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INFRA-RED EMISSION SPECTRA.[1]

By William W. Coblentz.

THE present experimental investigation was performed in the Physical Laboratory of Cornell University during the academic year 1904–1905. It forms the second part of an investigation of infra-red radiation, rendered possible by a grant from the Carnegie Institution of Washington. The first grant was for "Investigating infra-red emission and absorption spectra." Finding it impossible to complete the work in the time allotted, the Institution very generously renewed the grant, and the writer takes this opportunity to express his gratitude for the assistance rendered. In the Physical Laboratory he is under deep obligations to Professors E. L. Nichols and E. Merritt for advice and criticisms as well as for the numerous facilities placed at his disposal. His dealings with the two institutions have been so agreeable that it is with a feeling of regret that additional phases of the work could not be continued with them.

The present investigation deals with the question of the distribution of emission lines (bands) in the infra-red, especially with the question of presence of lines beyond 1.5 μ. All the infra-red lines predicted by our spectral series formulæ end in the short wavelength just beyond the red. Any information as to the presence of lines beyond this point will aid in establishing these formulæ upon

[1] Extracts from a memoir on this subject submitted to the Carnegie Institution of Washington for publication.

a firmer, less empirical basis than they have at present. From our knowledge of the radiation from the "black body," which is most intense in the region of 1.2 μ to 2.5 μ at high temperatures, one would expect the emission bands at 2 μ, if there be any, to be just as intense as those found by Snow[1] at 1 μ. Other points of interest which developed as the work progressed will be noted in their proper places.

All observers agree in thinking that when radiation is emitted by a gas, in one case by heating it, and in another case by sending an electric current through it, the mechanism which is brought into play must differ in some important respects in the two cases. The present work deals with the radiation from a gas when a current is sent through it.

The work divides itself into two parts, viz., emission spectra of the arc between metallic electrodes and of the chlorides of the alkali metals in the carbon arc; and emission spectra of gases in vacuum tubes. The contrast between these two forms of radiators is worthy of notice. The arc is noted for its enormous heat radiation in proportion to its light radiation. On the other hand the vacuum tube radiates but little heat. Consequently, in the study of these two kinds of radiators, the form of the device for exploring their spectra must differ. If a radiometer is used the period must be short, for the arc, to avoid heating of the window and the consequent shifting of the zero reading. This, however, is of less importance than the variation in intensity of the radiation from the arc which requires a recording instrument having a short period.

For the vacuum tube a much greater sensitiveness must be used, which means a longer period for a linear radiometer vane. Fortunately the radiation from the vacuum tube is uniform, which permits the use of an instrument having a slow period.

In the present work a Nichols radiometer, a 7 cm. rock-salt prism and a 35 cm. focal length mirror spectrometer were used.[2]

For the emission spectra of the metals, the radiometer vanes had an area of about 2 × 15 mm. each, and the short period was due to

[1] Snow, PHYS. REV., 1, p. 35, 1893.

[2] Described in the PHYS. REV., 16, pp. 35 and 77, 1903, and in "Infra-red Investigations," Washington, D. C. Published by the Carnegie Institution, October, 1905.

the heavy fiber suspension. The vacuum tube radiation being very weak, required great sensitiveness, which was obtained in part by reducing the size of the vanes (of mica) to 1 × 10 mm. and selecting a fine fiber. The behavior of such a vane is entirely different from a heavier one. At low pressures the vane before the window was suddenly repelled from it, due apparently to the radiation from the window. This repulsion occurred when both vanes were black, and when the unexposed one was not covered with lamp-black. It was not due to electrification, and throughout the vacuum tube work it was necessary to use a torsion head to keep the deflection on the scale.

I. Infra-red Emission Spectra of Metals.

This work was begun by examining the spark spectra of such metals like Zn, Al and Cu. An induction coil and condenser were used. No emission lines could be detected; instead of lines a weak continuous radiation was detected in the region of 2 μ to 3 μ, which appeared to be due to the hot particles from the electrodes. The arc between metallic electrodes of Fe, Zn and Cu was then tried; but no lines could be detected in the region of 1 μ, beyond which point the incandescent oxides gave such an intense continuous, "black body," spectrum that the emission lines would have been obliterated by the radiation from the oxides. The vapors from the copper arc had but little "black body" radiation. No emission lines were detected, however, although several have been predicted in the region of 2.5 μ.

In the Zn arc the oxides are formed so rapidly that it is almost impossible to work with this metal. The problem then is to separate the black body radiation of the oxides from that of the vapors, which is very different from the work in the visible spectrum.

Chlorides of Metals.

The chlorides of Na, Li and K were then examined in the carbon arc, using for the purpose hollow carