other, and a common connection to the gas apparatus was made through a very long flexible glass tube.

(b) The glass observation tubes were made from specially selected tubing. They were 20.0 cms. long and their ends were ground parallel to each other, the rock-salt end-plates were fixed with a small smear of grease to the ends of the tubes; an outer covering of vacuum wax was placed round the edges of the plates and the corresponding ends of the tubes. This method gave a very satisfactory vacuum-tight seal. The rock-salt end plates were 3.50 cms. in diameter and 0.5 cms. thick.

IX. Two observation tubes were used and were mounted on a rotating carriage, so that either of the two tubes could be placed in the path of the radiation. One tube was filled with the gas under investigation at a known pressure; the other was evacuated and used as a standard for comparison. Fig. 7 shows the type of carriage used. At first, great difficulty was experienced in obtaining exact compensation between the two tubes when both were evacuated. The precautions outlined by Sir R. Robertson[15] were observed, but before complete compensation could be obtained, the carriage had to be re-constructed and modified, so that either of the tubes could be easily displaced relative to the other; the supports for the tubes had also to be strengthened, as it was found that these were slightly displaced when the carriage was rotated. A brief description of the modified carriage illustrated in Fig. 7 is given below :-

Two circular end plates of $\frac{3}{8}$" brass were machined and bolted together by three long stout steel rods. Two strong V-shaped rests were bolted in corresponding positions on each end-plate; the observation tubes rested in these, and levelling screws S_1 were fixed in the sides of the Vs, in order to give the required tilting adjustment to the tubes. A fourth steel bar was fixed between the centres of the two brass end-plates, to act as an axle for the carriage. A support, fitted with two bearings to correspond with the ends of the axle, was arranged; also two fixed brass arms, to serve as stops, were screwed to one of the brass end-plates. On one side of the support was a brass bar fitted with two adjustable screws to register against the stops mentioned previously. A small spring arrangement was also attached to the support, to keep the rocking portion of the carriage fixed when set in any one position. When the carriage was properly adjusted the tubes could be brought in turn to one common position, and complete compensation was found between the two tubes.

X. For work on solids, a metal slider arrangement was devised whereby the specimen could be placed "in" or "out" of the path of the radiation. For the "out" position, where nothing but absorption by the atmosphere is taking place, an adjustable stop was provided so that the two galvanometer deflections could be arranged to be of the same order for the "in" and "out" positions if necessary. This arrangement, which increases the accuracy of the experimental method, was only used for regions of very intense absorption.

XI. A cell[17] for observation work on liquids was designed and constructed; it is shown in detail in Fig. 9. It was turned out from specially selected steel rod, & the outside of the rod was threaded and fitted with two brass "screw-on" caps. The centre of the rod, with the exception of a narrow flange, 1 mm. thick, was hollowed out as shown; the surfaces of the flange were ground parallel to each other, and a hole drilled through the flange in one part for the purpose of filling the cell. Two fluorite windows 3.50 cms. diameter, and of 0.5 cms. thickness, were used as windows for the cell, a rubber washer and brass plunger being placed in between the fluorite plate and the corresponding "screw-on" cap. With this arrangement there was an extremely small leakage from the cell due to evaporation. The cell was fixed to a metal slider device whereby it could be moved in and out of the path of the radiation. This slider device was fitted with an adjustable stop for work in regions of very intense absorption.

XII. A diagram of the apparatus used for the preparation of pure Nitric oxide gas is given in Fig. 13. The gas was prepared by dropping a solution of acidified ferrous sulphate from a funnel on to sodium nitrate solution contained in a generating flask. From there it passed either to a trap (T), where a sample could be collected and tested, or to a set of bubblers (W) containing an aqueous solution of potassium hydroxide for removal of acid fumes; from there it passed through the phosphorous pentoxide drying bulbs P_1, P_2, P_3, to a reservoir (R) where it was collected over mercury. The gas could be pumped over from the reservoir to the observation tube through the long flexible glass tube already described. The pressure of the gas in the observation tube was measured by means of a Bourdon[24] type of gauge fitted with a manometer arrangement. The whole apparatus could be evacuated by a Toepler pump and Hyvac pump. The Toepler pump was also used for recovering samples of gas for analysis from the observation tube. The bourdon type of gauge was primarily fitted for measuring the pressure of mixtures of nitric oxide and oxygen, since these mixtures attack mercury. It was used for measuring all the pressures recorded in the experiments described in the following chapters.

The carbon dioxide used in the experiments was prepared by heating pure sodium bicarbonate with hydrochloric acid; the gas was passed through concentrated sulphuric acid to remove all traces of water, and was then collected and stored in the mercury reservoir R until required.

CHAPTER II.

THE SPECTROMETER: ERRORS and THEIR ELIMINATION.

Section I.

I. This chapter deals exclusively with the spectrometer and the errors which may arise during its use; an account is given of all the possible errors, and the methods of correcting them.

II. The instrument used in these experiments was a large-scale Infra-Red Spectrometer supplied by Messrs. A. Hilger Ltd. It was furnished with a rock-salt prism of 60^o angle, and a wave-length drum for the prism table, calibrated to read directly in wave-lengths. The spectrometer was housed in a large plywood case fitted with the thermometer and heating lamp previously described (Chapter I, Sec. II, Para. IV). The temperature of the case was taken at intervals during the course of an experiment, and, as no observations were recorded until the temperature became reasonably steady, it was assumed that the temperature of the prism was equal to that of the air surrounding it.

III. The wave-length drum was recalibrated by a method similar to that described by Sir R. Robertson. A small plane mirror was set up vertically at the centre of the prism table, an accurate steel scale being placed parallel to it at a known distance away. An illuminated slit placed in line with the scale was so arranged that the light from it was reflected at the mirror and formed an image of the slit on the scale. Zero was taken as the position of the image of the slit on the scale, when the "wave-length drum" was set at the sodium wave-length graduation mark. The position of the image of the slit on the scale was read off when these conditions were fulfilled. The wave-length drum was given a slight rotation and set against some definite wave-length graduation mark; the position of the image of the slit on the scale was again read off. Such observations were repeated for several positions in the working range of the wave-length drum. (About 10 per μ, - see Column 1 of Table 1). The readings are given in Table 1; three representative sets, of the many observations made, have been given in the Table.

From a knowledge of the distance separating the scale from the mirror, the angle of rotation of the prism table corresponding to a rotation of the "wave-length" drum from one definite wave-length setting to another, could be determined.

Let us suppose that the distance between the scale and the mirror is equal to D; and the distance traversed by the image of the slit on the scale when the wave-length drum is rotated from one wave-length setting to another be d, then the angle through which the mirror and the prism table are turned when the wave-length drum is rotated, is given by the relation :-

$$\tan 2\alpha = d/D .$$

In Table 1, Column 1, the values of the "wave-length drum" settings are given; and in column 11 are given the values of the tangent of twice the angle of rotation of the prism table, caused by a rotation of the "wave-length drum" from the sodium wave-length graduation mark to the corresponding wave-length mark, λ . In columns III and IV are the duplicate values obtained with the scale and mirror separated by slightly different distances. These distances are given in brackets at the head of each column. Thus, the values of tan 2α given in column 11, correspond to a distance between the scale and mirror of 493.8 cms., column 111 shows experimental values of tan 2α for a distance 468.0 cms., and in column IV, values corresponding to a distance of 483.1 cms. are given. There is very close agreement between the three sets of values: the greatest difference between the maximum and minimum values of α for the three different settings being 5 seconds of arc. Column V contains the mean value of tan 2α , and in column VI is given the number of the observation.

IV. Now the spectrometer is so constructed that the rotation which must be given to the prism table or wave-length drum, for the radiation entering the thermopile slit to be changed from wave-length λ_1 to λ_2, is given by :-

$$\alpha = D_1/2 - D_2/2$$

where D_1 is the minimum deviation for radiation of wave-length λ_1 passing through the prism. D_2 is the minimum deviation for a radiation of wave-length λ_2 under the same conditions. A value for the semi-deviation of a ray of sodium light passing through a rock-salt prism of 60° angle and set in the minimum deviation position was assumed. This value is 20° 32' 52.4". From the relationship given above, the value of the semi-deviation for radiation of any other wave-length is easily calculated.

The value of α for a series of wave-lengths is given in column IIa of Table I, and the value of the semi-deviation for the same series of wave-lengths calculated by the above relation are given in Table I, column IIIa. These values of semi-deviation are called the "observed" values. A large-scale graph of these "observed" values plotted against

T A B L E 1.

Observations to shew the relationship between the rotation of the prism table and the rotation of the wave-length drum.

Column No.1	11	111	1V	V	V1	1a	11a	111a	1Va
WAVE-LENGTH DRUM READG. (λ IN μ)	Tan. 2α (Dist. = 493.8 cms)	Tan. 2α (Dist. = 468.0 cms)	Tan. 2α (Dist. = 483.1 cms)	Mean Value of Tan. 2A	No.	2α	Rotation α	Semi-Deviation D/2	No.
0.5893	-	-	-	-	1	-	-	20° 32' 52.4"	1
1.1	.0207371	.0207264	.0207409	.0207348	2	1° 11' 16.2"	- 35' 38.1"	19° 57' 14.3"	2
1.2	.0221142	.0221153	.0221072	.0221122	3	- 16' 0.2"	38' 1"	54' 52.3"	3
1.3	.0230862	.0230769	.0231007	.0230879	4	19' 21.3"	39' 40.6"	53' 11.8"	4
1.4	.0239975	.0240384	.0240115	.0240158	5	22' 32.6"	41' 16.3"	51' 36.1"	5
1.5	.0247873	.0247863	.0247981	.0247906	6	25' 12.3"	42' 36.1"	50' 10.6"	6
1.6	.0254354	.0254273	.0254191	.0254272	7	27' 23.6"	43' 41.8"	48' 10.7"	7
1.7	.0260024	.0260256	.0259986	.0260088	8	29' 23.4"	44' 41.7"	47' 24.3"	8
1.8	.0265289	.0265176	.0263298	.0264586	9	30' 56.2"	45' 28.1"	46' 29.4"	9
1.9	.0269744	.0270085	.0269923	.0269917	10	32' 46.0"	46' 23.0"	45' 43.1"	10
2.0	.0274402	.0274358	.0274476	.0274412	11	34' 18.7"	47' 9.3"	45' 0.3"	11
2.1	.0278452	.0278632	.0278616	.0278566	12	35' 44.3"	47' 52.1"	44' 20.3"	12
2.2	.0282503	.0282478	.0282342	.0282441	13	37' 4.2"	48' 32.1"	43' 41.1"	13

TABLE 1 (contd)

Column No. 1	11	111	1V	V	V1	1a	11a	111a	1Va
2.4	.0289996	.0289743	.0289794	.0289844	15	39' 36.7"	49' 48.3"	42' 29.8"	15
2.5	.0293136	.0293162	.0293106	.0293168	16	40' 45.2"	50' 22.6"	41' 43.5"	16
2.60	.0296881	.0297008	.0299109	.0297666	17	1° 42' 17.9"	51' 8.9"	41' 43.5"	17
2.70	.0300121	.0299999	.0300144	.0300132	18	43' 8.8"	51' 34.4"	41' 18.0"	18
2.80	.0303766	.0303846	.0303870	.0303827	19	44' 24.9"	52' 12.4"	40' 40.0"	19
2.90	.0307006	.0306837	.0307182	.0307008	20	45' 30.5"	52' 45.2"	40' 7.2"	20
3.00	.0310652	.0310256	.0310908	.0310605	21	46' 44.6"	53' 22.3"	39' 30.1"	21
3.10	.0314297	.0314102	.0314220	.0314206	22	47' 58.8"	53' 59.9"	38' 53.0"	22
3.20	.0317537	.0317521	.0317532	.0317530	23	49' 7.3"	54' 33.6"	38' 18.8"	23
3.30	.0321182	.0320939	.0321258	.0321126	24	50' 21.4"	55' 10.7"	37' 41.7"	24
3.40	.0324827	.0324786	.0324569	.0324727	25	51' 35.6"	55' 47.8"	37' 4.6"	25
3.50	.0328068	.0328204	.0328088	.0328120	26	52' 45.5"	56' 22.7"	36' 29.7"	26
3.60	.0331713	.0331623	.0332021	.0331786	27	54' 1.0"	57' 0.5"	35' 51.9"	27
3.70	.0335763	.0335897	.0335747	.0335802	28	55' 23.8"	57' 41.9"	35' 10.5"	28
3.80	.0339003	.0338888	.0338645	.0338845	29	56' 26.5"	58' 13.2"	34' 39.2"	29
3.90	.0343053	.0342948	.0343199	.0343066	30	57' 53.4"	58' 56.7"	33' 55.7"	30

TABLE 1 (contd)

Column No. 1	11	111	1V	V	V1	1a	11a	111a	1Va
4.10	.0351356	.0351281	.0351272	.0351303	32	2° 0' 43.1"	60' 21.5"	32' 30.8"	32
4.20	.0355407	.0355127	.0355205	.0355246	33	2' 4.3"	61' 2.1"	31' 50.3"	33
4.30	.0359659	.0359401	.0359759	.0359606	34	3' 34.2"	61' 47.1"	31' 5.3"	34
4.40	.0364317	.0364316	.0364313	.0364315	35	5' 11.2"	62' 35.6"	30' 16.8"	35
4.60	.0373430	.0373076	.0373421	.0373307	36	8' 16.2"	64' 8.2"	28' 44.2"	36
4.80	.0382746	.0382905	.0382942	.0382864	37	11' 33.2"	65' 46.6"	27' 5.8"	37
4.90	.0388416	.0388034	.0388117	.0388189	38	13' 22.9"	66' 41.4"	26' 11.0"	38
5.00	.0393276	.0393162	.0393292	.0393243	39	15' 7.0"	67' 33.5"	25' 18.9"	39
5.10	.0398946	.0398717	.0399088	.0398917	40	17' 3.8"	68' 31.9"	24' 20.5"	40
5.20	.0404009	.0403846	.0404056	.0403970	41	18' 47.9"	69' 23.9"	23' 28.5"	41
5.30	.0409477	.0409401	.0409438	.0409438	42	20' 40.5"	70' 20.2"	22' 32.2"	42
5.40	.0414742	.0414529	.0414406	.0414559	43	22' 26.0"	71! 13.0"	21' 39.4"	43
5.60	.0424868	.0424358	.0424756	.0424660	44	25' 53.9"	72' 56.9"	19' 55.4"	44
5.7	.0430943	.0430768	.0430551	.0430754	45	27' 59.4"	73' 59.7"	18' 52.7"	45
5.8	.0436208	.0436324	.0436347	.0436293	46	29' 53.4"	74' 56.7"	17' 55.7"	46
5.9	.0441879	.0441879	.0442143	.0441967	47	31' 50.3"	75' 55.1"	16' 57.3"	47

TABLE 1 (contd)

Column No. 1	11	111	1V	V	V1	1a	11a	111 a	1Va
6.2	.0459902	.0460042	.0459945	.0459963	50	38' 0.7"	79' 0.3"	13' 52.1"	50
6.3	-	.0465811	.0466155	.0465983	51	40' 4.6"	80' 2.3"	12' 50.1"	51
6.4	.0471850	.0471794	.0472158	.0471934	52	42' 7.1"	81' 3.5"	11' 48.9"	52
6.5	.0478331	.0478204	.0478161	.0478232	53	44' 16.7"	82' 8.3"	10' 44.1"	53
6.6	.0484608	.0484615	.0484784	.0484669	54	46' 29.1"	83' 14.5"	9' 37.9"	54
6.7	.0490886	.0491025	.0490994	.0490968	55	2° 48' 38.8"	84' 19.4"	19° 8' 33.0"	55
6.8	.0497164	.0497008	.0497204	.0497125	56	50' 45.5"	85' 22.7"	7' 29.7"	56
6.9	.0504252	.0504273	.0504242	.0504256	57	53' 12.2"	86' 36.1"	6' 16.3"	57
7.0	.0510733	.0510795	.0510866	.0510798	58	55' 26.8"	87' 43.9"	5' 9.0"	58
7.2	.0524908	.0525213	.0524941	.0525020	59	3° 0' 19.3"	90' 9.6"	2' 42.8"	59
7.3	.0532199	.0532050	.0532393	.0532214	60	2' 47.5"	91' 23.6"	1' 28.8"	60
7.4	.0539692	.0539743	.0539845	.0539760	61	5' 22.5"	92' 41.2"	0' 11.2"	61
7.5	.0547185	.0547008	.0546883	.0547024	62	7' 51.9"	93' 55.9"	18° 58' 56.5"	62
7.6	.0554880	.0555127	.0554749	.0554918	63	10' 34.2"	95' 17.1"	57' 35.3"	63
7.7	.0562170	.0562179	.0562201	.0562183	64	13' 36.0"	96' 31.8"	56' 20.6"	64
7.8	.0569461	.0569444	.0569239	.0569381	65	15' 31.6"	97' 45.8"	55' 6.6"	65
7.9	.0577561	.0577349	.0577518	.0577476	66	18' 18.0"	99' 9.0"	53' 43.4"	66

TABLE 1 (contd)

Column No. 1	11	111	1V	V	V1	1a	11a	111a	1Va
8.2	.0600647	.0600427	.0600702	.0600591	68	26' 13.2"	103' 6.6"	18° 49' 45.8"	68
8.3	.0608748	.0608760	.0608568	.0608692	69	28' 59.7"	104' 29.8"	48' 22.6"	69
8.4	.0616848	.0617093	.0617262	.0617401	70	31' 58.6"	105' 59.3"	46' 53.1"	70
8.5	.0625354	.0625213	.0625542	.0625369	71	34' 42.3"	107' 21.1"	45' 33.3"	71
8.6	.0633859	.0633974	.0634235	.0635023	72	38' 0.7"	109' 0.3"	43' 52.1"	72
8.7	.0642972	.0643162	.0642929	.0643021	73	40' 45.0"	110' 22.5"	42' 29.9"	73
8.8	.0651680	.0651709	.0651830	.0651739	74	43' 44.1"	111' 52.0"	41' 0.4"	74
8.9	.0660186	.0660042	.0660110	.0660112	75	46' 36.0"	113' 18.0"	39' 34.4"	75
9.0	.0668894	.0668803	.0668804	.0668834	76	49' 35.1"	114' 47.0"	38' 5.4"	76
9.1	.0677399	.0677349	.0677291	.0677346	77	52' 22.9"	116' 14.9"	36' 7.5"	77
9.2	.0686512	.0686324	.0686398	.0686411	78	55' 36.0"	117' 48.0"	35' 4.4"	78
9.3	.0696233	.0696366	.0696334	.0696311	79	58' 59.3"	119' 29.6"	33' 22.8"	79
9.4	.0705750	.0705555	.0705649	.0705651	80	4° 2' 11.0"	121' 5.5"	31' 46.9"	80
9.5	.0715268	.0715384	.0715171	.0715274	81	5' 28.5"	122' 49.2"	30' 3.2"	81
9.6	.0724584	.0724358	.0724486	.0724476	82	8' 37.3"	124' 18.6"	28' 33.8"	82
9.7	.0734102	.0734187	.0734008	.0734299	83	11' 58.8"	125' 59.4"	26' 53.0"	83
9.8	.0743620	.0743589	.0743529	.0743576	84	15' 9.2"	127' 34.5"	25' 17.8"	84

TABLE 1 (contd)

Column No. 1	11	111	1V	V	V1	1a	11a	111a	1Va
10.0	.0763061	.0763247	.0762987	.0763098	86	21' 49.5"	130' 54.7"	21' 57.9"	86
10.1	.0773592	.0773503	.0773337	.0773477	87	25' 22.4"	132' 41.2"	20' 11.2"	87
10.2	.0783312	.0783332	.0783479	.0783374	88	28' 24.8"	134' 12.4"	18' 40.0"	88
10.4	.0804778	.0804700	.0804800	.0804759	89	36' 3.6"	138' 1.8"	14' 50.6"	89
10.5	.0817334	.0817093	.0817220	.0817216	90	40' 18.9"	140' 9.4"	12' 43.0"	90
10.6	.0825232	.0825212	.0825086	.0825176	91	43' 2.0"	141' 31.0"	11' 21.4"	91
10.8	.0846091	.0846153	.0845785	.0846009	92	50' 8.7"	145' 4.3"	7' 48.1"	92
11.0	.0868975	.0869017	.0868969	.0868987	93	57' 59.2"	148' 59.6"	3' 52.8"	93
11.2	.0891049	.0891239	.0890910	.0891066	94	5° 5' 31.1"	152' 45.6"	0' 6.6"	94
11.4	.0913527	.0913461	.0913473	.0913487	95	13' 9.8"	156' 34.9"	17° 56' 17.5"	95
11.6	.0937019	.0936966	.0937071	.0937058	96	21' 11.1"	160' 35.5"	17° 52' 16.9"	96
11.8	.0960510	.0960683	.0960668	.0960620	97	29' 13.5"	164' 36.7"	48' 15.7"	97
12.0	.0984406	.0984829	.0984887	.0984707	98	37' 25.7"	168' 42.8"	44' 9.6"	98
12.2	.1009923	.1010250	.1010140	.1010104	99	46' 4.4"	173' 2.2"	39' 50.2"	99
12.4	.1036654	.1036960	.1036842	.1036818	100	55' 9.7"	177' 34.8"	35' 17.6"	100
12.6	.1061765	.1061960	.1062096	.1061940	101	6° 3' 42.2"	181' 51.1"	31' 1.3"	101
12.8	.1087282	.1087390	.1087557	.1087409	102	13' 21.6"	186' 10.8"	[illegible]	[illegible]

TABLE 1 (contd.)

Column No. 1	11	111	1V	V	V1	1a	11a	111a	1Va
13.0	.1114823	.1115170	.1115294	.1115096	103	21' 45.8"	190' 52.9"	21' 59.5"	103
13.2	.1141352	.1141880	.1141996	.1141742	104	30' 48.5"	195' 24.2"	17' 28.2"	104
13.4	.1169501	.1170085	.1169941	.1169842	105	40' 20.5"	200' 10.2"	12' 42.2"	105
13.6	.1198055	.1198717	.1198714	.1198492	106	50' 3.3"	205' 1.6"	7' 50.8"	106
13.8	.1226407	.1226923	.1226865	.1226731	107	59' 37.3"	209' 48.6"	3' 3.8"	107
14.0	.1255974	.1256624	.1251172	.1256090	108	7° 9' 33.7"	214' 46.8"	16° 58' 5.6"	108
14.2	.1287363	.1287820	.1287929	.1287704	109	20' 15.4"	220' 7.7"	52' 44.7"	109
14.4	.1316524	.1317307	.1317115	.1316982	110	30' 9.2"	225' 4.6"	47' 47.8"	110
14.6	.1347104	.1347649	.1347751	.1347501	111	40' 27.7"	230' 13.8"	42' 38.6"	111

wave-length is given on the calibration curves chart, Fig. 47.

V. The theoretical values of the semi-deviation for different wave-lengths were calculated from the values of the refractive index (η) of rock salt, given by Paschen[18].

According to Paschen, these values were determined at different temperatures (also given in his paper), and were corrected to a standard temperature, 18°C., assuming that the temperature coefficient of change of refractive index was constant for all wave-lengths, and equal to that for the sodium lines. The values of the corrected refractive indices, and the temperatures at which the uncorrected values were experimentally determined, are reproduced in the calibration chart (Fig. 46), columns 1, 2 and 3.

The coefficient of change of refractive index with temperature $d\eta/d\theta$ has been determined for several wave-lengths in the infra-red by Schaefer and Matossi[19], and their values show that $d\eta/d\theta$ varies with wave-length; such values are reproduced in column 4 of the calibration table, and are plotted against wave-length on the "calibration curves" chart; intermediate values of $d\eta/d\theta$ were read off from this graph, and when included in the calibration chart they are marked with an asterisk *. These values of $d\eta/d\theta$ must be used for an accurate correction of Paschen's original figures for the refractive index, and, moreover, the corrections for temperature originally applied by Paschen must first of all be removed.

Sir R. Robertson in his paper, has corrected Paschen's values assuming Paschen himself made no corrections. His method has been repeated and the results are given in column 5 of the chart; column 6 gives the values taken directly from Sir R. Robertson's paper, and it will be seen that general agreement exists between the two sets of values.

Paschen's values of η have been recorrected, after first removing Paschen's own corrections, and such values are given in column 7. These values were plotted against wave-length on a large scale graph (Fig. 48), and values of η given by Sir R. Robertson were also plotted alongside for comparison; values of η for intermediate wave-lengths were read off from the graph, and are distinguished from others in the tables by an asterisk.

The standard temperature to which the refractive index was corrected was 18°C.

Now :-

$$\eta = \frac{\sin (A+D)/2}{\sin A/2}$$

where A = angle of prism

" D = deviation of a ray when prism is set in minimum deviation position.

Since η and A are known, the value of $^D/2$ for any value of η can be determined. This calculation of $^D/2$ was carried out for all the values of 'η' given in column 7 of the calibration tables; a graph has been drawn to show the relationship between these theoretical values of the semi-deviation and corresponding wave-lengths; this is given in Fig. 47. This curve is found to intercept the "observed" semi-deviation wave-length curve in many places. There is, in short, a discrepancy between the observed and calculated semi-deviations for almost all wave-lengths. These arise from slight errors in cutting the threads of the screw which propels the wave-length drum and rotates the prism table. These differences between the values of the semi-deviation cause errors to occur in the readings given by the spectrometer. The makers of the instrument, in a leaflet issued with the spectrometer, claim an accuracy in the calibration which would allow for an error of $.03\mu$ at 4.71μ. Methods and correction charts have been devised whereby this error can be almost wholly eliminated.

To obtain the above correction in terms of wave-length, it is necessary to multiply the error in semi-deviation by the slope of the curve showing the relation between "observed semi-deviation" and "wave-length drum reading" $\left(= 2\frac{d\lambda}{dD}\right)$ for the particular wave-length under consideration. The correction has been evaluated for a range of wave-lengths in the infra-red, and a curve was plotted showing the variations of this correction with wave-length drum reading. The curve is periodic in character, and each complete undulation of the curve corresponds to one rotation of the wave-length drum. The values for the correction at different wave-length drum readings are given in column 20 of the calibration tables. This error may be classified as Error No. 1.

VI. Errors Due to Changes in Prism Temperature.

The effect of variations in prism temperature on the calibration of an infra-red spectrometer fitted with a rock-salt prism, was first pointed out by Sir R. Robertson[15]; the effect was later discussed by Bailey and Angus[13], and since the present work was completed, a further account appeared by P. C. Cross[20]. Some of his conclusions are reproduced in the calibration tables for the purposes of comparison. The effect has been summarised and divided into two main sections:-

(a)

The "semi-deviation wave-length" curve for radiations passing through a rock-salt prism set in the minimum deviation position is of the form shown in the figure. For prism temperature θ_1, (hereafter known as the standard temperature = 18°C) the curve is of the form AB; when the temperature is raised to θ_2, the refractive index of the rock salt varies in such a manner that the curve assumes the form CD. The "datum" line used with the present type of spectrometer is the wave-length of the sodium lines at 0.5893 μ, equivalent to a semi-deviation equal to OX in the figure. The Wadsworth mirror attachment is so adjusted that when the wave-length drum is reading the sodium wave-length (λ_{Na}), and the collimator slit is illuminated with sodium light, an image of the sodium lines appears on the exit slit of the spectrometer, i.e., the adjustment is such that the rays of sodium light have suffered a semi-deviation equal to OX, and just reach the exit slit of the spectrometer, provided the prism temperature is θ_1. Moreover, the instrument is so constructed that for a radiation of wave-length λ_1 to be deviated and fall on the exit slit of the spectrometer, a rotation equal to $(X-X_1)$ must be given to the prism table and wave-length drum; and the calibration is such that the wave-length drum should read λ_1 in this new position.

If the prism temperature were raised to θ_2, and the Wadsworth mirror again adjusted, the prism table rotation would be between Y and Y_1. It can be shown that :
$OX - OX_1 \doteq OY - OY_1$ for all wave-lengths in the near infra-red, provided ($\theta_2 - \theta_1$) does not exceed 4 degrees centigrade.(Error 1.5 x 10^{-5} rads. per degree). Hence, if the Wadsworth mirror is correctly re-set at a temperature θ_2 by means of the sodium lines, the wave-length of the

radiation falling on the thermopile slit of the spectrometer will be λ_1 when the wave-length drum setting reads λ_1, provided $(\theta_2 - \theta_1)$ does not exceed 4 degrees centigrade.

In general, however, it is not always possible to have the prism temperature so close to the standard temperature when the Wadsworth mirror is being set; the correction must therefore be fully evaluated and applied whenever experimental conditions differ from the ideal ones outlined above. The full correction for one degree difference in temperature of the prism is calculated as follows:

$\frac{D}{2}$ = semi-deviation of a ray passing through the prism at minimum deviation.

Now $$\eta = \frac{\sin.(A+D)/2}{\sin.A/2}, \quad \text{and} \quad \frac{dD}{d\eta} = \frac{2\sin.A/2}{\cos.(A+D)/2} \qquad (1)$$

Moreover, $$\frac{dD}{2d\eta} \times \frac{d\eta}{d\theta} = \frac{1}{2}\frac{dD}{d\theta} = \frac{\sin.A/2}{\cos.(A+D/2)} \cdot \frac{d\eta}{d\theta} \qquad (2)$$

which relation enables the change in semi-deviation of a ray with change of prism temperature to be calculated.

Again, since the spectrometer is so constructed, that in order to change the radiation transmitted by the thermopile slit from wave-length λ_{Na} to λ_1, the prism table must be rotated through an angle equal to the difference between the semi-deviations for radiations of wave-length λ_{Na} and λ_1.

Thus, rotation required to change from λ_{Na} to λ_1 at θ_1°C = $(OX - OX_1)$

and rotation required to change from λ_{Na} to λ_1 at θ_2°C = $(OY - OY_1)$

Correction for rotation of prism table to be applied for temperature change $(\theta_2 - \theta_1) = \Delta\theta$

$$
\begin{aligned}
&= (OX-OX_1) - (OY-OY_1) = (OX-OY) - (OX_1-OY_1) \\
&= \left\{OX-\left(OX-\left(\frac{dD}{d\theta}\right)_{\lambda_{Na}}\cdot\frac{\Delta\theta}{2}\right)\right\} - \left\{OY-\left(OY-\left(\frac{dD}{d\theta}\right)_{\lambda_1}\cdot\frac{\Delta\theta}{2}\right)\right\} \\
&= \left\{\left(\frac{dD}{d\theta}\right)_{\lambda_{Na}} - \left(\frac{dD}{d\theta}\right)_{\lambda_1}\right\}\frac{\Delta\theta}{2} \qquad (3)
\end{aligned}
$$

The term given in (3) gives the rotation correction factor for a change in prism temperature; similar correcting factors may be evaluated for other pairs of wave-lengths.

From the relationship (2), the values of $\frac{dD}{d\theta}$ for various wave-lengths in the infra-red region have been evaluated, and such values are given in column 12 of the calibration table; for comparison, in column 13 are corresponding figures taken from the Paper by P. C. Cross. From a knowledge of the value of $\frac{dD}{d\theta}$, the correction factor per degree, $\frac{1}{2}\left\{\left(\frac{dD}{d\theta}\right)_{\lambda_{Na}} - \left(\frac{dD}{d\theta}\right)_{\lambda_1}\right\}$ has been calculated for the same series of wave-lengths, and these values are given in column 14 of the calibration tables. It will be seen that for the shorter wave-lengths up to 8.0μ, the error involved per degree centigrade is very small indeed; for higher wave-lengths the correction becomes quite appreciable.

The absolute wave-length correcting factor $(\frac{d\lambda}{d\theta})$ is obtained by multiplying the above factor by $2\frac{d\lambda}{dD}$, this being derived from the slope of the "observed semi-deviation wave-length" curve.

for: $\frac{1}{2}\left\{\left(\frac{dD}{d\theta}\right)_{\lambda_{Na}} - \left(\frac{dD}{d\theta}\right)_{\lambda_1}\right\} \times 2\frac{d\lambda}{dD} = \frac{d\lambda}{d\theta}$

Column 17 in the calibration tables gives a series of values for this factor for different wave-lengths. In the region from $1.0\mu - 8.0\mu$, a change of temperature of 20 degrees centigrade only causes an error of 0.005μ.

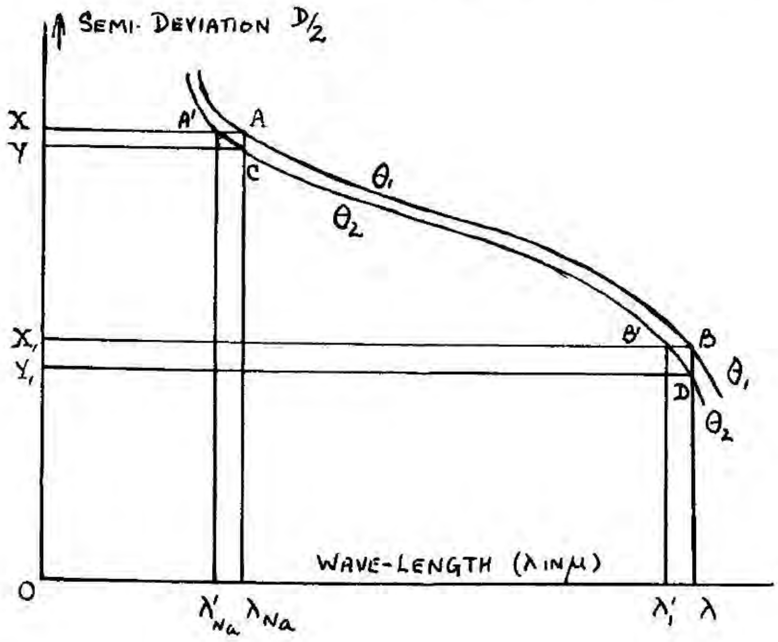
For experimental observations in these regions, where the dispersion of rock salt is small, this error may be neglected. A graph of the results plotted against wave-length is given with the calibration curves, Fig. 47, and is called "Wave-length temperature correction" curve. A better term would probably be "Rotation temperature correction."

(b) Error due to observations being taken at a different prism temperature from that at which the Wadsworth mirror is set.

This error, also due to fluctuations in prism temperature, is an additional one to that fully described in section (a). Suppose the Wadsworth mirror is correctly adjusted at prism temperature θ_1, so that when the wave-length drum is set at λ_{Na}, radiation of wave-length λ_{Na} is falling on the thermopile slit of the spectrometer. If the prism temperature is raised to θ_2 the radiation falling on the thermopile slit will be λ'_{Na} when the wave-length drum setting is λ_{Na}; and similarly, a difference will be noticed at other wave-lengths: for a drum setting of λ_1, the wave-length transmitted by the thermopile slit will be λ'_1. Thus, from a consideration of the figure, it will be seen that the error at λ_{Na} will be:

$$AX - A'X = d\lambda = \left(\frac{d\lambda}{d\theta}\right)\Delta\theta = \tfrac{1}{2}\left(\frac{dD}{d\theta}\right)_{\lambda_{Na}} \cdot \left(\frac{2\,d\lambda}{dD}\right)_{\lambda_{Na}} \cdot \Delta\theta \,,$$

and similarly for other wave-lengths.



The error has been evaluated for a series of wave-lengths in the infra-red, and the results are given in column 22 of the calibration tables. It will be seen that the error reaches a maximum value in the region between 2.0μ- 3.0μ, where the dispersion of rock salt is small. A graph of these results has been drawn with the calibration curves, and is called "Calibration temperature correction."

The errors due to prism temperature fluctuations may therefore be summed up as follows:-

(a) "Wave-length temperature correction" or "Rotation temperature correction" which becomes very noticeable beyond 8.0μ.

(b) "Calibration temperature correction ", due to the Wadsworth mirror being set at different temperature from that at which the final observations are taken. This error has its greatest effect in the near infra-red regions.

VII. Slit Width of the Spectrometer.

The resolving power of the spectroscope depends upon the range of wave-lengths included in the thermopile slit, measured by the drum setting on the spectrometer. To find the "width," the collimating slit of the spectrometer was closed to 2/1000" and illuminated with sodium light. The thermopile slit was then opened to 10/1000", and the rotation of the prism table which was necessary to cause the image of the collimator slit to traverse the width of the exit slit was measured. From the calibration curve, the difference in wave-length corresponding to this rotation of the prism table was evaluated for several positions throughout the spectrum. This gave the "equivalent width" of the thermopile slit. Such values were plotted on a graph to show the relation between slit-width and wave-length drum reading, Fig. 47; the graph shewed a maximum value for the "slit width" at about 2.8μ, corresponding to the point where the curvature of the "semi-deviation drum reading" graph changes sign. Column 18 in the calibration tables gives these values of the "slit width."

For most work the thermopile slit and collimator slit were opened to the same extent; occasionally, to obtain a greater amount of energy falling on the thermopile, the entrance slit was opened up - but never wider than twice the width of the thermopile slit.

VIII. The remainder of this chapter deals with the experimental work carried out to check the calibration outlined in the previous paragraphs, & also, the effects of variations in prism temperature on this calibration.

IX. The first experimental check on the calibration was that used by many previous investigators, namely, the use of the Emission line in the mercury arc spectrum at 1.014 μ. The Wadsworth Mirror was adjusted until the maximum emission from the lamp coincided with a "wave-length drum" setting of 1.014 μ, as observed by means of the telescope attached to the spectrometer. One of the many curves obtained during the course of the work is given in Fig. 21, which shows the emission as observed when the Wadsworth mirror is correctly adjusted; the corresponding experimental observations are given in Table 11. It should be noted that the errors due to both of the temperature effects, and to the faulty cutting of the "wave-length drum" screw, are all small in the region near 1.014 μ, so that this line at 1.014 μ is a most suitable one for calibration purposes. During the course of the work, the setting of the Wadsworth Mirror was often checked by this means, so that all values of wave-lengths given in the following pages are determined relative to the mercury line at 1.014 μ.

TABLE II.

Observations on the Line in the Mercury Arc Emission Spectrum at 1.014μ.
(After Wadsworth Mirror has been carefully adjusted).

Prism Temperature set at 27°C. Wadsworth set at 27°C.

Slits: 5/1000" Entrance.
5/1000" Exit.

W. L. Drum Readg. (λ in μ)	Temp. Corr. (λ in μ)	Corr. W. L. (λ in μ)	Galvo. zero cms.	Galvo. throw cms.	Galvo. Defl. cms.	Mean Defl. cms.
.98	-	.98	9.0 8.9	15.6	6.6 6.7	6.65
.99	-	.99	6.3 6.5	14.1	7.8 7.6	7.7
1.00	-	1.00	3.1 3.1	12.2	9.1 9.1	9.1
1.01	-	1.01	4.7 4.6	14.2	9.5 9.6	9.55
1.02	-	1.02	8.5 8.2	17.2	8.7 9.0	8.8
1.03	-	1.03	19.7 19.5	26.5	6.8 7.0	6.9
1.04	-	1.04	22.2 22.1	28.7	6.5 6.6	6.55
1.05	-	1.05	22.9 22.8	29.7	6.8 6.9	6.85

Repeat Observations:

.96	-	.96	32.4 32.8	26.1	6.3 6.7	6.50
1.01	-	1.01	20.0 20.3	10.4	9.6 9.9	9.7
1.02	-	1.02	22.9 23.4	14.15	8.75 9.25	9.0
1.03	-	1.03	25.7 26.0	18.8	6.9 7.2	7.1
1.04	-	1.04	28.6 28.8	22.4	6.2 6.4	6.3
1.05	-	1.05	31.0 31.0	24.1	6.9 6.9	6.9

X. When the mercury arc lamp was being used some trouble was experienced due to "flickering". This caused the energy emitted by the lamp to be unsteady, and the flickering also interfered with a true and steady deflection being given by the galvanometer. To compensate for any errors which might arise from this, the absorption bands of calcite were also used as an experimental check on the setting of the Wadsworth Mirror by the mercury arc lamp.

XI. When investigating true absorption curves, the following method was used for the actual taking and recording of observations. A good illustration of the method is probably given by a consideration of the actual experimental investigation of the absorption bands of calcite. Here, a crystal section cut perpendicular to the optic axis and of thickness 0.5 cms., was used. The section was placed on the metal slider arrangement previously described (Chap. I, Sec.II, para. X), and observations were recorded in the following manner. The Nernst Filament was started, and kept running for about an hour until the temperature conditions had become reasonably steady. The wave-length drum was set at some pre-determined position, and the setting noted. The crystal slider was set up in its appropriate position P. (Figs. I & II) and the crystal section was placed in the path of the radiation (Position A). The value of the galvonometer zero was measured and the shutter on the spectrometer case lifted. This allowed the radiations from the Nernst Filament to pass through the spectrometer and crystal section and fall on the thermopile; a corresponding deflection was produced in the galvanometer and this was measured. The final position of the galvanometer spot was noted, the shutter lowered, and the galvanometer spot returned to zero. This zero position was read off to allow for any "zero drift". The mean value of the galvanometer zero was estimated, and the difference between this figure and the greatest reading of the galvanometer gave the true galvanometer deflection corresponding to the energy passing through the specimen. This mean galvanometer deflection is given in the tables as "galvanometer deflection A". The crystal section was removed from the path of the radiation, the shutter on the spectrometer case was lifted, and the mean galvanometer deflection was observed as before. This deflection, corresponding to the energy passing without absorption to the thermopile, was called "galvanometer deflection B". The difference between the two values is a measure of the amount of energy absorbed by the crystal, and the ratio A/B gives the value of the transmission coefficient of the material for the radiation of the particular wave-length under consideration. The wave-length drum was rotated slightly to some new position, the wave-length graduation being noted, and the above procedure repeated. In this way a series of values for the transmission ratio (A/B) for radiations of different wave-lengths was obtained. When the values of the transmission ratio A/B were plotted against the corrected values of wave-length drum readings on a graph, the transmission curves given in the following pages were obtained.

XII. For the work on gases and liquids, the absorption cells previously described (Chap. I, Sect. I, Paragraphs VIII & XI) were used in place of the crystal holder. As will be understood from the next two chapters of this paper, it was possible to obtain exact compensation between the two empty cells used in such cases. That is, when the two cells were completely exhausted of either gas or liquid, each transmitted the same amount of energy to the thermopile. (This effect will be more fully discussed in Chapters III and IV). The "galvanometer deflection A" was then the value of the deflection when the cell containing the gas or liquid was in the path of the radiation, and the "galvanometer deflection B" was the deflection obtained when the compensation cell was in the path. The transmission ratio A/B was calculated in the same way as for solids.

XIII. A few representative results for the ratio A/B for different wave-lengths for a crystal of calcite are given in Table III. Column I gives the values of the wave-length drum readings; Column II, the values of the corrections to be applied due to the faulty cutting of the wave-length drum screw, and Column III, the values of the wave-length readings so corrected. Column IV gives the mean values of the "galvanometer deflection A", and Column V, the values of the "galvanometer deflection B", corresponding to the position when the crystal is out of the path of the radiation. The transmission power A/B is given in Column VI. These values are plotted on a graph in Fig. 14. Actually Section I, Table III, shows the values of the transmission ratio for various wave-lengths obtained with one setting of the Wadsworth Mirror on the spectrometer. The Wadsworth Mirror was given a very slight re-adjustment and the corresponding values of the transmission ratio A/B at various wave-lengths are given in Section II, Table III. The values for another setting of the Wadsworth Mirror are given in Section III, Table III. In the actual diagram of the absorption curves determined under these conditions (Fig. 14), it will be seen that the position of maximum absorption given by the spectrometer depends on the setting of the Wadsworth Mirror. Thus with the first setting, Section I, the maximum absorption is given at a wave-length of 3.89 μ; the second setting gives maximum absorption at 3.94 μ; and the third at 3.90 μ. Now the wave-lengths of some of the absorption bands of calcite are definitely known, so by adjusting the Wadsworth Mirror until the values of the wave-lengths for maximum absorption in calcite - as observed by the spectrometer - coincide with these known positions, one is assured that correct values of wave-length are being recorded by the spectrometer, provided the observations are made at the same prism temperature as that at which the Wadsworth Mirror is set; or, when such conditions do not hold, provided that suitable corrections are applied to the wave-length observations to compensate for any differance between these two temperatures. Such compensation to be applied according to scheme outlined earlier in this chapter. (Chap. II, Sect. I, Para. VIb). The effects produced by adjusting the Wadsworth Mirror are quite appreciable, so that it is absolutely essential for this adjustment to be carried out correctly. Moreover, it is very important to note the actual prism temperature at which the Wadsworth Mirror is set, so that all future observations or wave-length drum settings may be corrected for changes in temperature of the prism.

Of the three different settings described in this paragraph the correct one - corresponding to maximum absorption at 3.90 μ - was used for some of the work carried out on absorption bands of gases and liquids. The temperature of the prism when the Wadsworth Mirror received its final adjustment was carefully noted, and all future readings of wave-length obtained with this setting were corrected to the standard temperature of 18°C.

TABLE III.

OBSERVATIONS on the ABSORPTION BANDS of CALCITE in the INFRA-RED, SHOWING THE EFFECT of ADJUSTMENT of the WADSWORTH MIRROR of the SPECTROMETER on the OBSERVED WAVE-LENGTH for MAXIMUM ABSORPTION.

---

1. Experimental Readings for Setting A. Temperature 20.0°C.

Entrance Slit 5/1000"
Exit Slit 5/1000"

W. L. Drum Readg. (λ in μ)	W. L. Drum Error (λ in μ)	Corr. W. L. (λ in μ)	Mean Defl. A. cms.	Mean Defl. B. cms.	A/B % Trans.
3.80	-.001	3.80	3.11	24.25	12.8
3.84	-.002	3.838	2.43	23.58	10.3
3.86	-.002	3.858	2.33	23.42	9.9
3.88	-.003	3.877	2.23	23.13	9.6
3.90	-.003	3.897	2.20	22.82	9.6
3.92	-.004	3.916	2.38	22.53	10.5
3.96	-.005	3.955	3.02	21.86	13.7

II. Readings for Setting B. Temperature 20.3°C.

Entrance Slit 5/1000"
Exit Slit 5/1000"

3.76	-	3.76	6.46	25.76	25.0
3.80	-.001	3.80	5.06	25.10	20.1
3.84	-.002	3.838	3.79	24.40	15.5
3.86	-.002	3.858	3.14	24.17	12.9
3.88	-.003	3.877	2.73	23.88	11.4
3.90	-.003	3.897	2.45	23.44	10.4
3.92	-.004	3.916	2.22	23.20	9.6
3.94	-.004	3.936	2.13	22.85	9.3
3.96	-.005	3.955	2.16	22.60	9.5

(continued)

TABLE III (continued).

III. Readings for Setting C.

Temperature 20.9°C.

Entrance Slit 5/1000"
Exit Slit 5/1000"

W. L. Drum Readg. (λ in μ)	W. L. Drum Error (λ in μ)	Corr. W. L. (λ in μ)	Mean Defl. A. cms.	Mean Defl. B. cms.	A/B % Trans.
3.77	-	3.77	5.53	25.72	21.5
3.81	-.001	3.81	3.97	25.00	15.8
3.85	-.002	3.848	2.77	24.25	11.4
3.87	-.002	3.868	2.42	23.80	10.1
3.89	-.003	3.887	2.24	23.50	9.5
3.91	-.003	3.907	2.10	22.92	9.1
3.93	-.004	3.926	2.12	22.58	9.3
3.95	-.004	3.946	2.25	22.32	10.0
3.99	-.005	3.985	2.78	21.62	12.8
4.03	-.006	4.024	3.51	20.37	17.2
4.06	-.007	4.053	3.98	19.19	20.7

XIV. Some similar observations were made on the position of inflexion in the emission curves of the Nernst Filament, and these are included here as a matter of interest. The observations and energy curves show the effects produced when the Wadsworth Mirror is adjusted. The values of the galvanometer deflections, corresponding to the energy passing through the spectrometer slits from the Nernst Filament to the thermopile for definite settings of the spectrometer wave-length drum, are given in Table IV, Column IV. In figure XV, a graph is given showing the energy emitted by the

Nernst Filament at definite wave-lengths. Curve A shows the emission curve for one setting of the Wadsworth Mirror - the actual values being given in Table IV, Section I. This energy curve has minima at 6.25μ, 6.7μ, 7.72μ, 7.92μ and 11.92μ. The Wadsworth Mirror was readjusted slightly and the emission curve was once more determined. The actual values for the emission are given in Section II Table IV and the corresponding emission curve is given in curve B, fig. 15. This shows minima at 5.92μ, 6.41μ, 7.63μ, and 11.8μ. The minimum at 6.41μ is very slight indeed. A third setting of the Wadsworth Mirror gave an emission curve with minima at 6.03μ, 6.51μ, 7.76μ, and 11.9μ. This curve is drawn as curve C, fig. 15.

In general, therefore, when the Wadsworth Mirror is given a slight adjustment, there appears to be a shift in the position of the minima in the emission curves of the Nernst Filament. Moreover, it should be noticed, that on account of the higher dispersion of rock-salt in the further infra-red, the effect of adjustment of the Wadsworth Mirror (measured in terms of wave-length) on observed positions of the minima in that region is not so great as on the minima occurring in the very near infra-red. Thus, an inspection of the curves in Fig. XV shows that the adjustment required to produce quite a large shift in the position of minima occurring in the region of 5.0μ - 6.0μ, has very little effect on the minima occurring in the region beyond 10.0μ. When the adjustments of the Wadsworth Mirror are being made, therefore, it is far better to work on the minima occurring in the near infra-red, where the dispersion of rock salt is small; for it is in this region that a small adjustment of the Wadsworth Mirror produces quite an appreciable shift in the positions of the minima. This was one of the chief reasons why the absorption bands of calcite at 3.45μ and 3.80μ were chosen for checking the Wadsworth Mirror setting made by means of the emission line at 1.014μ in the mercury arc spectrum; and again, these bands are very sharp and pronounced, so that a correct setting of the Wadsworth Mirror by their aid is easily achieved. In all the work described in the following pages, the Wadsworth Mirror was adjusted first of all by means of the mercury arc lamp, and this setting was given a check (further) against the absorption bands of calcite. It was found that when the Wadsworth Mirror was correctly adjusted for the calcite bands between 3μ - 4μ, other well-known bands fell into line.

The method of adjustment was therefore as follows :-

The Wadsworth Mirror adjustment device was set in one position and the position of the emission line in the mercury arc spectrum determined. When this position did not coincide with 1.014μ, the Wadsworth adjustment was reset and the emission curve again plotted. This procedure was repeated until the spectrometer gave the correct value. The same method was then applied to the absorption bands of calcite and the Wadsworth was given suitable adjustments until the spectrometer gave the correct values for the positions of maximum absorption. The setting and the prism temperature were both noted, also the filament current and voltage in operation during the experiments.

TABLE IV.

Effect of adjustment of Wadsworth Mirror on the Observed Positions of Inflexion in the Energy Spectrum (Emission) of a Nernst Filament.

CASE A. 1st Position of Wadsworth. *Denotes change of sensitivity of galvanometer.

Entrance Slit 10/1000")
Exit Slit 10/1000") Prism Temp. = 21.2°C. (throughout)

Current for filament = 0.6 amps @ 87 volts.

W. L. Drum Readg. (λ in μ)	W. L. Drum Error. (λ in μ)	Corr. W. L. (λ in μ)	Mean Readings cms.	W. L. Drum Readg. (λ in μ)	W. L. Drum Error. (λ in μ)	Corr. W. L. (λ in μ)	Mean Readings cms.
5.285	+.004	5.289	31.35	6.2	+.021	6.221	6.95
5.372	+.007	5.379	29.8	6.30	+.018	6.318	7.6
5.48	+.010	5.49	26.27	6.41	+.014	6.424	7.75
5.60	+.013	5.613	22.9	6.50	+.011	6.511	7.95
5.72	+.017	5.737	18.4	6.60	+.007	6.607	7.9
5.85	+.020	5.87	13.70	6.7	+.004	6.704	7.62
5.97	+.022	5.992	9.7	6.75	+.002	6.752	7.85
6.10	+.022	6.122	7.0	6.86	-.0003	6.86	7.9
6.96*	-.002	6.958	16.8	7.69	+.009	7.699	10.5
7.04	-.003	7.037	16.65	7.71	+.010	7.72	9.5
7.10	-.003	7.097	16.0	7.72	+.010	7.73	9.6
7.20	-.001	7.199	15.45	7.75	+.0100	7.76	9.42
7.30	+.001	7.301	14.4	7.80	+.0113	7.811	8.75
7.4	+.003	7.403	13.65	7.85	+.0114	7.861	7.1
7.5	+.005	7.505	13.27	7.9	+.0115	7.912	6.9
7.6	+.008	7.608	11.9	7.95	+.0109	7.961	7.25
7.64	+.008	7.648	11.35	8.0	+.0104	8.010	8.35
7.68	+.008	7.688	10.5	8.05	+.0096	8.060	9.65

(Continued)

TABLE IV (continued).

CASE A.

W. L. Drum Readg. (λ in μ)	W. L. Drum Error. (λ in μ)	Corr. W. L. (λ in μ)	Mean Read-ings cms.	W. L. Drum Readg. (λ in μ)	W. L. Drum Error. (λ in μ)	Corr. W.L. (λ in μ)	Mean Read-ings cms.
8.10	+.0088	8.109	10.85	8.40	+.0060	8.406	12.45
8.205	+.0070	8.212	11.85	8.50	+.0057	8.506	11.95
8.30	+.0065	8.307	12.25				
		----------	----------	----------			
9.9*	+.0081	9.908	10.05	11.4	+.0089	11.409	9.30
10.0	+.0076	10.008	10.15	11.50	+.0091	11.509	7.77
10.1	+.0077	10.108	11.0	11.60	+.0084	11.608	6.42
10.2	+.0083	10.208	12.70	11.7	+.0075	11.708	5.85
10.30	+.0091	10.309	14.80	11.8	+.0064	11.806	5.25
10.40	+.0100	10.410	16.95	11.9	+.0057	11.906	5.00
10.5	+.0106	10.510	17.85	11.95	+.0053	11.955	5.00
10.6	+.0109	10.611	17.95	12.0	+.0053	12.005	5.10
10.7	+.0105	10.711	17.6	12.1	+.0054	12.105	5.65
10.8	+.0100	10.810	17.05	12.2	+.0057	12.206	6.55
10.9	+.0088	10.909	16.07	12.3	+.0061	12.306	7.55
11.0	+.0077	11.008	15.05	12.4	+.0066	12.407	8.95
11.1	+.007	11.107	13.8	12.5	+.0072	12.507	9.35
11.2	+.007	11.207	12.7	12.602	+.0074	12.609	9.95
11.3	+.008	11.308	11.1				

TABLE IV (continued).

CASE B. 2nd Position of Wadsworth Mirror.

Slits: Entrance 10/1000"
Exit 10/1000"

Prism Temperature 20.8°C. (throughout)

Filament current 0.6 Amps. @ 89 Volts.

W. L. Drum Readg. (λ in μ)	W. L. Drum Error (λ in μ)	Corr. W. L. (λ in μ)	Mean Readgs. cms.	W. L. Drum Readg. (λ in μ)	W. L. Drum Error. (λ in μ)	Corr. W.L. (λ in μ)	Mean Readgs. cms.
5.2	+.001	5.201	21.35	5.9	+.021	5.921	6.0
5.3	+.004	5.304	18.3	6.0	+.022	6.022	6.45
5.4	+.008	5.408	15.3	6.1	+.022	6.122	7.0
5.5	+.011	5.511	12.4	6.2	+.021	6.221	7.3
5.6	+.013	5.613	8.5	6.3	+.018	6.318	6.8
5.7	+.016	5.716	7.05	6.4	+.014	6.414	6.6
5.8	+.018	5.818	6.25	6.5	+.011	6.511	6.8
7.0*	-.003	6.997	15.0	7.65	+.0081	7.658	7.0
7.1	-.003	7.097	14.1	7.75	+.0105	7.751	8.0
7.2	-.001	7.199	13.51	7.85	+.0114	7.861	9.6
7.3	+.001	7.299	12.70	8.0	+.0104	8.010	12.0
7.4	+.0032	7.403	11.25	8.1	+.0088	8.109	12.5
7.5	+.0053	7.505	9.7	8.2	+.0073	8.207	12.3
7.6	+.0075	7.608	7.0	8.3	+.0065	8.307	11.8
10.75*	+.0102	10.760	15.5	11.3	+.008	11.308	8.68
10.8	+.0100	10.810	15.0	11.4	+.0089	11.409	7.25
10.9	+.0088	10.909	14.2	11.5	+.0091	11.509	5.75
11.0	+.0077	11.008	13.1	11.6	+.0084	11.608	4.81
11.1	+.007	11.107	11.8	11.7	+.0075	11.708	4.31
11.2	+.007	11.207	10.51	11.8	+.0064	11.806	4.0

(continued)

TABLE IV (continued)

CASE C. 3rd Position of Wadsworth Mirror.

Entrance Slit 10/1000")
Exit Slit 10/1000")

Prism Temperature 21.1°C.

Filament Current 0.6 Amps. at 88.0 Volts.

W. L. Drum Readg. (λ in μ)	W. L. Drum Error. (λ in μ)	Corr. W. L. (λ in μ)	Mean Readgs. cms.	W. L. Drum Readg. (λ in μ)	W. L. Drum Error (λ in μ)	Corr. W. L. (λ in μ)	Mean Readgs.
5.3	.004	5.304	25.6	6.10	.022	6.122	9.01
5.4	.008	5.408	22.61	6.2	.021	6.221	9.7
5.5	.011	5.511	19.0	6.3	.018	6.318	9.4
5.6	.013	5.613	16.41	6.4	.014	6.414	9.29
5.75	.016	5.766	11.31	6.5	.011	6.511	9.25
5.90	.021	5.921	9.2	6.6	.007	6.607	9.50
6.00	.022	6.022	8.5	6.7	.004	6.704	10.20
7.6 *	.0075	7.608	12.61	8.0	.0104	8.010	16.65
7.7	.0097	7.710	10.8	8.1	.0088	8.109	17.0
7.75	.0105	7.761	10.25	8.2	.0073	8.207	16.61
7.80	.0113	7.811	11.01	8.3	.0065	8.307	15.50
7.90	.0115	7.912	13.5				
10.6 *	.0109	10.611	18.70	11.5	.0091	11.509	8.2
10.7	.0105	10.710	18.20	11.6	.0084	11.608	7.0
10.8	.010	10.810	17.8	11.7	.0075	11.708	6.51
10.9	.0088	10.909	16.4	11.8	.0064	11.806	6.11
11.0	.0077	11.008	15.41	11.9	.0057	11.906	6.01
11.1	.007	11.107	14.1	12.0	.0053	12.005	6.25
11.2	.007	11.207	13.0	12.1	.0054	12.105	7.1
11.3	.008	11.308	11.30	12.2	.0057	12.206	8.1
11.4	.0089	11.409	9.6	12.25	.0059	12.256	8.70

XV. The effects of temperature on the calibration of the spectrometer were now considered. After the Wadsworth Mirror had been correctly adjusted, some experiments were tried with Nitric Oxide gas in one of the gas absorption tubes, and it soon became evident that the position of maximum absorption, as given by the spectrometer, depended upon the prism temperature. We have seen how this relationship can be theoretically explained (Chap. II, Section I, Para. III). It remained for us to demonstrate that this theoretical treatment was true. Observations were made on the absorption bands of calcite with the prism at different temperatures. In the case cited in this paragraph the following prism temperatures were used: 18.95°C, 19.8°C, and 20.1°C, and the absorption bands of calcite between 3.0μ and $4.0\ \mu$ were under investigation for the test. The actual values for the transmission ratio are given in Table V, Column VII; and the wave-length drum readings in Column I; the wave-length drum error in Column II; and the wave-length drum readings corrected to a standard temperature in Column IV. Column V gives the galvanometer deflection corresponding to the energy transmitted by the crystal, and Column VI, the deflection corresponding to the amount of energy passing to the thermopile without loss by absorption. In Fig. XVI, a graph has been drawn for the three cases, showing the relationship between values of the transmission ratio and the actual corrected values of the wave-length drum settings. The three resultant absorption curves differ considerably, but when corrections are applied for differences in prism temperature (so as to correct the wave-length drum readings to one standard temperature, 18°C) the three curves coincide. This definitely proves the efficiency of the correction factors which were deduced by the theoretical methods outlined in Chap. II, Section I, Para. VI. Further tests were made to illustrate the effects produced by variations in prism temperature.

TABLE V.

Effect of variations in temperature of the Prism on the observed wave-lengths of maximum absorption for Calcite, due to a change of the refractive index of prism material.

CASE 1. Prism Temperature 18.95°C. Wadsworth set at 20.90°C. Entrance Slit 5/1000" Exit Slit 5/1000"

W. L. Drum Readg. (λ in μ)	W. L. Drum Error. (λ in μ)	Temp. Corr. (λ in μ)	Corr. W. L. (λ in μ)	Mean Defl. A. cms.	Mean Defl. B. cms.	A/B %
3.80	-.0008	.0244	3.823	3.95	30.21	13.0
3.84	-.0015	.0241	3.862	3.11	29.46	10.5
3.88	-.0028	.0238	3.901	2.65	28.72	9.2
3.90	-.0034	.0236	3.921	2.64	28.40	9.2
3.92	-.0039	.0235	3.940	2.75	27.91	9.8
3.96	-.0049	.0234	3.978	3.41	26.85	12.7
4.00	-.0059	.0232	4.017	4.33	25.5	16.9

CASE II.

Temperature of Prism 19.8°C. Wadsworth Mirror set at 20.9°C. Entrance Slit 5/1000" Exit Slit 5/1000"

3.86	-.0018	.0135	3.868	2.82	28.28	9.9
3.88	-.0028	.0134	3.890	2.65	27.87	9.5
3.90	-.0034	.0133	3.910	2.35	27.53	8.5
3.92	-.0039	.0133	3.929	2.57	27.20	9.2
3.94	-.0044	.0133	3.949	2.75	26.84	10.2
4.00	-.0059	.0131	4.007	3.88	24.9	15.5
3.80	-.0008	.0137	3.813	4.14	29.44	13.9
3.84	-.0015	.0136	3.852	3.10	28.65	10.8

TABLE V (continued).

CASE III. Temperature of Prism 20.1°C.
Wadsworth Mirror set at 20.9°C.

Entrance Slit 5/1000"
Exit Slit 5/1000"

W. L. Drum Readg. (λ in μ)	W. L. Drum Error. (λ in μ)	Temp. Corr. (λ in μ)	Corr. W. L. (λ in μ)	Mean Defl. A. cms.	Mean Defl. B. cms.	A/B %
3.30	.0113	.0109	3.322	7.42	33.39	22.2
3.32	.0108	.0109	3.342	6.81	32.83	20.7
3.34	.0103	.0109	3.361	6.17	32.28	19.1
3.36	.0098	.0109	3.381	5.80	31.92	18.1
3.38	.0093	.0109	3.400	5.55	31.36	17.6
3.40	.0089	.0108	3.420	5.51	31.21	17.6
3.42	.0084	.0108	3.349	5.77	30.80	18.7
3.44	.0079	.0107	3.349	6.20	30.70	20.1
3.46	.0074	.0106	3.477	6.92	30.50	22.6
3.50	.0064	.0105	3.516	8.16	29.98	27.2
3.56	.0060	.0105	3.576	10.07	29.47	34.1
3.60	.0041	.0104	3.614	10.56	28.75	36.7
3.66	.0026	.0103	3.673	9.66	27.72	34.8
3.70	.0017	.0102	3.712	8.20	26.85	30.5
3.76	.0005	.0101	3.770	5.53	25.72	21.5
3.80	-.0008	.0100	3.809	3.97	25.00	15.8
3.84	-.0015	.0099	3.848	2.77	24.25	11.4
3.86	-.0028	.0098	3.867	2.42	23.80	10.1
3.88	-.0028	.0098	3.887	2.24	23.50	9.5
3.90	-.0034	.0097	3.907	2.10	22.92	9.1
3.92	-.0039	.0097	3.926	2.12	22.58	9.3

XVI. In tables VI are some results showing the effects observed on the absorption band of calcite at 4.60μ when the prism temperature of the rock-salt prism was varied. Fig. 17 gives the corresponding absorption curves. Corrections (corresponding to the difference between the prism temperature and the standard temperature of 18°C) were applied to the wave-length drum readings, and the corrected absorption curves were re-plotted to show the relationship between the transmission ratio and the true value of the wave-length settings. The corrected values all fall on the same absorption curve, once more demonstrating the accuracy of the recalibration and correcting factors of the spectrometer. Actually the prism was kept at two different temperatures during the experiments: Case I, Prism Temperature 20.2°C., and Case II, Prism Temperature 20.3°C.

TABLE VI.

Two sets of Observations on the Absorption Band of Calcite Crystal at 4.6μ, showing discrepancies, and the corrections to be applied for differences in temperature of the Prism.

CASE I. Wadsworth Mirror set at 20.9°C. Entrance Slit 5/1000"
Prism Temperature 20.2°C. Exit Slit 5/1000"

W. L. Drum Readg. (λ in μ)	W. L. Drum Error. (λ in μ)	Temp. Corr. (λ in μ)	Corr. W. L. (λ in μ)	Mean Defl. A. cms.	Mean Defl. B. cms.	A/B %
4.46	-.0161	.007	4.451	7.75	15.97	48.5
4.50	-.0163	.007	4.491	7.13	16.13	44.2
4.54	-.0163	.007	4.531	6.53	16.03	40.7
4.56	-.0163	.007	4.551	6.24	16.10	38.7
4.58	-.0163	.007	4.571	6.07	16.10	37.7
4.60	-.0163	.007	4.591	5.95	16.01	37.1
4.64	-.0161	.007	4.631	6.26	15.93	39.2
4.60	-.0163	.007	4.591	5.92	15.97	37.0

TABLE VI (continued).

CASE II. Wadsworth Mirror set at 20.9°C.
Prism Temperature 20.3°C.

Entrance Slit 5/1000"
Exit Slit 5/1000"

W. L. Drum Readg. (λ in μ)	W. L. Drum Error. (λ in μ)	Temp. Corr. (λ in μ)	Corr. W. L. (λ in μ)	Mean Defl. A. cms.	Mean Defl. B. cms.	A/B %
4.48	-.0162	.006	4.470	7.36	16.07	45.7
4.52	-.0163	.006	4.510	6.7	16.15	41.4
4.54	-.0163	.006	4.530	6.41	16.10	39.8
4.56	-.0163	.006	4.550	6.15	16.04	38.3
4.58	-.0163	.006	4.570	6.00	16.03	37.4
4.60	-.0163	.006	4.590	5.93	16.03	36.99
4.62	--.0162	.006	4.610	6.04	16.0	37.7
4.64	-.0161	.006	4.630	6.23	15.93	39.1
4.68	-.0158	.006	4.670	7.05	15.81	44.5
4.70	-.0155	.006	4.690	7.42	15.72	47.2

XVII. More experimental results on the absorption by calcite in the region $3.0\mu - 4.0\mu$, taken with the prism at different temperatures, are given in Table VII. The prism temperatures were :- 20.4°C., 20.9°C., 18.0°C., 17.5°C., with the Wadsworth Mirror set at 19.5°C. The corresponding absorption curves are drawn in Fig. 18. The uncorrected curves are all different, but when the corrections are applied for prism temperature differences, all the absorption curves fall on one common curve. These curves fully illustrate the effects of application of the temperature corrections to observed results of the wave-length drum settings. Thus, for a prism temperature of 20.4°C, the wave-length for maximum absorption actually given by the uncorrected spectrometer readings was 3.94μ; for a prism temperature of 20.9°C the wave-length was 3.92μ; for a prism temperature of 18.0°C, the value was 3.88μ; and for a temperature of 17.5°C, the value was 3.86μ. These discrepancies all disappeared when the corrections for temperature were applied, and the true wave-length for maximum absorption was found to be 3.90μ. For Case IV, D, there is an apparent discrepancy between the values of the transmission ratio A/B and the values of the same ratio in cases I, II and III. This difference was due to the crystal section becoming slightly displaced from its true position. In its new position (Case IV) it was not accurately at right angles to the path of the radiation. This had the effect of altering the effective thickness of the crystal section. It should be noticed that the corrected wave-length for maximum absorption was the same for Case IV as for Cases I, II and III.

TABLE VII.

Further observations to show the effect of change of Temperature of the Prism on the Apparent Wave-length for maximum Absorption in Calcite.

I. **CASE A.** Wadsworth Mirror set at 19.5°C.
Prism Temperature 20.4°C.

Entrance Slit 10/1000".
Exit Slit 10/1000".

W. L. Drum Readg. (λ in μ)	W. L. Drum Error. (λ in μ)	Temp. Corr. (λ in μ)	Corr. W. L. (λ in μ)	Mean Defl. A. cms.	Mean Defl. B. cms.	A/B %
3.70	.0017	.0114	3.691	6.46	26.02	24.8
3.75	.0005	.0114	3.739	5.52	25.15	21.9
3.80	-.0008	.0112	3.788	4.57	24.17	18.9
3.85	-.0015	.0110	3.837	3.82	23.28	16.4
3.90	-.0034	.0109	3.886	3.33	22.16	15.0
3.95	-.0046	.0108	3.934	3.16	21.01	15.0
4.00	-.0059	.0107	3.983	3.38	19.37	17.4
4.05	-.0070	.0106	4.032	3.76	17.82	21.0
4.10	-.0084	.0105	4.081	4.30	16.22	26.5

Wadsworth Mirror set at 19.5°C.
Prism Temperature 20.9°C.

II. **CASE B.**

Entrance Slit 10/1000".
Exit Slit 10/1000".

3.25	.0126	.0193	3.243	11.66	33.96	34.3
3.30	.0113	.0192	3.292	10.0	32.95	30.3
3.35	.0100	.0190	3.341	8.64	31.74	27.2
3.40	.0089	.0189	3.390	7.84	30.55	25.6
3.45	.0080	.0187	3.439	7.50	29.65	25.2
3.50	.0064	.0185	3.487	7.55	28.77	26.2
3.55	.0052	.0184	3.536	7.74	28.10	27.5
3.60	.0041	.0182	3.585	7.67	27.35	28.0
3.65	.0028	.0180	3.635	7.34	26.67	27.5

TABLE VII (continued)

II. Case B (ctd.)

W. L. Drum Readg. (λ in μ)	W. L. Drum Error. (λ in μ)	Temp. Corr. (λ in μ)	Corr. W. L. (λ in μ)	Mean Defl. A. cms.	Mean Defl. B. cms.	A/B %
3.70	.0017	.0178	3.684	6.54	25.75	25.3
3.75	.0005	.0177	3.732	5.60	25.04	22.3
3.80	.0008	.0175	3.781	4.57	24.25	18.8
3.85	.0020	.0172	3.830	3.83	23.27	16.4
3.90	.0034	.0169	3.880	3.22	22.28	14.4
3.95	.0045	.0168	3.929	3.04	21.02	14.4
4.00	.0059	.0166	3.976	3.20	19.68	16.2
4.05	.0070	.0165	4.026	3.55	17.71	20.0

III. CASE C.

Wadsworth Mirror set at 19.5°C.
Prism Temperature 18.0°C.

Entrance Slit 10/1000".
Exit Slit 10/1000".

3.75	.0005	.0188	3.768	4.68	23.82	19.6
3.80	-.0008	.0187	3.817	3.98	23.05	17.2
3.85	-.0020	.0184	3.866	3.28	22.14	14.8
3.90	-.0034	.0181	3.915	3.07	20.38	15.0
3.95	-.0045	.0180	3.964	3.17	19.08	16.6
4.00	-.0059	.0178	4.012	3.50	17.54	19.9

TABLE VII (continued)

Wadsworth set at 19.5°C
Prism Temperature 17.5°C.

IV. CASE D.

Entrance Slit 10/1000"
Exit Slit 10/1000"

W. L. Drum Readg. (λ in μ)	W. L. Drum Error. (λ in μ)	Temp. Corr. (λ in μ)	Corr. W. L. (λ in μ)	Mean Defl. A. cms.	Mean Defl. B. cms.	A/B %
3.25	.0126	.0274	3.290	9.34	30.49	30.6
3.30	.0113	.0274	3.338	8.4	29.52	28.4
3.35	.0100	.0272	3.387	7.53	27.59	27.2
3.40	.0089	.0270	3.436	7.39	27.03	27.3
3.45	.0080	.0267	3.485	7.36	26.39	27.8
3.50	.0064	.0264	3.532	7.35	25.47	28.8
3.55	.0052	.0262	3.581	7.19	24.86	28.9
3.60	.0041	.0260	3.630	6.67	24.26	27.4
3.65	.0028	.0257	3.679	5.92	23.22	25.4
3.70	.0017	.0254	3.727	5.10	22.59	22.5
3.75	.0005	.0252	3.775	4.28	21.94	19.5
3.80	-.0008	.0250	3.824	3.56	21.11	16.8
3.85	-.0020	.0246	3.873	3.17	20.40	15.5
3.90	-.0034	.0242	3.921	3.06	19.32	15.8
3.95	-.0045	.0240	3.970	3.26	18.18	17.9
4.00	-.0059	.0238	4.018	3.62	16.80	21.5
4.05	-.007	.0236	4.067	4.08	15.44	26.4
4.10	-.0084	.0234	4.115	4.66	14.38	32.4
4.15	-.0095	.0232	4.164	5.25	13.55	38.7

XVII. In Table VIII, some values are given for the transmission ratio obtained for a gas observation tube, filled with nitric oxide gas, compared with an evacuated gas observation tube. The prism temperature was kept constant throughout the experiments. It will be seen that the wavelength for maximum absorption was the same for both experimental determinations. This reveals that the readings given by the spectrometer depend on the prism temperature, and once more the need for taking accurate measurements of the prism temperature must be stressed. The corresponding absorption curves are drawn in figure 19. They show that maximum absorption occurs at 5.28 μ.

TABLE VIII.

Observations on the Absorption Band of Nitric Oxide at 5.28 μ showing readings are consistent when temperature of Prism is kept constant.

Monochromatic Method.

CASE I: Wadsworth Mirror set @ 20.8°C. Entrance Slit 10/1000"
Prism Temperature 20.7°C. Exit Slit 10/1000"

W. L. Drum Readg. (λ in μ)	W. L. Drum Error. (λ in μ)	Temp. Corr. (λ in μ)	Corr. W. L. (λ in μ)	Mean Defl. A. cms.	Mean Defl. B. cms.	A/B %
5.002	-.005	-	4.997	6.2	16.42	37.8
5.02	-.0047	-	5.015	5.8	16.2	35.8
5.04	-.0039	-	5.036	5.2	16.1	32.2
5.06	-.0030	-	5.057	4.67	16.02	29.1
5.08	-.0022	-	5.078	4.07	15.75	25.84
5.10	-.0012	-	5.099	3.55	15.62	22.70
5.12	-.0007	-	5.119	2.98	15.53	19.20
5.142	-.0002	-	5.142	2.50	15.30	16.33
5.16	.0003	-	5.16	2.10	15.12	13.88

(continued)

TABLE VIII (continued)

CASE I (ctd.)

W. L. Drum Readg. (λ in μ)	W. L. Drum Error. (λ in μ)	Temp. Corr. (λ in μ)	Corr. W. L. (λ in μ)	Mean Defl. A. cms.	Mean Defl. B. cms.	A/B %
5.18	.0008	-	5.181	1.70	14.9	11.40
5.20	.0012	-	5.201	1.42	14.77	9.61
5.22	.0018	-	5.222	1.12	14.55	7.69
5.24	.0024	-	5.242	.95	14.35	6.62
5.262	.0030	-	5.265	.90	14.05	6.40
5.28	.0036	-	5.284	.79	13.95	5.66
5.30	.0044	-	5.304	.81	13.72	5.90
5.321	.0050	-	5.326	.79	13.46	5.86
5.34	.0057	-	5.346	.92	13.25	6.94

CASE II. The above observations were repeated under identical conditions.

5.0	-.0055	-	4.995	6.30	16.47	38.2
5.02	-.0047	-	5.015	5.75	16.32	35.2
5.04	-.0039	-	5.036	5.30	16.20	32.7
5.06	-.0030	-	5.057	4.72	16.03	29.4
5.08	-.0022	-	5.078	4.12	15.86	25.97
5.104	-.0012	-	5.103	3.42	15.65	21.8
5.120	-.0007	-	5.119	3.11	15.57	19.9
5.141	-.0002	-	5.141	2.54	15.47	16.41
5.16	.0003	-	5.160	2.06	15.26	13.49
5.181	.0008	-	5.182	1.72	15.11	11.30
5.20	.0012	-	5.201	1.40	14.88	9.40
5.22	.0018	-	5.222	1.20	14.66	8.18
5.24	.0024	-	5.242	.97	14.45	6.71

(continued)

TABLE VIII (continued)

Case II (ctd.)

W. L. Drum Readg. (λ in μ)	W. L. Drum Error (λ in μ)	Temp. Corr. (λ in μ)	Corr. W. L. (λ in μ)	Mean Defl. A. cms.	Mean Defl. B. cms.	A/B %
5.26	.0030	-	5.263	.92	14.32	6.42
5.28	.0036	-	5.284	.85	14.12	6.01
5.30	.0044	-	5.304	.80	13.82	5.80
5.32	.0050	-	5.325	.88	13.62	6.46
5.34	.0057	-	5.346	.91	13.43	6.77
5.36	.0064	-	5.366	1.03	13.21	7.79
5.40	.0080	-	5.408	1.32	12.71	10.40

XIX. Finally, in Table IX are some further observations on the absorption by calcite in the region $3.0\mu - 4.0\mu$, measured with the prism at different temperatures. Four cases are given, the temperatures being: 21.3°C; 20.3°C; 20.1°C; and 19.2°C, the Wadsworth Mirror being set at 22.9°C. When the four uncorrected curves were plotted (Fig. 20) serious discrepancies were noticed. The corrections for differences in prism temperature were applied to readings of the wave-length drum, and the corrected values were plotted against the corresponding values of the transmission ratio, A/B. It will be seen that the corrected values all fall on the same smooth curve. These corrected curves are plotted in the same diagram as the uncorrected ones (Fig. 20), and the effectiveness of the temperature corrections is clearly demonstrated.

The conditions for this set of experiments are slightly different from those quoted in Chap. II, Sect. I, Para XV and Para XVII. In the latter cases, the prism temperatures were all different, but the Wadsworth Mirror was set at 20.9°C and 19.5°C respectively, instead of 22.9°C as in the case given above. The same correction principle applies, however, and when the corrections for differences in prism temperature are applied they are quite effective. The temperature corrections are therefore independent of the temperature at which the Wadsworth Mirror is set. Again, in Para. XV and Para XVII, the apparatus was set up as in Fig. II, whereas in the case of the results described in this paragraph, the apparatus was used as in Fig. I, i.e., as a monochromator. The temperature corrections are therefore a function of the spectrometer only, for they are independent of the position occupied by the spectrometer in the general arrangement of the apparatus.

TABLE IX.

An independent set of observations to show the effect of temperature on the observed wave-length for maximum absorption. The spectrometer was used in this case as a monochromator.

CASE I: Prism Temperature 21.3°C. Entrance Slit 5/1000".
Wadsworth Mirror set @ 22.9°C. Exit Slit 5/1000".

W. L. Drum Readg. (λ in μ)	W. L. Drum Error. (λ in μ)	Temp. Corr. (λ in μ)	Corr. W. L. (λ in μ)	Mean Defl. A. cms.	Mean Defl. B. cms.	A/B %
3.80	-.0008	.0212	3.820	3.4	21.27	15.9
3.84	-.0015	.0210	3.859	2.35	20.62	11.3
3.88	-.0028	.0208	3.898	1.95	20.2	9.6
3.92	-.0039	.0204	3.937	1.97	19.70	10.0
3.96	-.0049	.0202	3.975	2.30	19.15	12.0
3.98	-.0054	.0200	3.995	2.52	18.7	13.4
4.02	-.0064	.0200	4.034	3.22	17.67	18.2
4.06	-.0074	.0197	4.073	3.72	16.07	23.1

TABLE IX (continued)

CASE II (ctd.)

W. L. Drum Readg. (λ in μ)	W. L. Drum Error. (λ in μ)	Temp. Corr. (λ in μ)	Corr. W. L. (λ in μ)	Mean Defl. A. cms.	Mean Defl. B. cms.	A/B %
3.90	-.0034	.0314	3.928	1.88	18.94	9.9
3.92	-.0039	.0312	3.947	1.98	18.58	10.6
3.94	-.0044	.0310	3.967	2.22	18.32	12.1
3.96	-.0049	.0308	3.986	2.43	17.93	13.5
4.00	-.0059	.0306	4.025	3.07	16.90	18.1

CASE III:

Prism Temperature 20.1°C.
Wadsworth Mirror set at 22.9°C.

Entrance Slit 5/1000";
Exit Slit 5/1000".

3.30	.0113	.0383	3.349	6.80	31.62	21.5
3.34	.0103	.0380	3.388	5.87	30.52	19.2
3.38	.0093	.0380	3.427	5.59	29.72	18.8
3.42	.0084	.0378	3.464	6.28	29.30	21.4
3.46	.0074	.0374	3.507	7.47	28.85	25.8
3.50	.0064	.0369	3.543	8.67	28.43	30.5
3.54	.0056	.0367	3.583	9.70	27.99	34.6

(Continued)

TABLE IX (continued)

CASE III (ctd.)

W. L. Drum Readg. (λ in μ)	W. L. Drum Error. (λ in μ)	Temp. Corr. (λ in μ)	Corr. W. L. (λ in μ)	Mean Defl. A. cms.	Mean Defl. B. cms.	A/B %
3.65	.0029	.0359	3.689	8.76	26.1	33.5
3.70	.0017	.0355	3.738	6.92	25.15	27.5
3.75	.0005	.0352	3.785	5.03	24.42	20.5
3.80	-.0008	.0350	3.834	3.22	23.6	13.6
3.82	-.0011	.0347	3.854	2.76	23.25	11.8
3.84	-.0015	.0345	3.873	2.45	22.96	10.6
3.86	-.0020	.0343	3.892	2.25	22.62	9.9
3.88	-.0028	.0341	3.911	2.04	22.39	9.1
3.90	-.0034	.0339	3.931	2.12	22.16	9.5
3.92	-.0039	.0337	3.950	2.35	21.87	10.7
3.96	-.0049	.0333	3.988	2.87	21.08	13.6
4.00	-.0059	.0330	4.027	3.61	20.12	17.9
4.04	-.0069	.0305	4.063	4.21	19.51	21.5

CASE IV. Prism Temperature 19.2°C.
Wadsworth Mirror set at 22.9°C.

Entrance Slit 5/1000"; Exit Slit 5/1000".

3.80	-.0008	.0462	3.845	2.9	24.38	11.8
3.82	-.0011	.0460	3.865	2.60	24.06	10.8
3.84	-.0015	.0458	3.884	2.40	23.90	10.0
3.86	-.002	.0455	3.904	2.25	23.56	9.5
3.88	-.0028	.0453	3.922	2.25	23.35	9.6
3.90	-.0034	.0448	3.942	2.37	23.00	10.3
3.92	-.0039	.0446	3.961	2.60	22.68	11.4
3.94	-.0044	.0443	3.980	2.88	22.20	12.9

(Continued)

XX. It appears, therefore, that a knowledge of the temperature of the rock-salt prism is entremely important for all experimental work in this region of the infra-red. Actually, the prism temperature was recorded at fairly frequent intervals throughout the course of all the experiments, and the corrections for differences in prism temperature were applied to all measurements taken on the wave-length drum, according to the methods outlined at the beginning of this chapter. Whenever it has been possible for the veracity of these corrections to be tested experimentally, the theoretical work has been completely substantiated. Some very serious discrepancies found in the earlier part of the work were readily explained by means of the temperature correction factors.

For accurate work, it is also extremely important that corrections be applied to compensate for errors in cutting the thread of the screw which propels the prism table and wave-length drum. This correction has been applied to all measurements of wave-length given in this paper.

XXI. And finally, the two experimental arrangements have been compared by means of an investigation of the absorption bands in a crystal of calcite. The two methods gave identical results. The amount of energy falling on the thermopile was greatest in the case of the second experimental arrangement; but a reasonable explanation of this has already been given in Chap. I, Sect. II, Para. III.

CHAPTER III

AN EXPERIMENTAL STUDY OF ABSORPTION DUE TO GASES.

SECTION 1

THE OBSERVATION TUBES.

1) A very lucid description of an apparatus used for the accurate determination of infra red absorption bands for gases has been given for Sir R. Robertson in the paper already cited. He describes the experimental method very carefully, and all the necessary precautions outlined by him were observed in the present work, which is described in this chapter. Some unforeseen difficulties arose, however, and these will first of all be discussed.

2) It was decided to use two observation tubes for the experiments: one to be filled with the gas at a known pressure; the second to be identical with the first, but completely evacuated, so that the true absorption effect due to the gas could be determined. If only one tube had been used a direct comparison would have been impossible. There would have been a time lag between the estimation of the transmission power of the same tube when completely evacuated, corresponding to the time taken to evacuate the tube and to fill it with gas to a desired pressure. During this interval, a change in the prism temperature and also in the concentration of any absorbing gases in the atmosphere might occur. Corrections for these changes would be somewhat difficult to calculate. It was chiefly because of

of this that two tubes were used in the experiments.

The first step was to prepare two identical tubes fitted with rock-salt end-plates. These have already been described in Chap.1, Sec.2, 8. They were placed on the rotating carriage (Chap.1, Sect. 2 Para.9), and, after they had been completely evacuated, measurements of their transmission powers were made. The transmission powers of the two tubes were found to be unequal.

3) The apparatus was set up according to the arrangement shown in Fig.1, and the gas observation tubes were evacuated. The manometer attached to the tubes showed a gradual rise in pressure inside the tubes, corresponding to some small leakages. These leaks were stopped by smearing a little shellac varnish over the joints between the rock-salt end-plates and the ends of the tubes. In all cases this treatment overcame the trouble. To make quite certain, the tubes were left overnight and if any further leaks developed, more varnish was painted over the joints.

The Nernst filament was started up, and, after it had run for some considerable time and the temperature conditions had become reasonably steady, attempts were made to adjust the tubes so that they transmitted equal amounts of radiation for all settings of the wave-length drum. It was found impossible to obtain complete compensation between the two tubes. The value of the transmission for any wave-length was determined in the following manner. The wave-length drum was set at some predetermined position and the setting noted, together with the value of the prism temperature. The gas observation tube was placed in the path of the radiation and the galvanometer zero position noted; the shutter on the spectrometer case was raised, to allow the radiation to pass through the spectrometer and tube to the thermopile, and the corresponding galvanometer deflection was observed; finally, the shutter was closed, the new position of the galvanometer spot noted, and from the results, the mean galvanometer deflection was estimated. This deflection corresponds to the energy transmitted by the tube. For the sake of convenience in the tables given in the remainder of this chapter, the energy transmitted by the tube which contains (or is to contain) the gas under observation is called, "Galvanometer deflection A". Likewise the energy transmitted by the evacuated tube is termed "Galvanometer deflection B". The ratio of these two is called "%TRANSMISSION A/B". If a gas is contained in the tube A, the value of this ratio gives the transmission of the gas for the particular pressure and wave-length under consideration. When both tubes are evacuated and there is complete compensation between the tubes, the ratio A/B should be exactly unity. Table X gives the values of the ration A/B at different wave-lengths. It will be seen that these values of the ratio are neither uniform nor equal to unity. The values of the ratio are plotted against wave-length on a graph which is shown in Fig.XXII. Curve 1 in this figure shows the variation of the ratio with wave-length; it reveals that the ratio is not constant and that the difference in transmission powers is greatest in the region where strong absorption occurs in the emission spectrum of the Nernst filament. (=10% at 2.96 μ). The experimental results obtained after one tube had been slightly tilted with respect to the other are also given. The variation of the ratio with wave length under these conditions is shown in Fig.XXII, Curve 2. The region covered is from 2.5 μ - 4.0 μ , a region where a pronounced minimum occurs in the emission spectrum of the Nernst filament. The ratio A/B is still not equal to unity and it is not uniform. These curves show that tilting one tube does not entirely remove the trouble.

In Table X, column 1, are the values of the wave-length observations corrected for temperature; column 2 gives the corresponding values of the transmission ratio A/B, and column 3 gives a series of values obtained under slightly different conditions of prism temperature; column 4 gives the values obtained after one tube had been tilted slightly with respect to the other.

TABLE X

Observations to show the inequality of transmission of the two gas tubes, and the effect of tilting one with respect to the other.

1 Corrected Wave-length (λ in μ)	2 A/B % TRANS.	3 A/B % TRANS.	4 A/B % TRANS.
2.522	95.6	95.9	-
2.572	96.4	96.6	-
2.623	96.0	96.4	-
2.674	96.0	97.0	-
2.703	-	-	97.6
2.723	96.0	96.25	-
2.754	-	-	96.9
2.774	95.0	95.3	-
2.805	-	-	95.6
2.825	93.4	94.5	-
2.855	-	-	94.1
2.875	93.0	93.6	-
2.906	-	-	93.3
2.926	90.8	92.3	-
2.955	-	-	92.6
2.975	90.8	91.9	-
3.005	-	-	92.1
3.025	90.5	91.5	-
3.054	-	-	92.3
3.073	91.3	91.0	-
3.102	-	-	92.9
3.119	91.8	92.3	-
3.151	-	-	93.2
3.168	92.9	92.3	-
3.200	-	-	94.2
3.217	92.8	92.67	-
3.248	-	-	94.0
3.265	93.2	93.6	-
3.297	-	-	94.7
3.314	94.0	93.8	-
3.346	-	-	94.6
3.363	93.8	93.3	-
3.395	-	-	94.9
3.412	93.6	93.8	-
3.444	-	-	94.3
3.461	93.1	94.3	-
3.492	-	-	95.2
3.509	94.0	94.0	-
3.541	-	-	94.4
3.590	-	-	95.1
3.635	-	-	95.4
3.688	-	-	95.8

Column No.	Prism Tempre. °C	Wadsworth set at °C	Entrance and Exit Slits 1/1000"
2	20.5°C	21.2°C	5) 5)
3	20.6°C	21.2°C	5) 5)
4 One tube tilted.	22.1°C	21.2°C	5) 5)

4) In table XI are given similar values of the transmission ratio for different wave-lengths in the region from 4.0μ to 7.0μ. The relationship between values of the ratio and wave-length are shown in Fig. XXIII. The curves show that the difference between the transmission powers is greatest in the regions round 4.25μ, 4.75μ, and 6.05μ. Moreover, measurements of the emission curves of the Nernst filament show that strong absorption occurs in these regions. Hence the difference in the transmission powers of the tubes is greatest in the regions where strong absorption occurs in the emission curves of the Nernst filament.

TABLE XI

Observations to show the inequality in transmission powers of the tubes in the region 4.0 μ to 8.0 μ.

Corrected W.L. Drum Reading (λ in μ)	% TRANS A/B	Corrected W. L. Drum Reading (λ in μ)	% TRANS A/B	Corrected W.L. Drum Reading (λ in μ)	% TRANS A/B
x3.982	98.65	4.819	96.02	xxx 7.465	92.9
4.03	98.38	4.871	96.2	7.567	89.9
4.079	98.29	4.922	96.2	7.669	89.8
4.127	98.25	4.973	96.79	7.771	82.0
4.176	97.5	xx5.786	100.0	7.871	81.0
4.224	96.68	5.832	89.6	7.971	87.3
4.273	94.48	5.882	96.6	7.465	92.0
4.321	97.05	5.933	95.0	7.567	90.1
4.369	97.9	5.984	87.8	7.669	88.04
4.418	97.26	6.034	87.9	7.571	84.1
4.468	97.75	6.084	90.0	7.871	83.2
4.517	98.79	6.134	90.9	7.971	88.0
4.566	99.06	6.184	96.25	8.070	92.8
4.616	98.71	6.233	97.8	-	-
4.666	98.0	6.281	99.5	-	-
4.716	96.61	6.33	96.4	-	-
4.767	95.85	6.378	101.5	-	-

Case No.	Prism Temperature	Wadsworth set at	Entrance and Exit Slits 1/1000"
x	18.1°C	21.2°C	5 5
xx	19.6°C	21.2°C	5 5
xxx	19.4°C	21.2°C	5 5

5) Further attempts were made to adjust the tubes so that they transmitted equal amounts of radiation for all wave-lengths, but these were not successful. An experiment was then made to see if the trouble was due to the rock-salt end-plates. The end-plates were removed from the tubes and the transmission ratio was again determined for different wave-lengths. The actual results observed are given in Table XII, and the corresponding transmission curves are drawn in Fig. XXIV. These curves give the value of the transmission ratio for different wave-lengths. The curves show that the transmission ratio is constant for all wave-lengths when the rock-salt end-plates are removed from the tubes. Only a slight adjustment to the carriage was necessary in order to make the two tubes transmit equal quantities of radiation.

TABLE XII

Observations to show that the Observation Tubes transmit equally when the rock-salt end-plates are removed from the tubes.

	Corrected W.L. Drum Reading (λ in μ)	% TRANS A/B	Corrected W.L. Drum Reading (λ in μ)	% TRANS A/B
1	4.865	98.0	3(7.466	98.0
	4.968	98.1	3(7.568	98.11
	5.07	98.02	3(7.671	98.2
	5.174	98.2	3(7.773	98.1
	5.277	98.0	3(7.872	98.1
2	5.372	98.0	3(7.972	97.97
	5.38	98.1	4(8.06	98.0
2	5.47	98.03	4 8.158	98.1
	5.48	98.0	4 8.257	98.01
2	5.578	98.09	5 4.129	98.2
	5.585	98.03	4.177	98.23
2	5.68	98.2	4.226	98.1
	5.688	98.2	4.274	98.2
2	5.782	98.25	4.323	98.2
	5.789	98.2	4.373	98.0
2	5.885	98.2	4.419	98.0
	5.891	98.0	4.469	98.05
2	5.985	98.1	4.519	98.15
	5.992	98.03	4.568	98.2
2	6.086	98.01	4.618	98.25
	6.092	97.9	4.668	98.3
2	6.186	98.11	4.717	98.1
	6.192	98.1	4.769	98.2
	6.289	97.9	4.820	98.0
	6.385	98.2		

Case No.	Prism Temperature.	Wadsworth set at	Entrance and Exit Slits.
1	18.7°C	21.2°C	20/1000" 10/1000"
2	19.5°C	21.2°C	20 10
3	19.1°C	21.2°C	20 10
4.	21.1°C	21.2°C	20 10
5	18.0°C	21.2°C	20 10

6) The rock-salt end-plates were replaced on the tubes and it was found that the trouble due to inequality in the transmission power of the tubes returned. There was, therefore, no doubt that the trouble was in some way connected with the rock-salt end-plates. The observations made are given in Table XIII, and the relationship existing between the values of transmission ratio and wave-length is shown in Fig. XXV. Once more it is seen that the maximum difference between the transmission powers of the two tubes coincides with the wave-length where maximum absorption occurs in the emission spectrum of the Nernst filament; also, tilting one tube with respect to the other does not improve the position.

TABLE XIII

Observations to show that the tubes still transmit unequal amounts of radiation after the rock-salt end-plates are replaced in the tubes.

Corrected W.L. Drum Reading (λ in μ)	% TRANS A/B	Corrected W.L. Drum Reading (λ in μ)	% TRANS A/B	Corrected W. L. Drum Reading (λ in μ)	% TRANS A/B
1					
6.909	95.07	6.118	91.2	6.797	97.45
-	94.26	6.217	93.05	6.895	96.03
7.008	93.99	6.314	94.9	6.994	95.86
-	93.8	6.410	96.4	7.094	95.5
7.107	95.68	6.508	97.66	7.47	91.9
-	93.26	6.604	97.14	-	91.85
7.209	95.15	6.701	97.16	7.571	92.4
-	95.7	6.797	94.43	-	89.4
7.311	95.48	6.895	93.54	7.674	84.96
-	97.18	6.994	93.3	-	87.7
7.413	99.24	7.094	91.85	7.775	87.5
-	97.38			-	84.8
		2			
7.515	98.95	5.399	97.4	7.875	86.6
-	98.02	5.504	97.6	-	86.62
7.618	98.13	5.606	98.1	7.975	88.6
-	100.0	5.709	100.6	-	90.5
7.719	105.9	5.716	99.28	8.074	91.85
-	105.9	5.812	98.0	-	93.5
7.82	108.0	5.819	98.35	8.171	93.3
-	108.9	5.915	93.3	-	94.6
7.92	100.6	5.921	94.2	8.27	95.4
-	103.9	6.016	92.3	-	96.7
8.02	98.6	6.022	91.9	8.368	92.5
-	97.1	6.116	94.7	-	94.7
8.119	95.88	6.122	96.23	-	-
-	95.1	6.118	94.26	8.468	91.3
8.215	94.71	6.217	95.83	-	91.5
-	93.6	6.314	97.39		
8.315	93.5	6.41	99.78		
-	92.7	6.508	99.88		
8.413	97.6	6.608	99.86		
-	95.7	6.701	99.77		

Case No.	Prism Temperature	Wadsworth set at	Entrance Exit Slits	Remarks.
1	19.6°C	21.2°C	20/1000" 10/1000"	-
2	22.0°C	21.2°C	20/1000" 10/1000"	one tube tilted slightly.

7) The carriage and tubes were therefore examined to see if any defect could be discovered which would explain the trouble. The rests for the tubes on the carriage were found to be too weak, so that one tube was slightly displaced when the carriage was rotated from one position to the other. It was deemed advisable to alter the construction of the carriage to correct this fault. The "V" shaped rests for the observation tubes were altered and strengthened, and further adjustment devices were fitted, so as to ensure finer adjustment when setting the tubes in position. The modified form of carriage is fully described in Chapter 1, Section 2, Para. 9.

The gas tubes were also examined to make quite certain that their ends had been ground parallel to each other. No such defect was discovered. The two tubes were now placed on the reconstructed carriage and adjusted accurately by means of a goniometer device. By this means it was possible to place the tubes so that they were exactly parallel to each other, and their end plates were normal to the axes of the tubes. No displacement of the tubes in the carriage took place when the carriage was rotated. The carriage, with tubes, was now placed in the appropriate position (see Fig. 1) and the tubes were once more evacuated. Observations showed that the transmission powers of the tubes were not exactly equal, but only a slight adjustment to one of the tubes was required to produce equality for all wave-lengths. Some of the actual results obtained are given in Table XIV, but no corresponding transmission ratio graphs have been drawn.

TABLE XIV.

Observations to show the complete compensation between the tubes when placed on the modified carriage.

Corrected W.L. (λ in μ)	% TRANS A/B	Corrected W.L. (λ in μ)	% TRANS A/B	Corrected W.L. (λ in μ)	% TRANS A/B
1					
3.903	99.9	5.525	99.97	6.134	100.1
3.952	99.89	5.529	100.1	6.233	100.0
4.00	100.0	5.627	100.1	6.330	100.1
4.049	100.1	5.631	99.9	5 7.31	99.9
4.098	99.9	3 5.729	99.8	7.41	101.4
4.146	99.9	5.83	100.0	7.51	100.0
4.194	100.0	5.933	100.0	7.62	99.95
4.243	99.8	6.034	99.8	7.719	100.0
4.292	99.7	6.134	99.7	7.819	100.4
4.34	100.2	6.233	100.1	7.919	99.82
4.389	99.1	6.330	99.9	6 7.412	99.9
4.439	99.9	4 5.318	100.1	7.514	100.3
4.439	100.1	5.422	99.9	7.617	100.0
4.539	100.1	5.525	99.95	7.719	99.6
4.589	99.7	5.627	99.93	7.819	99.7
2 5.014	100.0	5.729	99.9	7.92	100.1
5.118	99.9	5.832	99.5	8.02	100.2
5.218	100.1	5.934	99.2	8.117	100.0
5.32	99.7	6.03	100.0	8.214	99.9
5.43	99.9	6.084	100.2		

Case No.	Prism. Temp.	Wadsworth set at	Entrance Slit	Exit Slit
1.	20.8°C	21.2°C	20/1000"	10/1000"
2	19.1°C	21.2°C	"	"
3	19.6°C	21.2°C	"	"
4	19.8°C	21.2°C	"	"
5	19.8°C	21.2°C	"	"
6	19.6°C	21.2°C	"	"

8) A very reasonable explanation of this inequality of transmission of the two tubes has been given by Sir R. Robertson in his paper. (10). It is

very doubtful, however, if the conditions in this case were similar to those which Sir R. Robertson considers essential for the production of unequal transmission. The first carriage constructed for carrying the observation tubes was definitely faulty in that it allowed one of the tubes to shift slightly when the carriage was rotated. When the supports for the tubes were strengthened the trouble was overcome. It is very important, therefore, in all work of this kind to have a strong carriage for the gas tubes, and also the necessary adjusting screws for aligning the tubes in the carriage.

A brief description of the explanation given by Sir R. Robertson is given below. He showed that it was essential to have the tubes placed exactly parallel to each other in the carriage, and also for the rock-salt end-plates to be parallel to each other and placed at right angles to the axes of the tubes.

Let us suppose that the two tubes are incorrectly aligned, and that one tube is placed with its end-plates exactly normal to the axes of the tube, and to the central ray of the beam of radiation passing through the tube. When the second tube is rotated into position, its end-plates will not be normal to the central ray. The rays will, therefore, be displaced laterally and brought to a focus slightly different from that for corresponding rays passing through the first tube. Now both these sets of rays should finally come to a focus on the thermopile junctions, and under the conditions outlined above, this will not be the case. There will therefore be a difference between the amounts of energy falling on the thermopile in the two cases. It can be shown that this difference, when expressed as a percentage of the maximum amount of energy, will show a maximum value for wave-lengths in the regions where there is strong atmospheric absorption in the emission curves of the Nernst filament. These accurate adjustments of the tubes were fulfilled when the observations quoted at the beginning of this chapter were made, but even so, the results show that incomplete compensation resulted. It was only by redesigning the carriage for the gas tubes, so that no "rock" could take place when the carriage was rotated, that complete compensation was obtained.

Section II.

Absorption Bands of Carbon Dioxide.

1. When complete compensation of the tubes had been obtained, the first investigation of gases was undertaken. This work was a complete study of the absorption bands due to carbon dioxide, which are known to occur at 2.72 μ, 4.25 μ, and 14.87 μ. (21, 22 and 23). The verification of these positions of maximum absorption gave a complete check on the calibration of the spectrometer which has been described in detail in previous pages. Many experimental values were obtained; an account of some of these is now given, together with a brief description of the method used for making the experimental observations.

The gas tube "A" was filled with carbon dioxide at a known pressure, measured on the manometer attached to the system, and the tube "B" was completely evacuated. Having set the wave-length drum at some desired position, the wave-length setting was noted, also the temperature of the prism. The gas tube "A" was placed in the path of the radiation and the shutter in front of the spectrometer entrance slit was raised. In this way energy was allowed to pass through the system causing a deflection in the galvanometer. This galvanometer deflection was measured, and an allowance made for any galvanometer zero drift. Tube "B" was now placed in the position previously occupied by "A", and the mean deflection was again measured. The ratio, deflection A ÷ B, gave the transmission ratio of the tubes for the particular wave-length under consideration. The wave-length drum was rotated slightly and the above procedure repeated. The results were tabulated and the following table, which is taken from the actual experimental records, gives a typical example of the total number of observations made. Corrections were always applied to the wave-length drum readings to allow for :

a) Prism temperature being different from that at which the Wadsworth Mirror was set and from the standard temperature of 18°C.

b) Errors in cutting the wave-length drum screw.

These corrections have been calculated and are given in the specimen table below. (Table XV).

TABLE XV.

SAMPLE TABLE OF EXPERIMENTAL OBSERVATIONS.

Nitric Oxide Absorption Band at 5.29 μ.

Prism Temperature 20.5°C. Wadsworth Mirror set at 23.9°C.

Slit Widths: Entrance 10/1000"; Exit 10/1000".

Wave-Length Drum Reading. (λ in μ)	Corr. for Calibr. Error. (λ in μ)	Corr. for Temp. of Prism. (λ in μ)	Corr. Wave-Length. (λ in μ)	Gas Tube "A"				Evacuated Tube "B"				A/B % Trans-mission.
				Galvo. Zero CMS.	Galvo. Throw CMS.	Galvo. Defl. CMS.	Mean Galvo. Defl. CMS.	Galvo. Zero CMS.	Galvo. Throw CMS.	Galvo. Defl. CMS.	Mean Galvo. Defl. CMS.	
5.00	-.006	.033	5.027	38.48 38.48	22.23	16.25 16.25	16.25	38.1 38.1	21.52	16.58 16.58	16.58	98.0
5.02	-.005	.033	5.048	38.45 38.48	22.89	15.56 15.59	15.58	38.15 38.12	21.72	16.43 16.40	16.42	94.9
5.04	-.004	.033	5.069	38.55 38.50	23.54	15.01 14.96	14.98	38.15 38.10	21.82	16.33 16.28	16.30	91.9
5.06	-.003	.033	5.09	38.55 38.55	24.27	14.28 14.28	14.28	38.3 38.3	22.2	16.1 16.1	16.1	88.7
5.08	-.002	.033	5.111	38.7 38.65	25.07	13.63 13.58	13.60	38.35 38.35	22.4	15.95 15.95	15.95	85.3
5.10	-.001	.033	5.132	38.60 38.60	25.61	12.99 12.99	12.99	38.30 38.30	22.5	15.8 15.8	15.8	82.2
5.12	-.001	.033	5.152	38.7 38.7	26.37	12.33 12.33	12.33	38.40 38.34	22.7	15.7 15.64	15.67	78.7
5.14	-	.033	5.173	38.7 38.75	26.96	11.74 11.79	11.77	38.40 38.40	22.92	15.48 15.48	15.48	76.0

In the tables actually reproduced in the following pages, only the values of the corrected wave-length drum settings and the transmission ratio are given; corrected wave-length drum reading is denoted by "Corr. W. L. Reading (λ in μ)" and transmission ratio by "% Trans. A/B".

2. Observations were first made on the absorption due to carbon dioxide at 2.72 μ. A wide range of gas pressures was used, but results are given for only two of these pressures, namely, 40.3 cms. and 65.0 cms. of mercury. The spectrometer slits were widened when the pressure of gas was 40.3 cms. mercury, and the effect of this increase on the resolving power of the apparatus is seen from an examination of the transmission curves which are plotted in Fig. XXVI. Table XVI contains the corresponding experimental values. The curves show that maximum absorption occurs at a wave-length corresponding to 2.72 μ, and also, that the value of the transmission ratio for the wave-length corresponding to maximum absorption is directly proportional to the gas pressure. Thus, for a gas pressure of 40.3 cms. mercury, the maximum percentage absorption was 46%, and for a pressure of 65.0 cms. mercury, this value was 66%. The ratio of percentage absorption/gas pressure is equal to 1.14 for a pressure of 40.3 cms. mercury, and 1.04 for a pressure of 65.0 cms.

A point worthy of note is this: the corrections applied for variations in prism temperature give consistent results for the position of maximum absorption. A difference of five degrees centigrade in the temperature of the prism does not upset the calculated position of the wave-length for maximum absorption.

TABLE XVI.

Observations on the Absorption Band of Carbon Dioxide at 2.72 μ.

Corrected W. L. (λ in μ)	% TRANS A/B	Corrected W. L. (λ in μ)	% TRANS A/B	Corrected W. L. (λ in μ)	% TRANS A/B
1					
2.501	82.5	2.545	58.5	2.98	70.5
2.524	81.00	2.555	57.3	2.999	71.8
2.541	79.3	2.579	54.0	3 2.568	73.0
2.564	77.0	2.596	51.1	2.592	71.0
2.582	74.5	2.619	48.0	2.609	69.4
2.594	72.4	2.637	45.2	2.632	67.8
2.622	67.8	2.637	45.2	2.650	65.3
2.644	64.0	2.660	42.0	2.673	63.5
2.664	61.3	2.677	38.8	2.69	61.7
2.685	58.0	2.697	36.3	2.713	60.4
2.702	55.0	2.700	36.0	2.731	60.0
2.725	54.2	2.718	34.0	2.764	60.5
2.743	54.0	2.721	34.5	2.771	61.0
2.782	55.8	2.748	33.7	2.794	62.5
2.803	58.3	2.758	34.0	2.802	65.5
2.824	61.7	2.761	34.0	2.835	67.0
2.846	64.0	2.778	36.0	2.852	71.0
2.864	68.5	2.781	36.0	2.875	73.1
2.886	73.0	2.799	40.0	2.893	76.0
2.902	79.0	2.822	42.7	2.916	78.4
2.925	80.0	2.839	47.0	2.933	80.3
2.942	82.5	2.86	53.0	2.956	82.1
2.964	84.0	2.88	56.6	2.972	83.5
2.994	85.4	2.902	60.0	3.012	85.8
3.001	86.3	2.92	62.2		
2 2.515	60.8	2.94	66.0		
2.538	59.0	2.959	68.0		

Case No.	Prism Temperature	Wadsworth set at	Entrance Slit 1/1000"	Exit Slit 1/1000"	Gas Pressure cms. Hg.
1	28.8°C	23.2°C	5	5	40.3
2	24.7°C	23.2°C	5.	5	65.0
3	23.7°C	23.2°C	7.5	7.5	40.2

3. A few of the several observations made on the absorption band of carbon dioxide at 4.25 μ are given in Table XVII. This Table contains results for one gas pressure, namely, 35.0 cms. of mercury. The corresponding absorption curve is drawn in Fig. XXVII. Maximum absorption (equal to 23.5%) occurs at 4.25 μ.

TABLE XVII.

Observations showing absorption by Carbon Dioxide at 4.25μ.

Corrected W. L.Drum (λ in μ)	% TRANS A/B	Corrected W.L. Drum (λ in μ)	% TRANS A/B	Corrected W.L. Drum (λ in μ)	% TRANS A/B
1 4.057	94.0	2 4.186	83.9	3 4.067	93.7
4.106	91.5	4.225	76.3	4.086	93.0
4.154	83.4	4.264	76.0	4.125	90.7
4.203	77.9	4.303	81.2	4.164	86.2
4.252	76.5	4.343	90.2	4.203	78.9
4.30	83.8	4.360	92.2	4.241	74.5
4.349	93.0	4.404	95.0	4.28	78.9
4.398	95.0	4.459	96.5	4.30	81.7
4.448	96.0	4.499	97.0	4.358	92.8
2 4.069	93.96	4.539	97.5	4.407	95.0
4.108	92.0	4.559	97.4	4.457	96.8
4.147	88.5	4.619	97.9		

Case No.	Prism Temperature	Wadsworth set at	Entrance Slit	Exit Slit	Gas Pressure
1	19.7°C	20.1°C	7.5	7.5 1000"	35.0 cms HG
2	18.7°C	20.1°C	7.5	7.5/ 1000"	
3	18.9°C	20.1°C	7.5	7.5/ 1000"	

4. The results of some of the work carried out on the absorption band of carbon dioxide between 14.0μ and 15.0μ are given in the Table XVIII. The pressure of the gas used for the experiments was 50.0 cms of mercury. The curve showing the relationship between the values of the transmission ratio and wave-length is given in Fig. XXVIII. Maximum absorption is found to occur at 14.87μ. It will be noticed that the "slit widths" used for these experiments are much greater than those used for experiments in the near infra-red region. However, on account of the higher dispersion of rock-salt at such high wave-lengths, the resolving power of the spectrometer is still quite good, and the peak of the absorption band is well defined (Fig. 28). Some experimental observations on this band were made

using the arrangement depicted in Fig. 2; the results obtained were found to be in complete agreement with those obtained by experimental arrangement, No. 1 (see Fig. 1).

TABLE XVIII.

Observations to show the absorption by Carbon Dioxide near 14.9μ.

Correct. W.L. (λ in μ)	% TRANS A/B	Correct. W.L. (λ in μ)	% TRANS A/B	Correct. W.L. (λ in μ)	% TRANS A/B
1 14.501	91.9	1 14.801	82.77	14.921	80.8
14.501	91.7	14.801	82.3	14.941	81.9
1 14.601	90.95	14.841	72.26	14.951	83.3
14.601	91.26	1 14.851	71.99	14.961	84.0
1 14.701	86.9	14.861	71.22	14.981	86.3
14.701	87.2	14.901	79.28	15.001	87.6
				15.051	90.9

Case No.	Prism Temperature	Wadsworth set at	Entrance Exit Slits	Gas Pressure.
1	23.3°C 20.2°C	24.1°C 24.1°C	20/1000" 20/1000"	50 cms Hg

5. In the literature dealing with infra-red absorption bands, we have found some evidence of absorption by carbon dioxide in the region between 1.0 μ and 2.0 μ. A paper has been published by Dennison[23] in which he predicts an absorption band at 1.20 μ for carbon dioxide. A search was made for this band, using experimental arrangement No. 1, and a wide range of pressures of gas in the absorption tube. The results, given in Table XIX, do not point to any region of pronounced absorption.

The absorption curve in Fig. XXIX shows the variation of the transmission ratio with wave-length. The absorption is seen to be almost uniform for all wave-lengths from 1.0 μ to 2.0 μ: varying from a transmission of 71.0% to one of 75.0% for a gas pressure of 75.0 cms mercury; and from 68.0% to 71.0% for a gas pressure of 101.1 cms mercury. The variation in both cases is uniform. The slits were reduced in width as far as possible, consistent with a reasonable galvanometer deflection, but no selective absorption could be detected. A very wide range of gas pressures was used, but results for only two of them are given :- 75.0 cms and 101.1 cms of mercury. Later, some experiments were tried using a mixture of carbon dioxide dissolved in water. An account of these will be given in Chapter IV.

TABLE XIX.

Observations to show the Absorption produced by Carbon Dioxide in the region of 1.0μ - 2.0μ.

Correct. W.L. Drum Reading (λ in μ)	% TRANS A/B	Correct. W.L.Drum Reading (λ in μ)	% TRANS A/B	Correct. W.L.Drum Reading (λ in μ)	% TRANS A/B
1 1.994	71.3	1.607	72.3	1.356	71.7
1.114	71.0	1.626	72.3	1.376	71.8
1.134	71.0	1.646	72.5	1.396	71.9
1.153	71.3	1.666	72.8	1.416	72.0
1.173	71.3	1.686	72.9	1.437	71.9
1.192	71.4	1.706	72.8	1.456	72.0
1.213	71.6	1.767	73.1	1.475	72.1
1.232	71.6	1.806	73.35	1.497	71.9
1.252	71.5	1.827	73.7	1.817	71.8
1.271	71.5	1.866	73.9	1.537	72.2
1.291	71.7	1.886	74.0	1.557	72.0
1.311	71.6	1.984	74.9	1.577	72.25
1.331	71.8	2 1.097	71.4	1.597	72.4
1.35	71.6	1.117	71.4	1.617	72.3
1.37	71.7	1.137	71.3	1.637	72.2
1.388	71.7	1.157	71.2	1.657	72.5
1.408	71.7	1.177	71.4	1.698	72.6
1.428	71.8	1.197	71.5	1.748	72.85
1.447	71.8	1.217	71.6	1.798	73.6
1.467	71.9	1.237	71.4	1.849	73.5
1.488	72.0	1.257	71.7	1.900	74.1
1.507	71.9	1.276	71.9	1.950	74.2
1.547	72.2	1.296	71.8	2.000	74.91
1.567	72.3	1.316	71.7		
2 1.587	72.2	1.337	71.7		
1.030	67.2	1.228	67.9	3) 1.395	68.2
1.07	67.6	1.248	68.1	1.404	68.1
1.09	67.7	1.267	68.1	1.423	68.4
				1.444	68.4
1.108	67.7	1.286	67.9	1.464	68.6
1.148	67.6	1.306	68.1	1.483	68.4
1.17	67.8	1.325	68.1	1.504	68.6
1.188	67.9	1.346	68.2	1.542	68.6
1.208	68.0	1.365	68.0	1.582	68.8

Case No.	Prism Temperature	Wadsworth set at	Exit Slit 1/1000"	Entrance Slit 1/1000"	Gas Pressure cms. hg.
1	21.5°C	20.1°C	2.5	2.5	75.0
2	20.9°C	"	2.5	2.5	75.0
3	22.8°C	"	2.5	2.2	101.1

We are compelled to reach the following conclusions from these experiments :

a) There is no selective absorption by carbon dioxide in the region near 1.20μ,

or

b) The absorption is so weak that it is impossible to detect it with the apparatus described in the preceding pages.

Section III.

The absorption Bands of Nitric Oxide.

1. Absorption bands due to nitric oxide have been investigated by Warburg and Luthauser[25] using a prism spectrometer, and by Snow, Rawlins and Rideal[26] using a grating and rock-salt prism spectrometer.

The fundamental band (frequency 1883 cms^{-1}.) was observed by Snow and his collaborators, and they were able to resolve it sufficiently to show that a first harmonic should occur at about 2.69μ; they were unable, however, to demonstrate the existence of this band, chiefly because of its very weak intensity, but also, because of the "masking effect" produced by the strong absorption of atmospheric carbon dioxide near these wave-lengths (the 2.72μ band of carbon dioxide). Before proceeding in the present work to search for the first harmonic at 2.69μ, it was first of all necessary to verify the existence of the fundamental band at 5.29μ, observed by Warburg and Luthauser, and by Snow and his co-workers. This work will be described in the next paragraph. It is interesting to record that no bands have ever been observed in the region 6.0μ - 20.0μ for nitric oxide. Moreover, none were discovered during the present work.

2. An account is now given of the results obtained during the investigation of the absorption band at 5.29μ. The experimental observations summarised in Table XX are some of the many results obtained during the course of the work when nitric oxide was contained in the observation tube "A". The gas pressures used were 64.0 cms, 65.0 cms and 69.0 cms of mercury, the gas tube "A" being completely evacuated and refilled with freshly generated gas after the recording of each set of observations. The corresponding transmission curves are given in Fig. XXX; these show the values of the transmission ratio plotted against wave-length. They demonstrate clearly that maximum absorption occurs at a wave-length of 5.29μ; and also, that the values of maximum absorption for different gas pressures are proportional to the corresponding values of the gas pressure. Thus, for a gas pressure of 69 cms. mercury, the value of the maximum absorption is 35%. These two figures give a value of 0.51 for the ratio, $\frac{\%\ \text{absorption}}{\text{gas pressure}}$. The corresponding value of this ratio, for a pressure of 65 cms. mercury, is 0.52, and for a pressure of 64 cms the ratio is 0.48. Pressures of gas very much above or below these values, gave absorption bands of poor definition. Results corresponding to such pressures are not, however, included in this account.

TABLE XX

The Absorption Band of Nitric Oxide at 5.29 μ.

Correct W.L. Reading (λ in μ)	% TRANS A/B	Correct W.L. Reading (λ in μ)	% TRANS A/B	Correct W.L. Reading (λ in μ)	% TRANS A/B
1 5.026	97.8	5.377	65.7	5.272	66.8
5.047	94.8	5.387	66.8	5.293	66.3
5.068	91.6	5.397	66.8	5.313	66.2
5.089	88.8	5.418	67.5	5.333	66.1
5.11	85.4	5.439	68.8	5.354	66.5
5.131	81.8	2 5.026	97.8	5.375	66.7
5.151	79.2	5.045	95.3	5.395	67.9
5.172	76.0	5.063	92.8	5.416	68.6
5.192	73.2	5.087	89.3	5.437	70.3
5.213	70.6	5.108	86.0	3 5.018	97.9
5.232	68.7	5.129	82.7	5.039	95.6
5.253	67.5	5.149	79.7	5.06	92.7
5.273	65.8	5.17	76.5	5.08	89.01
5.294	65.0	5.19	73.8	5.101	86.5
5.315	64.8	5.211	71.5	5.122	83.47
5.337	64.9	5.231	69.5	5.142	80.8
5.356	65.0	5.252	68.3	5.163	78.00
3 5.183	75.5	5.265	69.5	5.348	69.95
5.204	73.8	5.285	69.2	5.369	70.9
5.224	71.7	5.307	69.2	5.389	71.6
				5.41	73.1
5.245	70.6	5.327	69.3	5.43	74.2

Case No.	Prism Temp.	Wads. set at	Exit Slit	Entrance Slit.	Maxm. Abs. %	Gas Press cms. Hg.	% abs. Gas Press.
1	20.5 °C	23.9 °C	10/1000"	10/1000"	35	69	0.51
2	20.8 °C	"	"	"	34	65	0.52
3	19.5 °C	"	"	"	31	64	0.48

3. Two other absorption curves for nitric oxide in this region have been drawn; these are given in Fig. XXXI, and the experimental results are tabulated in Table XXI. The gas pressures used were 52.0 cms. and 73.0 cms of mercury. Both the curves show maximum absorption occurring at 5.29μ, maximum absorption being 26% for a pressure of 52.0 cms. mercury, and 35.5% for a pressure of 73.0 cms. These results give a value for the ratio $\frac{\%\ \text{Absorption}}{\text{Gas pressure}}$ of 0.50 for a pressure of 52.0 cms., and 0.50 for a pressure of 73.0 cms. mercury. We see, therefore, that the value of maximum absorption is proportional to the gas pressure, a result reached in the records given in the previous paragraph (Table XX). The resolving power of the apparatus was insufficient to resolve the band, but the existence of the band was successfully demonstrated. It should be observed that the uncorrected curves (for prism temperature variations) were very inconsistent; it was only after corrections had been applied to all wave-length readings, that complete uniformity in the results for wave-length of maximum absorption was obtained.

TABLE XXI

Absorption Bands of Nitric Oxide at 5.29μ.

Correct. W.L. Reading (λ in μ)	% TRANS A/B	Correct. W.L. Reading (λ in μ)	% TRANS A/B	Correct. W.L. Reading (λ in μ)	% TRANS A/B
4) 5.097	96.0	4) 5.385	75.1	5) 5.236	66.5
5.122	92.3	5.406	76.4	5.257	64.5
5.143	89.0	5.427	77.0	5.278	64.0
5.163	85.9	5.447	78.3	5.303	63.7
5.184	83.8	5.468	80.2	5.319	63.3
5.199	82.0	5.488	82.1	5.342	63.6
5.220	79.2	5.509	84.3	5.360	64.3
5.240	77.3	5) 5.093	90.2	5.381	65.5
5.261	75.7	5.113	87.1	5.402	67.0
5.282	74.5	5.134	82.8	5.423	68.5
5.302	74.0	5.159	78.0	5.443	70.5
5.327	74.05	5.175	74.2	5.464	72.0
5.344	74.2	5.195	71.0	5.484	74.0
5.364	74.3	5.216	68.1	5.505	76.02

Case No.	Prism Temp.	Wads. set at	Exit Slit	Maxm. Abs. %	Gas Press. cms.Hg.	% abs. ÷ Gas Press
4	20.3°C	20.1°C	10/1000"	26.0	52	0.50
5	20.8°C	20.1°C	10/1000"	36.5	52	0.50

In all five cases described in the previous two paragraphs it has been shown that the percentage maximum absorption is directly proportional to the gas pressure. As the pressure of gas increased, the % absorption increases accordingly. This demonstrates that the absorption band is clearly one caused by the nitric oxide gas. Moreover, there does not seem to be any shift in the position of the band as the pressure of gas is increased. This is in accordance with results obtained by different observers with other gases.

4. It will be remembered that Snow and Rawlins were unable to detect the overtone of nitric oxide near 2.70μ. They thought this result was possibly due to the great absorption produced by atmospheric carbon dioxide in this region. The work described in the present paragraph was carried out in an endeavour to discover the band. The experimental results given in Table XXII, and the absorption curves drawn in Fig. XXXII show the amount of absorption produced by nitric oxide at different wavelengths in the region near 2.70μ. A pressure of gas equal to 52.0 cms. of mercury was used for the two experiments, the results of which are given in these tables. The "slit-width" was increased by 50% for the second set of observations, and the result of this is seen in the general "blunting" of the peak of the absorption curve. Both the absorption curves show maximum absorption at 2.68μ. It is of interest to note that the absorption curves reproduced in Fig. XXXII were the very first two obtained with the apparatus after nitric oxide had been placed in the tubes. Further, the curves are entirely untouched in any way with the exception of corrections applied for variations in prism temperature. The application of these corrections is, as we have seen, very essential.

TABLE XXII.

The Absorption Band of Nitric Oxide in the region near 2.70μ.

Correct. W.L. Reading (λ in μ)	% TRANS A/B	Correct. W.L. Reading (λ in μ)	% TRANS A/B	Correct. W.L. Reading (λ in μ)	% TRANS A/B
1) 2.498	87.8	2.781	87.2	2) 2.728	87.6
2.508	87.7	2.79	87.7	2.753	88.0
2.527	87.5	2.81	88.1	2.768	88.3
2.538	87.0	2.821	88.5	2.794	88.5
2.547	86.9	2.857	90.0	2.809	88.5
2.579	86.5	2) 2.552	89.0	2.834	89.3
2.619	86.1	2.566	88.8	2.85	89.4
2.627	86.4	2.592	88.6	2.875	90.0
2.639	86.0	2.606	88.5	2.889	90.5
2.668	86.2	2.633	88.0	2.905	90.8
2.700	86.2	2.647	87.5	2.929	91.5
2.708	86.2	2.673	87.6	2.948	91.8
2.741	86.8	2.687	87.65	2.954	92.2
2.747	87.0	2.713	87.9		

Case No.	Prism Temp.	Wads set at	Entrance Slit	Exit Slit	Gas Pressure cms. Hg.
1	27.1°C	20.8°C	5/1000"	5/1000"	52.0
2	23.2°C	20.8°C	7.5/1000"	7.5/1000"	52.0

5. To show that this band was really due to nitric oxide, it was essential to demonstrate the variation in intensity of absorption as the gas pressure was increased. The results obtained in the course of this experiment are given in this paragraph, Table XXIII, Fig. XXXIII, shows the absorption bands for the several cases. Four different gas pressures were used for the tests, namely 143.0 cms., 114 cms., 86 cms. and 46 cms mercury respectively. Each curve shows maximum absorption at 2.68μ, and also, that the percentage maximum absorption is proportional to the gas pressure. Thus, for a gas pressure of 114 cms. mercury, the value of the ratio % Absorption $\div$ Gas Pressure is equal to 0.16; and for

a gas pressure of 46 cms.mercury, 86.0 cms. mercury and 143 cms. mercury, the values of the ratio are 0.17, 0.18 and 0.17 respectively, which values are practically identical. These results show that the % absorption is proportional to the gas pressure, and there is, therefore, no doubt that the band is an absorption band of nitric oxide. The value of the wave-length corresponding to maximum absorption is 2.68μ - an average of the values obtained from the four curves which correspond to four different gas pressures.

TABLE XXIII.

The Absorption Bands of Nitric Oxide at 2.68μ.

Corr.W.L. Reading (λ in μ)	% TRANS A/B	Corr. W.L. Reading (λ in μ)	% TRANS A/B	Corr.W.L. Reading (λ in μ)	% TRANS A/B
3) 2.414	97.0	4) 2.425	93.5	5) 2.487	89.95
2.416	96.8	2.476	92.1	2.538	87.75
2.465	96.5	2.527	90.01	2.588	84.5
2.516	95.0	2.561	89.1	2.640	82.2
2.568	93.5	2.577	87.92	2.681	80.95
2.617	92.6	2.628	86.4	2.721	81.8
2.619	92.6	2.679	85.2	2.741	82.4
2.668	92.3	2.730	86.1	2.782	83.97
2.718	93.0	2.770	88.2		
2.720	92.93	2.781	88.5		
2.771	94.0				

Case No.	Prism Temp.	Wads. set at	Entrance Slit	Exit Slit	Max. Abs.%	Gas Press. cms.Hg.	Max.Abs. Gas Press.
3	19.2°C	19.3°C	5/1000"	5/1000"	8.0	46.0	0.17
4	18.4°C	19.3°C	"	"	15.0	86.0	0.18
5	17.6°C	"	"	"	19.0	114.0	0.16

6) Some further observations in this region were made with gas pressures of 62.0 cms. and 94.0 cms. mercury. The record of these results is given in Table No. XXIV, and the corresponding absorption curves are drawn in Fig. XXXIV. It will be seen that maximum absorption occurs at 2.68μ,

and the table also shows that the % maximum absorption is directly proportional to the gas pressure. The ratio of $\frac{\text{Maxm. Absorption}}{\text{Gas pressure}}$ has a value of 0.17 for both gas pressures.

TABLE XXIV.

Absorption Curves of Nitric Oxide at 2.68 μ.

Corr. W.L. Reading (λ in μ)	% TRANS A/B	Corr. W.L. Reading (λ in μ)	% TRANS A/B	Corr. W.L. Reading (λ in μ)	% TRANS A/B
6)		7)		8)	
2.549	83.0	2.577	91.5	2.584	88.1
2.589	80.5	2.598	90.5	2.605	87.5
2.599	79.5	2.618	90.2	2.625	86.2
2.630	77.9	2.649	89.9	2.630	85.6
2.651	76.5	2.659	89.5	2.640	85.0
2.671	75.6	2.699	89.7	2.676	83.5
2.692	76.0	2.74	90.4	2.686	83.8
2.712	76.8	2.78	91.2	2.719	84.1
2.722	77.5	2.806	91.3	2.762	85.7
2.733	78.47	2.951	92.0	2.807	88.5
2.773	81.0			2.828	89.0
2.783	82.1				

Case No.	Prism Temp.	Wads. set at	Entrance Slit	Exit Slit	Maxm. Abs.%	Gas Press. cms.Hg.	Abs. Gas Press.
6	16.8°C	19.3°C	5/1000"	5/1000"	24.0	143.0	0.17
7	19.9°C	20.1°C	"	"	10.5	62.0	0.17
8	19.6°C	20.1°C	"	"	16.0	94.0	0.17

It should also be noted that for cases 7 and 8, the Wadsworth Mirror was set at a prism temperature of 20.1°C, whereas for cases 1 and 2, it was set at 20.8°C., and for cases 3, 4, 5 and 6, it was set at 19.3°C. Nevertheless, the wave length for maximum absorption is the same for all the cases, provided the corrections for prism temperature are applied. The importance of this correction for prism temperature cannot be stressed too strongly. Before the corrections were applied to the results recorded in Tables Nos. XXII and XXIII, the absorption curves derived therefrom were very inconsistent. Application of the correction factors removed all anomalies, and the position given for the maximum absorption was independent of the temperature at which the Wadsworth mirror was set, or the temperature of the prism when the observations were recorded.

6. To complete the investigation of the absorption spectrum of nitric oxide, it was necessary to see if any band existed near the region round 1.6μ, where a second harmonic would occur. The recorded observations summarised in Table XXV and graphically represented in Fig. XXXV, are some of these obtained during the course of this investigation. Actually, the results tabulated are for gas pressures of 57.0 cms., 70.0 cms. and 84.0 cms. mercury. Generally speaking, there is no very marked absorption due to the gas in this region (from 1.0μ - 2.0μ). The absorption actually varies very uniformly; the transmission ratio, A/B, varies from 95% to 94.8% over the range 1.0μ to 2.2μ for a gas pressure of 70.0 cms. mercury; and so on for other gas pressures. We may conclude, therefore, that the absorption is very small in this region, so small that it is impossible to detect it with the apparatus described in these pages. Pressures very much above or below those mentioned in these tables gave the same result. The corresponding observations at these pressures have not, however, been recorded.

TABLE XXV.

Absorption by Nitric Oxide in the region from 1.0μ - 2.0μ.

Corr.W.L. Reading (λ in μ)	% TRANS A/B	Corr.W.L. Reading (λ in μ)	% TRANS A/B	Corr.W.L. Reading (λ in μ)	% TRANS A/B
1) 1.055	95.1	1) 2.034	94.7	3) 1.622	94.0
1.105	95.1	2.085	94.7	1.672	94.1
1.156	95.2	2.143	94.7	1.727	94.0
1.206	95.3	2.185	94.7	1.777	93.9
1.257	95.2	2) 1.11	96.1	1.829	94.0
1.308	95.1	1.16	96.5	1.890	93.85
1.358	95.2	1.211	96.4	1.933	94.0
1.409	95.1	1.251	96.6	1.985	94.0
1.459	95.2	1.262	96.3	2.035	93.86
1.512	95.3	1.30	96.9	2.086	94.0
1.568	95.5	1.314	96.2	2.138	94.1
1.621	95.0	1.355	96.5	3a) 1.529	94.1
1.673	95.0	1.364	96.45	1.576	94.6
1.725	94.9	1.40	96.95	1.628	94.0
1.777	95.0	1.416	96.2	1.689	94.1
1.829	95.0	1.45	97.0	1.732	93.8
1.880	94.9	1.514	97.05	1.784	93.9
1.932	94.8	3) 1.521	94.5	1.836	94.0
				1.888	94.0
1.982	94.7	1.570	94.4	1.945	93.9
				2.043	94.0
				2.095	93.9

Case No.	Prism Temp.	Wadsworth set at	Entrance Slit	Exit Slit	Gas Pressure cms. Hg.
1	(18.7°C (17.8°C	(20.1°C (20.1°C	2.5/ 1000"	2.5/ 1000"	70.0
2	20.1°C	20.1°C	"	"	57.0
3	17.4°C	20.1°C	"	"	84.0
3a	16.6°C	20.1°C	"	"	

7. The examination of the bands of carbon dioxide with the apparatus described reveals several facts. It has been shown that bands occur at 2.72μ, 4.25μ and 14.87μ; and that the percentage absorption for radiations of these wave-lengths is proportional to the gas pressure. This result is to be expected. A

study of the experimental curves drawn for these absorption bands also shows there is some critical pressure of gas for which the absorption bands are most pronounced. The same result was obtained with nitric oxide gas. In every investigation of this character one would suggest that experiments be first made to discover the value of this critical pressure. Afterwards, the resolving power of the apparatus should be increased, by diminishing the slit widths of the spectrometer, so that the absorption bands can be fully resolved.

No absorption bands for carbon dioxide in the region $1.0\mu - 2.0\mu$ could be detected. The selective absorption in this region is either negligible, or too small to be detected with the apparatus used in the present work. A similar conclusion was reached from a series of experiments in the same region on the system "water and carbon dioxide". An account of these experiments is given in Chapter IV, Section IV. The effect of adjusting the Wadsworth mirror at different prism temperatures is also clearly demonstrated in the experiments described in this Chapter. Provided the necessary temperature corrections are applied to the wave-length drum readings, the apparatus will give consistent results. These results are independent of the temperature of the prism at which the Wadsworth mirror is set. Thus, for the series 1 to 8 for the nitric oxide band at 2.68μ given in Tables XXII, XXIII and XXIV, the Wadsworth mirror was set at three different prism temperatures: 20.8°C, 19.3°C and 20.1°C; and the observations were recorded at prism temperatures varying from 16.8°C to 27.1°C. The eight corrected experimental absorption curves all show maximum absorption at 2.68 μ.

For nitric oxide, the fundamental band at 5.29 μ was measured for a wide range of gas pressures. Here again, the value of the maximum absorption so determined is proportional to the gas pressure. Different widths of the spectrometer slits were used for some of the experiments, and although wide slits give a small resolving power, the positions for maximum absorption when obtained with wide and narrow slits were identical. In some of the earlier experiments, slight discrepancies were noticed when different slit widths were used. These, however, were traced to variations in prism temperature, and when corrections for these variations were applied, the discrepancies disappeared and all the experimental values gave consistent results.

The overtone for nitric oxide at 2.68 μ was easily distinguished with the instrument, and a large number of experimental observations on this band are included in the account. The value for maximum absorption depends on the gas pressure, and for the best definition of the band there is a critical value of the gas pressure; an examination of the experimental curves drawn in Figs. XXXII, XXXIII and XXXIV reveals this fact.

The fact that the percentage absorption increases as the gas pressure is raised shows that the band is really due to the gas under observation. This is conclusive evidence, and the method of attack should be used for the investigation of all problems of this character.

The several attempts made to discover selective absorption in the region near the position which the second harmonic would occupy, were unsuccessful. There is either no selective absorption by nitric oxide in this region, or it is too small to be measured with the apparatus. This minimum value for the measurable absorption is approximately 2.0%.

CHAPTER IV

AN INVESTIGATION of ABSORPTION by LIQUIDS.

LIQUIDS.

Section I.

1) The accurate determination of the infra-red absorption spectra of liquids has always been rather difficult. This has been due, in general, to the great absorption of infra-red radiation exhibited by most liquids. In the case of pure water, for example, most infra-red radiations of wave-length greater than 3.0μ are cut off completely by a layer of liquid of thickness 0.2 cms. Other liquids are not quite so opaque as this to infra-red radiations, but the general principle remains, and to get good definition of the absorption bands, extremely thin films of liquid must be used. The thickness of these films must also be accurately known for a correct value of the absorption coefficient to be elucidated. The measurement of these thicknesses presents further difficulties. Although a great deal of work has been done and a large number of results published, the work is still only in its infancy. For solids and gases more or less definite results have been obtained, both from the theoretical and experimental points of view. For liquids much less progress has been made.

II) The chief interest lies in the chemical data obtained. For example, in all cases where a homologue series of organic liquids has been examined, it has been possible to attribute one definite absorption band, which occurred in all members of the series, to some particular chemical radicle. Ellis[27], Coblentz[28], and J. Lecomte[29] have worked on the series of saturated aliphatic hydrocarbons, and a careful analysis of their results reveals that the main regions of absorption occur in the same part of the spectrum. The intensities of the corresponding bands are also of the same order. Thus, in each of the absorption spectra of the following three members of the series, octane, hexane and pentane, absorption bands occur at 1.02μ, 1.2μ, 1.40μ, 1.7μ, 2.2μ, 3.45μ, 6.85μ and 13.8μ. The intensities of these bands are approximately the same for each member of the series. The same is true for other members of the series. In addition to these strong characteristic bands, a number of fainter bands have been observed by many workers for individual members of the series. The positions of these bands do not appear to be accurately known. A possible explanation of these bands is given later in this chapter.

III) For pure water a fair amount of work has been done. It is now generally considered that the principal bands of water occur at approximately 2, 3, 4.7 and 6.0μ. At this stage it is noteworthy that the bands of carbon dioxide definitely occur at

2.72 μ, 4.25 μ, and 14.87 μ. This illustrates the difference between gases and liquids as far as absorption is concerned. Moreover, for some gases, the fine structure of the bands has been investigated. Such accuracy has not been attained for liquids in the infra-red for reasons already given. Above 6.0 μ the absorption coefficient for water increases rapidly and uniformly with wave-length. There is no selective absorption between 6.0 μ and 18.0 μ.

Many workers have attacked the problem of the investigation of the absorption bands of water. Aschkinass[30], one of the earlier workers, used a prism and worked in the region 2.0 μ to 9.0 μ; Tamman[31] also used a prism and studied the band near 4.70 μ; and Ellis[32], Collins[33] and Dreisch[34], with prism and grating spectrometers, have studied the bands. For very long wave-lengths, the residual rays of salt, potassium chloride, and bromide are absorbed completely by a layer of water 1 mm. thick. These rays all lie between the limits 52 μ and 83 μ. Some observations recorded during the course of the present work in the region 2.0 μ - 8.0 μ are described in this chapter, (Section II).

IV) Very intriguing phenomena are noticed when aqueous solutions of substances are examined. Salts which easily form hydrates give aqueous solutions which are more transparent to infra-red radiations than pure water itself. This is a surprising result, and several theories have been advanced to account for it. The solvate theory is probably the one generally accepted. This suggests that the dissolved salts form slightly stable compounds with the water, these salts being more transparent than water in the infra-red regions. Another theory assumes that the water consists of several kinds of molecules which possess different types of infra-red absorption spectra. When the crystals are dissolved in water, probably some of the more transparent molecules are liberated, which causes the solution to be more transparent than the pure liquid. However, there are several facts which are not accounted for by any of these theories, so that further work in this field would help considerably in the elucidation of the outstanding problems.

V. The reflection spectra of the liquids have not been extensively studied. They are, therefore, far less accurately known than those of solids. The reflecting powers, in cases where they have been measured, are found to be very low indeed. The phenomenon of residual rays, which is so pronounced in the case of solids, is non-existent.

Generally speaking, the reflexion spectra of liquids are similar to the absorption spectra. Thus for water, reflexion maxima occur at 3.2, 6.3 and 19.5 μ, and absorption maxima occur at 3.0, 6.25 and 20.0 μ. (It is worth noting that no reflexion maximum has been recorded near 4.70 μ, where an absorption band for water occurs). A similar result is obtained with ethyl alcohol. The majority of this work has been carried out by Rubens[35].

VI) Most studies of the infra-red absorption spectra of liquids show that some connection exists between their infra-red absorption spectra and their chemical constitution. One case of this nature has already been cited, namely, the homologous series of saturated hydrocarbons; and there are others. The spectra of the primary alcohols, i.e., those containing a CH_2OH group, are very similar up to 8.0 μ, both in the position and intensity of the bands. A few feeble bands are the only differences between individual members of the series. The same result is true of the series of secondary alcohols, and the series of tertiary alcohols. The absorption spectra are definitely characteristic for each series, and this is undoubtedly due to the different chemical groups which characterise the three series. Thus, for primary alcohols, strong bands are found at 3.35 μ, 6.2 μ, 7.2 μ and 9.7 μ; for secondary alcohols, bands occur at 3.60 μ, 5.8 μ, 7.0 μ and 9.0 μ; and for tertiary alcohols, at 3.7 μ, 6.1 μ, 7.5 μ, and 8.5 μ. These bands are characteristic of the radicles occurring in the series. Again, aliphatic ketones are found to contain a characteristic band at 5.9 μ; and the aromatic ketones give a double band at 6.20 μ (approx.). Amongst other compounds having similar characteristic bands are the primary amines, secondary amines, aldehydes, isomeric ketones and esters. In some cases where substances have been investigated it has been possible to work conversely, and substances have been identified by means of the characteristic bands of different radicles occurring in their infra-red absorption spectra.

When crystals have been examined, it has been possible to distinguish between "water of constitution" and "water of crystallisation". Salts containing water of crystallisation possess the characteristic bands of water. In other substances, where the water appears to be in chemical combination with the substance, the infra-red absorption spectra show striking effects. In these cases, the infra-red absorption bands of water completely mask the ordinary absorption spectra of the substance. A study of similar cases should give interesting information about the chemical structure of various substances.

VII) In Chapter I, a brief account was given of the theoretical explanation of the absorption bands of solids and gases. This explanation was based on a study of rotation and vibration of the molecules contained in the substances. The explanation of the absorption spectra of liquids is naturally more complex, and only small progress in this direction has been made.

Considering the case of organic liquids containing carbon and hydrogen atoms, it has been found that these all possess bands of approximately the same wave-length. These bands can be attributed to the groups CH_3, CH_2 and CH, or more correctly, to the vibrations of the carbon and hydrogen atoms composing the group. In a similar way characteristic bands have been found for the CCN, CBr, CH_2OH, and NH groups. The bands produced in this way are vibration spectra, and are generally found below 14.0μ.

A consideration of the movements or rotation of the molecule as a whole, shows how the rotation bands may be produced. These rotation spectra are usually found beyond 8.0μ to 10μ. Between 8.0μ and 14.0μ, we have, therefore, a region where rotation and vibration spectra may occur. These theories account reasonably well for the majority of the known facts. They show, for instance, why the members of a homologous series, which contain the same chemical group, should have different absorption spectra in the region beyond 10μ. For it is in this region that the rotation spectra occur; and, since the rotation spectra depend on the Moment of Inertia of the molecule, which varies from member to member in a homologous series, it is reasonable to expect the absorption spectra beyond 10.0μ to vary as we pass from member to member in the series.

Working on these general principles, attempts have been made to treat the absorption spectra of liquids on a mathematical basis. Coblentz, some years ago, suggested that the absorption bands for members of the series of hydrocarbons form a harmonic series. In short, each of the bands is some multiple of a fundamental, or more simply, if ν_0 is the frequency of the fundamental, the frequency of any other band, ν, is given by the relation: $\nu = n\nu_0$, where n is some simple multiple.

Later, work by Kratzer on gases showed that the vibrations of the molecule may be anharmonic. This causes the absorption bands to form an anharmonic series. A correction must be applied for this deviation from the strictly harmonic vibration, and this makes the simple relation given above assume the modified form : $\nu = n\nu_0(1-nx)$

, where x is some constant. This modified relation has explained several of the better known absorption spectra of liquids, and in many cases it has been possible to evaluate the constants in the relation. Moreover, this equation does not exclude the combination of frequencies giving rise to the combination bands. Such combination bands have been definitely observed in the case of gases. An idea of this combination of frequencies may be gained from a study of the relation given below. In this relation, ν is the frequency of the combination band and,

$$\nu = \nu_1 x + \nu_2 y + \nu_3 z + ----$$

where x,y,z are simple multiples, and ν_1, ν_2 and ν_3 -- are the frequencies of the fundamentals. This simple equation accounts for many absorption spectra which would be otherwise inexplicable. For example, the faint absorption bands in the absorption spectra of the aliphatic hydrocarbons are typical cases of combination bands.

Other theories have been advanced by Henri, Bonino and Gapon, but they do not give such satisfactory explanations of all the known facts. These workers have chiefly been concerned in attempts to find a formula to fit their observed results. These attempts have produced nothing better than the simple relation given above, and developed by Kratzer. The theory of the infra-red spectra of liquids presents great difficulties, and it is only by the careful analysis of large collections of experimental observations on the spectra of different liquids, that further progress will be attained.

Section II.

The Absorption Bands of Water.

I) In Chapter III an account was given of some experiments which were made with the apparatus to see if carbon dioxide exhibited any reasonable selective absorption in the region 1.0 μ to 2.0 μ. A wide range of pressures was used for these experiments; some of the experimental results are given in Table XIX, and they are graphically represented in Fig. 29. The results show no traces of selective absorption; in fact, the absorption is practically uniform until the band at 2.72 μ is encountered.

The possibility existed that either an aqueous solution of carbon dioxide or liquefied carbon dioxide might show some selective absorption in the region $1.0\mu - 2.0\mu$. Accordingly, a cell was constructed which could be adapted to contain either of these two liquids, so that an investigation of their absorption spectra could be made. A description of the cell is given in Chapter I. Fluorite plates of thickness 0.5 cms. and reasonably transparent to radiations of wave-length up to 8.0μ, were fitted to the cell. Afterwards, it was thought that it might be possible to fill the cell with an aqueous solution of carbon dioxide, sufficiently concentrated to show the existence of the carbon dioxide band at 2.72μ. This proved to be impossible, and only general absorption was found in the region near 2.72μ.

The experimental method used, is briefly described below. The empty cell was first fixed to a metal slider, which could be placed in the path of the radiation at the point P in the second experimental arrangement. (Fig. 2) It is at the point P that the cone of almost pure radiation is brought to a focus. The metal slider and cell were adjusted so that the central ray of the cone of radiation passed normally through the fluorite plates of the cell. The slider arrangement enabled the cell to be easily moved into, or out of, the path of the radiation. A measurement of the galvanometer deflection for the "in" and "out" positions of the cell was made, and the ratio of the two values was calculated. In the tables given in the remainder of this chapter, the galvanometer deflection for the "in" position is called, "Galvanometer Deflection A", and that for the "out" position is called "Galvanometer Deflection B." The ratio of the two values is given as "% TRANS A/B". The value of this ratio was recorded for several wave-length drum settings, and the absorption curve for the cell itself was plotted. This "blank" test showed that no Spurious bands were produced by the cell, provided that the central ray of the beam of radiation passed normally through the cell. None of the experimental observations recorded in this preliminary survey are included in this account.

II) For the investigation of the absorption produced by carbon dioxide dissolved in water, it was necessary to carry out some preliminary tests with the absorption cell filled with water. A mixture of water and carbon dioxide was afterwards placed in the cell, and the absorption produced by this mixture was measured. By difference, the effect of the dissolved carbon dioxide was elucidated.

The chief water bands of water near 1.20 μ, the region where the carbon dioxide band predicted by Dennison should occur, are at 1.21 μ, 1.45 μ and 1.96 μ (approx..). These bands have been investigated by Henri[36], Collins[39], Dreisch[38] and others. Moreover, Collins was able to show that a displacement of the bands occurred when the temperature of the water was altered. An increase in the intensity of some of the bands with increase of temperature was also noted.

In Table XXVI, and in Figs. 36 and 37, a summary is given of some recorded observations on the absorption bands of water. These measurements were made with the apparatus described in the previous paragraph. Several thicknesses of water film were used for the tests. These thicknesses covered a range of 0.05 cms.; from 0.05 cms. to 0.1 cms. All the corrected absorption curves for the region 1.0 μ - 2.0 μ, show absorption bands at 1.18 μ, 1.45 μ and 1.96 μ. The temperature of the water in the cell was maintained reasonably constant at 28°C. This is an important observation, for it is known that the position of some of the water absorption bands depends on the temperature of the water. The difference of 0.03 μ, between the accepted position of the band at 1.21 μ and the experimental value of 1.18 μ, is accounted for by the difference (= 8.0 degrees centigrade) in the temperature of the water used in the two cases.

TABLE XXVI.

The Absorption Bands of Water in the near infra-red region.

rrected um Reading λ in μ)	% TRANS A/B	Corrected Drum Reading (λ in μ)	% TRANS A/B	Corrected Drum Reading (λ in μ)	% TRANS A/B
1.098	69.5	1.74	62.5	5) 1.563	73.5
1.147	65.9	1.79	49.4	1.583	75.0
1.197	62.5	1.84	30.3	1.605	75.2
1.246	64.8	1.90	17.8	1.626	76.0
1.346	64.4	1.95	13.7	1.646	76.5
1.798	20.9	2.00	16.6	1.666	77.05
1.848	12.6	2.053	22.5	1.687	76.8
1.899	7.42	2.104	30.0	1.708	77.1
1.948	5.2	2.157	29.2	1.728	76.9
1.998	4.85	4) 1.114	83.6	1.75	76.2
2.049	5.5	1.134	81.4	1.771	75.0
2.099	6.39	1.155	79.3	1.791	72.15
2.15	6.50	1.176	79.7	1.812	69.2
2.20	6.10	1.196	81.9	1.833	66.0
1.102	81.1	1.217	81.4	1.853	62.1
1.152	79.5	1.238	80.8	1.874	60.0
1.202	79.2	1.259	80.5	1.896	58.0
1.253	79.34	1.28	80.0	1.916	56.2
1.303	75.0	1.30	81.5	1.938	55.5
1.353	59.6	1.32	79.9	1.959	55.0
1.404	41.46	1.341	78.5	1.979	55.2
1.454	38.7	1.362	74.95	2.000	55.8
1.506	46.6	1.382	70.6	2.021	56.3
1.556	55.6	1.403	66.55	2.042	58.0
1.607	61.34	1.424	67.4	2.093	60.4
1.658	63.0	1.445	67.1	2.145	64.0
1.708	60.6	1.466	66.5	2.197	65.2
1.80	40.2	1.487	68.1		
1.862	24.5	1.508	70.0		
1.913	19.0	1.530	72.5		
1.963	17.78	5) 1.110	84.3		
2.015	20.18	1.13	82.4		
2.066	24.1	1.151	81.0		
2.116	27.1	1.172	79.4		
2.167	27.9	1.193	80.07		
2.217	26.85	1.213	81.5		
2.269	24.5	1.233	81.25		
2.320	20.25	1.254	81.16		
2.370	16.3	1.274	80.4		
2.421	12.92	1.294	80.0		
1.114	87.0	1.315	80.0		
1.166	84.98	1.336	79.1		
1.217	85.9	1.356	76.8		
1.27	84.29	1.377	73.3		
1.32	79.2	1.397	68.9		
1.37	55.5	1.418	66.5		
1.42	35.3	1.438	66.15		
1.476	39.5	1.459	66.3		
1.53	51.8	1.479	67.1		
1.58	61.2	1.500	68.5		
1.63	66.1	1.522	70.5.		
1.684	66.8	1.542	72.3		

TABLE XXVI (contd).

e No.	Prism Temperature.	Wadsworth set at	Entrance Slit	Exit Slit	Thickness of film.
I	27.6°C	27.0°C	5/1000"	2.5/ 1000"	0.1 cms
II	26.4°C	"	"	"	0.05 "
III	22.9°C	"	"	"	0.05 "
IV	22.95°C	"	"	"	0.01 "
V	24.0°C	"	"	"	0.01 "

A careful examination of the absorption curves of water drawn from these experimental results (Figs. 36 and 37), shows that absorption bands occur at 1.18 μ , 1.45 μ , and 1.96 μ . The band at 1.45 μ has undoubtedly the greatest intensity; the bands at 1.18 μ and 1.96 μ are only weak ones. An interesting point arises from the results obtained with different slit widths of the spectrometer. A reduction of 50% in the width of the slit increases the resolving power of the apparatus and gives a more defined absorption maximum. The same effect is produced by diminishing the thickness of the liquid layer used in the experiments. The effect produced on these bands by dissolving carbon dioxide in the water, is discussed in Section IV of the present chapter.

III. The positions of the bands in the region from 2.0 μ to 7.0 μ are not accurately known. It is extremely difficult to obtain accurate results, because of the extreme opacity of water to radiations whose wave-lengths lie in that region. Many workers have attacked the problem, the chief of them being Tamman 39), Collins 40), Dreisch 41) and Reinkober 42). It appears that the infra-red absorption bands of water occur near 3.0 μ, 4.70 μ, and 6.0 μ; the positions, with the possible exception of the weak band at 4.7 μ, are not known accurately. These workers obtained the absorption curves with apparatus which had been calibrated in the particular region concerned, without reference to any bands which occur in other parts of the spectrum. Some experiments have been made with the present apparatus, and these will now be discussed. It will be remembered that the present apparatus was calibrated against bands and emission lines in the region 1.0 μ - 4.0 μ, so that the positions of the water bands in the region 2.0 μ - 6.0 μ, determined with this apparatus, are obtained relative to such well known bands and emission lines.

The cell was filled with water, and observations were recorded in the usual way. It was soon found that only very thin films of water will transmit radiations of wave-length greater than 3.0 μ, and some of the films used in the final experimental work were only 1/100 mm. in thickness. The thickness of the films was measured by means of a Michelson Interferometer in the usual way.

An interesting method for building up such films was devised, and a brief description of the method may not be out of place. The two fluorite plates of the observation cell were removed, and a layer of liquid was poured into the surface of one of them. The other plate was placed over this, and the two plates, with the film of water between them, were placed in the cell holder previously described. The screw-cap was then screwed up quite tightly. Slight evaporation took place from a cell constructed in this way, but this was overcome by painting shellac varnish over the edges of the cell. No further troubles due to evaporation from the cell were encountered after this method of sealing the cell was adopted.

In Table XXVII, a record is given of some observations made with cells of this type, the thickness of liquid film used being $\frac{1}{2}$mm. and 1/200 mm. The corresponding absorption curves are reproduced in Fig. 38. These absorption curves show maximum absorption at 2.94 μ. An inspection of curve No.2, which corresponds to a liquid layer of $\frac{1}{2}$ mm., shows that a layer of this thickness gives only general absorption in this region. The temperature of the water used for the experiments was 28°C. The generally accepted value for the wave-length of maximum absorption is 3.0 μ. Now the experimental results summarised in Table XXVII give a value of 2.94 μ, a difference of 0.06 μ. This discrepancy is probably due to the difference in temperatures of the water used for the different experimental estimations. This is a point which should be investigated in future work. The band of water vapour near 3.0 μ is known to occur at 3.11 μ, and it is quite conceivable that a shift in the band takes place as the liquid phase is approached. A spectrometer of very high resolving power would be required for this work.

TABLE XXVII

Observations showing the absorption produced by water in the near infra-red region round 3.0 μ.

Corrected rum Reading λ in μ)	% TRANS A/B	Corrected Drum Reading (λ in μ)	% TRANS A/B	Corrected Drum Reading (λ in μ)	% TRANS A/B
2.535	90.0	2.831	7.2	3.054	31.6
2.586	86.9	2.872	5.8	3.102	36.7
2.637	79.1	2.912	3.8	3.151	43.3
2.688	69.2	2.954	3.3	3.200	49.9
2.738	58.8	2.994	2.1	3.248	56.2
2.789	50.2	3.033	2.6	3.296	63.4
2.840	43.6	3.073	1.2	3.338	68.6
2.890	41.1	3.111	0.94	3.345	70.4
2.941	40.05	3.15	1.25	3.387	74.2
2.99	42.2	3.228	1.6	4 2.637	78.5
3.04	45.85	3.267	1.9	2.688	73.9
3.088	51.6	3.314	4.4	2.738	67.7
3.137	58.2	3.318	4.2	2.789	63.9
3.186	64.4	3.356	8.3	2.840	61.8
3.235	68.6	3.405	12.3	2.890	60.99
3.283	74.3	3 2.651	69.3	2.941	60.7
3.332	78.3	2.692	60.4	2.99	62.0
3.380	81.7	2.732	50.9	3.04	63.96
3.429	85.9	2.773	43.1	3.088	67.3
3.478	87.3	2.813	35.5	3.137	71.1
3.526	89.2	2.854	31.5	3.144	70.8
2 2.669	23.7	2.894	27.3	3.186	74.8
2.710	17.7	2.935	26.5	3.193	74.05
2.750	13.4	2.975	26.3		
2.791	9.9	3.014	28.1		

Case No.	Prism Tempre.	Wadsworth set at	Entrance Slit	Exit Slit	Thickness of film	% TRANS
I	25.5°C	27.°C	2.5/1000"	2.5/1000"	1/1000 mm	41
II	23.2°C	27 °C	"	"	½ mm.	4
III	24.5°C	27 °C	"	"	1/50 mm.	26
IV	25.4°C	27 °C	"	"	1/200 mm	61

A simple analysis of the results given in Table XXVII discloses an interesting fact. When values of the mimimum transmission for different thicknesses of film are plotted against the corresponding values of film thickness, an exponential curve is obtained. The transmission power, in the region of greatest absorption, diminishes exponentially as the thickness of the film is increased. If T is the value of the minimum transmission, and D is the value of the corresponding thickness of film, then the two factors are connected by the relation,

$$T = T_0 e^{-ad}$$

where T_0 is the transmission power corresponding to zero thickness of liquid film, and a is a constant factor.

IV. The absorption spectrum for water in the region 4.5 μ to 6.0 μ was afterwards investigated. All the experimental curves reveal a faint band at 4.7 μ, and several experiments had to be made before the most favourable thickness of film was discovered. Very thin films did not show the selective absorption very clearly, and thicker films gave more or less intense absorption. A film of thickness 1/250 mm. was finally chosen and this film gave a very sharply defined absorption band at 4.7 μ , a transmission power of 20% being obtained near the maximum of absorption. The corrected absorption curve gave 4.68 μ as the position of the absorption maximum, when the temperature of the water in the cell was maintained reasonably constant at 28°C. Most other observers have given the position of maximum absorption as 4.7 μ . The discrepancy equal to 0.02 μ is no doubt due to the difference in temperature of the water used for the various investigations. However, it is noteworthy that Tamman, during his researches on this band, proved that it existed in the absorption spectra of water and water vapour. He records its wave-length as 4.70 μ . There is no other experimental evidence regarding the variation of its position with temperature, and this is a point which should be investigated in the near future.

In this paper, the experimental results for only two different films thicknesses are given. Other values were derived, but the absorption curves plotted from them are not of very great interest. The experimental observations are tabulated below in Table XXVIII, and the corresponding absorption curves have been drawn in Fig. 39. Both curves show maximum absorption at 4.68 μ , and there is a minimum in the curves at 5.30 μ . The absorption band is so feeble that an increase of 20% in the thickness of film only increases the percentage absorption at the maximum by 3% . (See Fig. 39).

TABLE XXVIII

Experimental results showing the Absorption produced by water in the region 4.0 μ to 5.0 μ.

Corrected rum Reading (λ in μ)	% TRANS A/B	Corrected Drum Reading (λ in μ)	% TRANS A/B	Corrected Drum Reading (λ in μ)	% TRANS A/B
3.83	53.5	4.762	19.7	5.687	19.0
3.879	52.8	4.814	21.0	5.738	14.7
3.927	51.96	4.864	22.5	2 4.328	30.4
3.975	50.1	4.914	24.3	4.376	27.8
4.024	48.4	4.968	26.8	4.426	25.4
4.072	46.4	5.018	29.1	4.475	23.5
4.121	44.07	5.02	28.8	4.525	21.7
4.170	41.0	5.07	32.2	4.575	20.5
4.218	37.1	5.123	33.8	4.624	20.0
4.267	32.9	5.174	35.2	4.674	20.0
4.315	29.5	5.225	35.97	4.724	20.2
4.363	26.8	5.277	36.1	4.765	21.2
4.412	24.5	5.328	35.96	4.827	22.6
4.461	22.6	5.379	35.5	4.878	24.4
4.511	20.8	5.431	34.1	4.929	26.4
4.561	19.4	5.482	32.8	4.981	28.9
4.61	18.6	5.534	30.0	5.031	30.9
4.66	18.0	5.585	26.8	5.081	32.5
4.710	18.8	5.636	23.1	5.110	32.8

Case No.	Prism Tempre.	Wadsworth set at	Entrance Slit	Exit Slit	Thickness. of film.
I.	22.8°C	27.0°C	7.5/1000"	5/1000"	1/200 mm.
II	24.3°C	27.0°C	"	"	1/250 mm.

V. Early measurements of the absorption spectrum of water in the region between 6.0 μ and 7.0 μ showed that an absorption band exists close to 6.0 μ. In Table XXIX are some of the results obtained during the measurement of the absorption produced by water in this region. The investigations show that the band is quite strong, and to get good definition of the absorption band only thin films of water should be used in the absorption cell. Three different cases have been chosen for the purposes of illustrating this paper; the three thicknesses of the water film being 1/100 mm, 1/200 mm, and 1/250 mm. Corresponding absorption curves have been drawn in Fig. 40, and these suggest that the absorption increases as the thickness of liquid film is increased. This fact itself shows that the band is due entirely to water. A fair estimate of the wave-length of maximum absorption derived from these results is 6.10 μ. A slight "kink" in the curve at 6.62 μ, for a film of thickness 1/200 mm, remains unexplained. Only freshly distilled water was used for the experiments, and several independent surveys of this region showed the same dip in the absorption curve. The dip does not appear in the absorption curves plotted for different thicknesses of liquid film, and a survey of the empty cell in the same region did not disclose any selective absorption by the cell near 6.6 μ. No explanation of this "kink" in the absorption curve was discovered.

TABLE XXIX

Experimental Observations on the Absorption Spectrum of water in the region 6.0 μ to 7.0 μ .

rrected m Reading (λ in μ)	% TRANS A/B	Corrected Drum Reading (λ in μ)	% TRANS A/B	Corrected Drum Reading (λ in μ)	% TRANS A/B
5.829	74.1	6.047	67.2	3 6.186	60.0
5.860	70.1	6.097	64.4	6.235	61.16
5.931	67.2	6.147	65.2	6.283	62.26
5.982	64.6	6.197	67.4	6.332	64.75
6.032	63.2	6.240	70.1	6.38	66.4
6.082	62.1	6.294	73.3	6.428	68.0
6.132	61.9	6.342	75.8	6.477	69.4
6.182	64.0	6.390	78.0	6.524	70.6
6.231	65.3	6.438	79.6	6.572	71.2
6.279	68.7	6.486	80.7	5.834	68.9
6.327	70.0	6.534	81.0	5.885	65.5
6.376	72.9	6.582	81.8	5.936	63.1
6.424	74.3	6.630	81.5	5.987	61.6
6.473	75.7	6.674	81.7	6.037	60.5
6.521	76.0	6.722	81.5	6.086	59.2
6.569	77.1	3 5.732	75.5	6.136	59.5
6.617	76.8	5.782	72.0	6.186	60.0
6.622	75.8	5.834	68.1	6.235	61.6
6.670	76.3	5.885	65.4	6.283	63.0
6.717	76.1	5.936	62.9	6.332	64.6
5.845	86.0	5.987	61.5	6.380	66.9
5.896	80.8	6.037	60.0	6.428	67.9
5.946	74.8	6.086	59.4	6.477	70.2
5.997	70.3	6.136	59.3		

Case No.	Prism Tempre.	Wadsworth set at	Entrance Slit	Exit Slit	Thickness of film.
I	25.°C	27 °C	7.5/1000"	7.5/ 1000"	1/200 mm.
II	23.9°C	27°C	"	"	1/250 mm.
III	25.2 C	27 C	"	5/1000"	1/100 mm.

SECTION III.

The Absorption Bands of Ethyl Alcohol.

1. Some interesting results obtained with pure dry ethyl alcohol in the cell will now be given.

Many research workers have investigated the infra-red absorption spectrum of ethyl alcohol. In the near infra-red, i.e., from 1.0 μ - 2.0 μ , the bands appear to be well defined, but at higher wave-lengths the results of different workers are not in complete agreement. The chief work has been done by Lecomte 43), Meyer, Bronk and Levin 44), Plyler and Burdine 45), Smith and Boord 46), V. Henri 47), and Reinkober 48).

Lecomte, using a prism, found the positions of maximum absorption to be 3.0 μ , 3.5 μ , 6.85 μ , and 8.0 μ . The bands at 3.5 μ and 6.85 μ were feeble ones. Henri found a band at 3.34 μ , and others at 3.05 μ and 5.00 μ . M$\overset{e}{\text{a}}$yer, Bronk and Levin found pronounced bands at 3.36 μ and 3.45 μ . Their results are summarised in table No.XXX below.

TABLE XXX

The Absorption Bands of Ethyl Alcohol by different observers.

Worker.	Bands observed at (* Faint Bands)				
Lecomte	3.0μ	$\overset{*}{3.5}\mu$	-	6.85μ	$\overset{*}{8.0}\mu$
Henri	3.05μ	3.34μ	5.0μ	-	-
Meyer Levin	-	3.36 & 3.45μ	-	-	9.3μ
Present Work	3.05μ	3.41μ	5.90μ 6.05	7.2μ	9.5μ

The results given by various workers differ considerably, and because of these discrepancies, an independent set of observations was made. The investigation made was only a very short one, but it sufficed to show the positions of the main absorption bands. The wave-length of the observed bands are included in Table XXX for the purposes of comparison. The results differ from those of previous workers, and a probable explanation of these differences is given later in this section.

II. In Table XXXI, a summary is given of the experimental results obtained during the investigations of the absorption spectrum of ethyl alcohol in the region 1.0 μ to 2.0 μ . The corresponding absorption curves are plotted in Fig. 41. Results are given for two different thicknesses of liquid film, namely, 1.0 mm. and 0.75 mm. The curves show maximum absorption at 1.17 μ , 1.48 μ , 1.65 μ , and 2.41 μ , with possibly a slight absorption at 1.95 μ .

The bands at 1.18 μ and 1.48 μ may be due to the (OH) group in the ethyl alcohol molecule. It will be remembered that with water, bands were found at 1.18 μ and 1.48 μ . The bands at 1.18 μ and 1.48 μ for ethyl alcohol may have similar origin, for the (OH) radicle is common to both liquids. It would be extremely interesting to see if these bands disappear in the case of compounds made from ethyl alcohol in which the (OH) group has been substituted by some other radicle.

TABLE XXXI.

The Absorption Bands of Ethyl Alcohol in the region 1.0 μ to 2.5 μ.

Corrected Drum Reading (λ in μ)	% TRANS A/B	Corrected Drum Reading (λ in μ)	% TRANS A/B	Corrected Drum Reading (λ in μ)	% TRANS A/B
1 1.114	79.5	2.209	27.1	1.788	71.2
1.166	77.3	2.26	23.5	1.839	66.1
1.217	78.48	2.312	20.84	1.89	61.8
1.270	79.5	2.364	18.8	1.945	58.2
1.321	76.1	2.415	18.2	1.997	56.6
1.372	69.1	2.467	18.5	2.049	55.4
1.424	61.7	2.518	18.31	2.100	53.9
1.476	59.5	2.570	16.18	2.152	49.7
1.530	59.7	3 1.113	81.7	2.204	45.0
1.58	61.5	1.165	80.2	2.256	40.3
1.633	59.5	1.215	80.5	2.307	37.2
1.684	60.7	1.267	81.7	2.36	34.7
1.737	62.5	1.319	81.3	2.409	33.4
1.79	59.4	1.370	76.0	2.461	33.6
1.843	51.7	1.422	70.2	2.513	34.1
1.896	46.7	1.474	69.1	2.564	32.3
1.949	43.6	1.526	68.9		
2.000	41.8	1.578	70.0		
2.053	40.9	1.630	69.5		
2.104	39.0	1.681	69.8		
2 2.157	33.4	1.734	71.2		

Case No.	Prism Tempre.	Wadsworth set at	Entrance Slit	Exit Slit	Thickness of film
I	23.1°C	27.°C	2.5/1000"	2.5/1000"	1 mm.
II	23.4°C	27.°C	2.5/1000"	2.5/1000"	0.75 mm.

III. An investigation of the absorption effects produced in the region 2.0 μ to 4.0 μ was then made. In Table XXXII, a summary is given of the experimental values obtained for the absorption in this region. The recording of these observations was made in the usual manner. Three different thicknesses of liquid film was used, and in each case there was definite evidence of the existence of two absorption bands in this region. The thicknesses of film used for the experiments were 1.0 mm, 0.5 mm, and 0.7 mm. The absorption curve for the film 1mm. thickness shows that nearly all the radiation between wave-lengths 2.8 μ & 3.8 μ is cut off by such a film. However, even with such strong absorption, it is possible to distinguish the two maxima of absorption. All the absorption curves are drawn in Fig.42. Two bands are disclosed, one at 3.05 μ , and the other at 3.41 μ . It would appear that the best definition of the band at 3.05 μ is given by a liquid film of thickness 0.7 mm, and for the band at 3.41 μ , better definition is given by a film of thickness equal to 0.5 mm. The correct thickness of film for good definition of the bands is very important, and experiments must always be made to determine this thickness before the main investigations are carried out. If this is not done, it is possible for very weak bands to be completely masked by a more general absorption.

TABLE XXXII

The Absorption Spectra of Ethyl Alcohol in the region 2.5μ - 4.0μ .

Corrected Drum Reading (λ in μ)	% TRANS A/B	Corrected Drum Reading (λ in μ)	% TRANS A/B	Corrected Drum Reading (λ in μ)	% TRANS A/B
1)		2)		3)	
2.870	8.2	3.459	68.2	2.939	39.6
2.92	5.3	3.508	71.05	2.99	35.3
2.971	4.0	3.556	73.8	3.039	34.6
3.02	3.16	3.654	81.3	3.089	38.3
3.07	3.2	3.703	83.9	3.137	42.8
3.118	3.1	3.752	86.1	3.186	45.6
3.166	3.94	3.801	87.9	3.235	50.3
3.215	4.1	3.849	88.9	3.284	53.2
3.264	3.4	3.898	90.2	3.332	54.0
3.313	3.95	3.937	90.5	3.381	54.1
3.361	4.7	3.985	90.9	3.43	55.7
3.41	7.59	4.034	91.2	3.48	58.7
3.459	10.6	4.083	92.3	3.53	63.4
3.507	16.36	4.132	92.2	3.58	68.9
3.556	22.2	4.18	91.5	3.625	73.3
3.605	29.65	4.23	92.5	3.674	76.7
3.654	36.8	4.278	92.6	3.713	80.3
3.703	43.8	4.327	90.6	3.762	83.2
2) 2.767	83.0	4.375	97.3	3.811	85.2
2.818	76.7	4.424	93.3	3.859	86.9
2.869	65.3	4.474	93.2	3.908	87.8
2.919	58.0	3) 2.505	89.9	3.957	88.9
2.97	53.1	2.555	89.5	4.005	89.5
3.07	50.3	2.585	84.5	4.054	90.6
3.12	53.6	2.635	83.1	4.103	89.3
3.215	61.7	2.686	81.06	4.152	90.6
3.264	65.8	2.737	77.7	4.20	91.5
3.313	67.2	2.787	68.3	4.239	92.0
3.361	67.1	2.838	57.4		
3.41	67.2	2.889	47.3		

Case No.	Prism Tempre.	Wadsworth mirror set at	Entrance Slit	Exit Slit	Thickness of film.
I	23.4°C	27 °C	4/1000"	4/1000"	1.0 mm.
II	23.4°C	27 °C	"	"	0.5 mm.
III	22.1°C	27 °C	5/1000"	2.5/1000"	0.7.mm.

IV. An examination of the spectrum in the region 5.0μ to 8.0μ was also made. Only one set of the observations—recorded in Table XXXIII-are given in this paragraph. The corresponding absorption curve is given in Fig.43. In this curve, it is possible to distinguish maxima of absorption at 5.90μ, 6.05μ, 6.96μ, 7.2μ, and 7.5μ. The bands at 5.90μ and 6.05μ are quite faint. The band at 6.05μ is interesting, because it is very similar to the band at 6.10μ observed in the infra-red absorption spectrum of water. It is probably due to the (OH) radicle in the molecule, a view which is supported by the similarity of this band and the corresponding water band; and the (OH) radicle is common to both ethyl alcohol and water. If this is the case, it would fall in with the other members of wave-lengths 1.48μ and 3.05μ, to form a harmonic series. (1.48μ, 3.05μ and 6.05μ). The band at 1.18μ, which is quite a feeble band, is no doubt a combination band. It could arise from a suitable combination of the frequencies of the bands at 3.05μ and 6.05μ, which would then be the fundamentals of the band. The frequency of the band at 1.18μ is 8474 cm^{-1}, the band at 3.05μ has a frequency of 3278 cm^{-1}, and the one at 6.10μ is 1639 cm^{-1}.

Now 8474 is approximately equal to

$$2 \times 3278 + 1629$$
$$= 8195$$

so that $\gamma = 2\gamma_1 + \gamma_2$

where $\gamma_1 \equiv 1{\cdot}18\mu, \gamma_1 \equiv 3.05\mu$ and $\gamma_2 \equiv 6.10\mu$.

γ = frequency of the combination band, γ_1 & γ_2 are the frequencies of the two fundamentals.

TABLE XXXIII

The Absorption Bands of Ethyl Alcohol in the region $5.0\,\mu$ to $8.0\,\mu$.

Corrected rum Reading (λ in μ)	% TRANS A/B	Corrected Drum Reading (λ in μ)	% TRANS A/B	Corrected Drum Reading (λ in μ)	% TRANS A/B
5.551	91.5	6.358	86.3	7.127	62.3
5.602	90.7	6.396	85.9	7.178	62.0
5.653	90.4	6.444	83.5	7.23	63.8
5.704	88.7	6.49	83.7	7.278	67.3
5.756	87.2	6.54	82.2	7.33	68.3
5.807	86.1	6.59	78.7	7.38	68.1
5.859	84.37	6.64	77.7	7.431	67.6
5.91	84.38	6.69	75.3	7.481	66.4
5.96	84.8	6.73	71.1	7.532	66.9
6.012	83.5	6.782	67.9	7.539	65.8
6.062	83.3	6.832	65.0	7.589	66.9
6.112	85.5	6.882	63.1	7.641	70.4
6.162	85.25	6.93	62.56	7.691	71.2
6.212	86.1	6.98	61.1	7.742	73.05
6.261	86.4	7.027	62.1	-	-
6.309	86.7	7.077	63.0		

Thickness of film - 1/5°mm.

Wadsworth mirror set at 27°C Exit Slit 7.5/1000"

Prism Temperature 23.4°C Entrance Slit 5/1000"

SECTION IV

Infra-Red Absorption Spectra of Some Aqueous Solutions.

I. In Chapter III mention was made of a paper published by Dennison, in which he predicted that an infra-red absorption band for carbon dioxide should occur at 1.20 μ. An investigation during the experiments on gases with carbon dioxide in the observation tube, did not reveal any traces of selective absorption by carbon dioxide in this region. The experimental results obtained during the investigation are given in Chapter III, Table XIX, and the corresponding absorption curves are drawn in Fig.29. It was therefore decided to study the infra-red absorption spectrum of water containing carbon dioxide, in the hope that the band at 1.20 μ would be more pronounced under such conditions. Many experimental determinations of the absorption effects produced by a solution of carbon dioxide were made, to see if the dissolved carbon dioxide showed any traces of absorption near 1.20 μ. Several thicknesses of liquid layer were used, but none of the results for these showed any trace of absorption near 1.20 μ, other than that due to water. The results of one of these experiments are tabulated in Table XXXIV, Case I, and the corresponding absorption curves are drawn in Fig. 44. The transmission powers in the Table A are for a given thickness of freshly distilled water in the cell; those summarised in Table B are for a corresponding thickness of water containing dissolved carbon dioxide. The graph drawn in Fig.44 shows that all the results lie on the same curve, showing that the carbon dioxide dissolved in the water is either insufficient to produce selective absorption near 1.20 μ, or that the carbon dioxide itself has no absorption band in this region.

With the same solution, an investigation was made of the absorption spectrum near 2.80 μ. Some of the results are also tabulated in Table XXXIV, Case II, and the corresponding absorption curves are drawn in Fig. 44. The curve shows that there is no absorption at 2.72 μ due to the carbon dioxide; only general absorption due to the water is found round 3.0 μ. A thicker film of water containing carbon dioxide transmitted no radiation of wave-length greater than 2.5 μ, and a thinner film of water showed no traces of absorption at 2.72 μ. The experimental results, on which these conclusions are based, have not been given in detail in this account.

Apparently, therefore, there was insufficient carbon dioxide dissolved in the water to produce the characteristic absorption band of carbon dioxide at 2.72 μ. The results for the region round 1.20 μ are therefore not surprising. It is hardly possible for a liquid containing a very small quantity of dissolved gas to show selective absorption at 1.20 μ, when no selective absorption is found corresponding to the strong absorption band of the gas at 2.72 μ. Many experimental observations on the system of water containing dissolved carbon dioxide confirm this view.

The question of the band at 1.20 μ will have to remain until an investigation of the absorption spectrum of the liquefied gas can be carried out. All the experimental results discussed in this paragraph are summarised in the table below.

TABLE XXXIV.

The Absorption Spectrum of water containing dissolved carbon dioxide.

Part A: Water in the Cell.			Part B: Water + Carbon Dioxide.		
Drum Reading (λ in μ)	Corrected Drum Reading (λ in μ)	% TRANS A/B	Drum Reading (λ in μ)	Corrected Drum Reading (λ in μ)	% TRANS A/B
I) 1.069	1.059	79.1	1.06	1.06	79.7
1.10	1.099	72.7	1.08	1.08	79.6
1.14	1.139	51.99	1.10	1.10	75.26
1.18	1.179	40.97	1.12	1.12	65.7
1.20	1.200	39.7	1.14	1.14	54.2
1.22	1.218	39.67	1.16	1.16	45.2
1.24	1.24	39.0	1.18	1.18	40.9
1.26	1.258	36.9	1.20	1.20	40.0
1.28	1.278	31.1	1.22	1.22	39.1
1.30	1.298	24.4	1.26	1.26	37.8
I) 2.65	2.653	36.48	2.60	2.602	47.28
2.70	2.703	27.3	2.65	2.653	36.8
2.75	2.754	18.9	2.70	2.703	26.2
2.80	2.805	13.1	2.75	2.754	17.5
2.85	2.855	8.95	2.80	2.805	11.79
2.90	2.906	7.00	2.85	2.855	8.0
2.95	2.955	5.23	2.90	2.906	6.3
3.00	3.005	4.3	2.95	2.955	5.3
3.05	3.054	4.16	3.00	3.005	3.8
3.10	3.102	3.8	3.10	3.102	3.05
3.15	3.151	3.7	3.15	3.151	3.2
3.20	3.20	3.9	3.20	3.201	3.5
3.25	3.249	4.7	3.26	3.261	4.5
3.3	3.297	5.4	3.31	3.31	5.7

Case No.	Prism Tempre.	Wadsworth set at	Entrance Slit	Exit Slit	Thickness.
I	26.6°C	27.0°C	2.5/1000"	2.5/1000"	1/40 mm.
	27.2°C	27.0°C	2.5/1000"	2.5/1000"	
II	28.0°C	27.0°C	2.5/1000"	2.5/1000"	

II) A few interesting results obtained with an aqueous solution of potassium permanganate are included here. A liquid film of 1/100 mm. thickness was used for the tests, and the results obtained with this film are summarised in Table XXXV. The corresponding absorption curve is drawn in Fig. 45. This curve shows the relationship between the transmission power of the cell, when filled with the aqueous solution, and the wavelength of the radiations used. It reveals a band due to potassium permanganate at 5.52μ. It is definitely due to the permanganate, for when the cell is filled with freshly distilled water, the absorption band is not obtained. So far as the present writer is aware, the existence of this band has never previously been reported.

TABLE XXXV.

The Absorption Spectrum of an Aqueous Solution of Potassium Permanganate ($KMnO_4$).

Corrected Drum Reading (λ in μ)	% TRANS A/B	Corrected Drum Reading (λ in μ)	% TRANS A/B	Corrected Drum Reading (λ in μ)	% TRANS A/B
x 5.407	92.9	5.715	85.1	6.012	60.8
5.459	91.4	5.766	82.0	6.062	59.2
5.509	88.95	5.817	78.6	6.112	58.2
5.561	89.8	5.869	75.5	6.162	59.6
5.612	90.9	5.92	70.1		
5.663	88.6	5.961	66.2		

x Intermediate values not included.

Prism Temperature 22.5°C Entrance Slit 7.5/1000"
Wadsworth Mirror set at 27.0°C Exit Slit 5/1000"
Thickness of film - 1/100 mm.

CHAPTER V.

SUMMARY and BIBLIOGRAPHY.

Section I.

SUMMARY.

I) An infra-red spectrometer has been set up complete with all the necessary accessories for use in the accurate investigations of infra-red absorption spectra of solids, liquids, and gases over a wide range of pressures.

II) The spectrometer used during the work was a large-scale model "Infra-Red Spectrometer" supplied by A. Hilger, Ltd., and fitted with a rock-salt prism, Wadsworth mirror device and specially calibrated wave-length scale. This scale was re-calibrated by a method similar to that described by Sir R. Robertson in his paper[10], using the values ~~of the~~ values of the refractive index of rock-salt quoted by Paschen[18]. These values were corrected to one standard temperature of 18°C by means of the coefficient of change of refractive index with temperature, given by Schaefer and Matossi[19]. A chart showing the observed errors in this calibrated wave-length scale at different wave-lengths has been compiled.

III. The effect of adjusting the Wadsworth mirror was fully investigated. Several graphs have been drawn to illustrate the absorption bands of calcite observed with different settings of the Wadsworth mirror. In these graphs, the effects of altering the Wadsworth mirror setting are clearly demonstrated. Similar illustrations are afforded by some observations on the positions of inflexion in the emission curves

curves of the Nernst filament. It was found that the points of inflexion changed as the adjustment of the mirror was altered.

IV) Nernst filaments were used as a source of radiation, the filament current being accurately controlled by means of the potentiometer device mentioned by Sir R. Robertson[10].

V. The calibration of the wave-length drum of the spectrometer was found to depend on the temperature of the rock-salt prism, due to the variation of the refractive index of rock-salt with temperature. This point was also stressed by Sir R. Robertson. A calculation of the change in the calibration with temperature was undertaken, and all the wave-length drum observations taken during the experiments at different prism temperatures were corrected to one standard temperature of 18°C. The effect of these changes in prism temperature has been illustrated by experimental observations on the absorption bands of calcite made at different prism temperatures. It was found that the positions of the bands, as given by the apparatus, varied as the temperature of the prism was altered. Graphs are included in the account to show the actual displacement of the bands; and for the purpose of comparison, the same curves corrected to 18°C are also shown. It will be seen that, provided the corrections for the prism temperature variations are applied, the same consistent position is given by the instrument for the maximum absorption - no matter what value the prism temperature may have.

The actual study of the errors caused by changes in the prism temperature showed that the errors fall into two classes :

a) Error due to the Wadsworth mirror being set at a prism temperature different from the standard temperature of 18°C. This error is very small for wave-lengths less than 8.0μ, provided the temperature difference does not exceed four degrees centigrade.

b) Error due to the actual observations being made with a prism temperature different from that at which the Wadsworth mirror is set. This error has its greatest value for wave-lengths below 8.0μ.

All the wave-length drum readings given in this account have been corrected for these two errors, and the values of these essential corrections appear in the tables given in Chapter II. The values of the corrections have not been given in the tables in the other chapters. It cannot be too strongly emphasised that for accurate values of wave-length to be obtained, these corrections must be applied whenever any one of the two conditions given above is fulfilled. It is absolutely necessary to know, therefore, the exact value of the prism temperature when the Wadsworth mirror is set, and also the prism temperature when the final observations are being made. Many previous workers have tried to maintain a constant prism temperature, but it is not always possible to have such favourable conditions; it is far better, and more practicable, to note the prism temperature variations and to apply the necessary corrections for them. The makers of the instrument claim an accuracy for the instrument of 0.03 μ at 4.7 μ; provided the three corrections are applied as outlined above, there is no reason why observers should not be able to obtain an accuracy of .005 μ throughout the whole working-range of the spectrometer (1.0 μ - 15.0 μ). There is no record of any previous work with a rock-salt prism in the region 1.0 μ to 8.0 μ, where such an accuracy has been obtained. Experimenters have usually preferred to work with quartz and fluorite prisms in this region, chiefly on account of their greater dispersion and freedom from very large variations of refractive index with change of temperature. Undoubtedly, the dispersion of the rock-salt prism is not very good in this region, so that the bands occurring in the region from 1.0 μ - 8.0 μ cannot be fully resolved. Nevertheless, the wave-length of maximum absorption (especially in the case of gases where the absorption bands are sharp and well defined), can be accurately determined; the results on the bands of carbon dioxide at 2.72 μ and 4.25 μ confirm this view.

VI. An actual determination was made of the range of wave-lengths embraced by a definite slit-width of the thermopile slit of the spectrometer for different settings of the wave-length drum. The value of this term, called the "slit-width", has been plotted against wave-length, and the resultant curve shows a maximum value for the slit-width at 2.50 μ. The "resolving power" of the spectrometer is inversely proportional to the value of the "slit-width", and the slit-width wave-length curve shows that the resolving power is least at a wave-length of about 2.5 μ, and gradually increases as the wave-length is increased. It has its greatest value in the region beyond 8.0 μ.

In the earlier stages of the work, the wave-lengths for some absorption maxima, when observed with different slit-widths of the spectrometer, appeared to be proportional to the value of the slit-width. It was found, however, that when corrections were applied for the differences in prism temperature, this relationship disappeared, and all the results were identical, regardless of the value of the slit-width used for their elucidation.

VII) The calibration and Wadsworth mirror setting were checked against the strong emission line of the mercury spectrum at 1.014 μ, and several absorption bands of calcite. Some of the actual observations recorded during this check are reproduced in the account.

VIII) The infra-red absorption spectrum of carbon dioxide was then investigated; the experiments showed that bands occur at 2.72 μ, 4.25 μ and 14.87 μ. No selective absorption by the gas in the region 1.0 μ - 1.50 μ could be detected.

Absorption bands of nitric oxide were found at 5.29 μ, and 2.68 μ. The latter was predicted by Snow in his paper. There was no selective absorption shown by the gas at 1.60 μ, where a second harmonic should occur.

A wide range of pressures was used in these investigations, which revealed that a simple relationship exists between the value of the maximum absorption and the values of the gas pressure. The increase in the value of the maximum absorption is proportional to the corresponding increase in gas pressure. Only a few of the many results obtained in support of this view are included in this paper. A large number of duplicate readings are included in order to demonstrate the accuracy of the experimental method. All the diagrams are actually copies of untouched experimental curves, and almost without exception, the duplicate readings follow closely the first experimental observations. This is noteworthy, when it is considered that on some occasions a change of six degrees centigrade occurred in the prism temperature between the recording of the duplicate observations.

IX) The weak band at 1.20 μ predicted by Dennison for carbon dioxide could not be detected with the apparatus, although very high pressures of gas were used in the gas observation tubes. It was thought possible that the band might be more pronounced in an aqueous solution of carbon dioxide or with liquefied carbon dioxide. A cell was therefore constructed for work on liquids, so that an investigation of this point could be made.

During this work on liquids, some interesting figures for the absorption spectrum of pure distilled water were obtained. Absorption bands were found at 1.18 μ, 1.45 μ, 1.96 μ, 2.94 μ, 4.70 μ, 6.09 μ, when the temperature of the water was 28°C. Authorities can only say that absorption bands of water occur at about 3.0μ, 4.7μ, and 6.0μ, whereas the absorption bands of water vapour are known to occur definitely at 3.11μ, 4.7μ and 6.26μ. Moreover, Collins has shown that a displacement and alteration in intensity of the bands at 1.18μ, 1.45μ and 1.96μ occurs as the temperature of the water is altered. A suggestion is made that a similar displacement may occur with the water bands of higher wave-length. This will make an interesting study for future work.

Some interesting figures for the absorption spectrum of ethyl alcohol were also elucidated, and these are included in the account. Different thicknesses of liquid film were used and the results showed that absorption bands occur at 1.17μ, 1.48μ, 1.65μ, 2.41μ, 3.00μ, 3.41μ, 5.9μ, 6.05μ, 6.96μ, 7.20μ and 7.5μ. These figures are contrasted with those obtained by previous workers,and the differences are discussed. The similarity of some of the bands with those of water is also noted; this similarity is no doubt due to the bands being formed by the (OH) radicle which is common to both ethyl alcohol and water. An investigation should be made of liquids analogous to ethyl alcohol, but in which the (OH) radicle is substituted by some other group, to see if the bands disappear.

The experimental investigation of the absorption produced by an aqueous solution of carbon dioxide showed that the amount of carbon dioxide in solution was too small to show the strong characteristic band of carbon dioxide at 2.72μ, and no absorption band at 1.20 μ due to the dissolved carbon dioxide could be detected. Unfortunately there was insufficient time to carry out the investigation on the liquefied gas.

A few interesting facts are given at the end of Chapter IV, regarding the absorption produced by an aqueous solution of potassium permanganate. A band was found at 5.52 μ arising from the potassium permanganate, and so far as is known, this band has never previously been reported.

X) In an account such as this, it is impossible to give an adequate description of all the attempts made, the many different lines of attack used, and the disappointing failures recorded, before an accurate and speedy technique was developed. Moreover, when this technique was finally worked out, the method had to be thoroughly practised before complete agreement between duplicate sets of observations was obtained, and consistent results recorded. Of the two experimental arrangements used, method No. 2 is by far the most sensitive. There is less energy lost during the passage of the radiation from the source, via the specimen and spectrometer, to the thermopile, and this increase in energy causes a definite increase in the galvanometer deflections. Such a big increase in the galvanometer deflections outweighs any advantages which the experimental method No. 1 may possess. The account contains a large number of duplicate observations, but these are only included to show the efficiency of the apparatus, the accuracy of the experimental method, and the precision of the instruments used.

XI) In conclusion, I should like to place on record my gratitude to all those who have given helpful advice during the course of the work; and especially to Dr. J. E. P. Wagstaff do I offer my very best thanks, for his unfailing help, advice and encouragement so freely given throughout the whole research.

::: ::::: :::

WBW.
/735.

Section II.

BIBLIOGRAPHY.

1.	F. Paschen	Wied. Ann.	53, 301,	- 1894.
		Ann. Physik	4, 299,	- 1901.
		"	26, 120,	- 1908.
		"	35, 1005,	- 1911.
2.	Langley	Wied. Ann.	22, 598,	- 1884.
		Smithsonian Inst.	Vol. 1,	- 1902.
3.	Rubens.	Wied. Ann.	45, 238,	- 1892.
			46, 529,	- 1892.
			53, 267,	- 1894.
4.	Trowbridge	Wied. Ann.	60, 724,	- 1897.
5.	Angstrom	Phil. Trans.	172, 887,	- 1882.
6.	Aschkinass	Ann. Physik.	(3) 55, 406,	- 1895.
7.	Paschen	Ann. Physik.	53, 336,	- 1894.
8.	Ransohoff	Ann. Physik.	56, 302,	- 1896.
9.	Publications of the Carnegie Institute, Washington,		1905	- 1908.
10.	R. Robertson	Proc. Roy. Soc.	120, 128, 149,	- 1928.
11.	Drude	Ann. Physik,	14, 4, 677,	- 1924.
12.	Kratzer	Zeit. Physik.	3, 289,	- 1920
13.	Bailey, Caissie, Angus,	Proc. Roy. Soc.,	A.130, 812, (Part III).	-
14.	Wadsworth.	Phil. Mag.,	Vol. 38,	- 1894.
15.	R. Robertson & J. J. Fox,	Proc. Roy. Soc.,	A.120, 784, B.128.	-
16.	Taylor	Proc. Roy Soc.	A.142, 598.	

17.	Smith & Boord	Journ. Americ. Chem. Soc.	48,	1512,	- 1925
18.	Paschen	Ann. der Phys.	26,	128,	- 1908
19.	Schaefer & Matossi	Das Ultra Rote Spectrum,	p. 41.		
20.	P. Cross	Review of Scientific Instruments,	4,	4,	- 1933
21	Schaefer & Phillips	Zeit. for Physik,	36,	641,	- 1926
22.	Wimmer	Ann. der Physik.	81,	1091,	- 1926
23.	Dennison	Phys. Review,	43,	No.9,	
24.	Bourdon	Journ. Chem.Soc.761,			- 1927
25.	Warburg	Ann. der Physik.	28,	313,	- 1909
26.	Snow, Rawlins & Rideal	Proc. Roy. Soc.,		A.124,	- 1929
27.	Ellis	Phys. Review	22,	200,	- 1923
28.	Coblentz	Publ. Carnegie Inst.,		1905	- 1908
29.	Purvis	Proc. Camb. Phil. Soc.,	21,	556,	- 1923
30.	Aschkinass	Wied. Ann.	55,	401,	- 1895
31.	Tamman	Naturw.	15,	1632,	- 1927
32.	Ellis	Phys. Review,	23,	48,	- 1924
33.	Collins	Phys. Review	18,	339,	- 1921
34.	Dreisch	Z. Physik.	30,	200,	- 1924
35.	Rubens	Verh. Physik.	40,	714,	- 1927
36.	V. Henri	Etudies de Photo. Chem.			- 1919
37.	Collins	Phys. Review	20,	486,	- 1922
38.	Dreisch	Zeit. fur Physik.	30,	200,	- 1924
39.	Tamman	Die Naturw.	15,	632,	- 1927
40.	Collins	Phys. Review,	26,	771,	- 1925
41.	Dreisch	Zeits. fur Physik.	30,	200,	- 1924

42.	Reinkober	Zeits. fur Physik.	35,	179,	- 1926
43.	J. Lecomte	Comptes Rendus.		1698, 825,	- 1924 - 1925
44.	Meyer, Bronk & Levin	Phys. Review	21,	712,	- 1923
45.	Plyler & Burdine	Phys. Review	35,	605,	- 1930
46.	Smith & Boord	Jnl. Opt. Soc., Americ.,	48,	1512,	- 1926
47.	Henri	Etudies de Photochimie,			- 1919
48.	Reinkober	Zeits. fur Physik.	35,	179,	- 1926

::: ::::::: :::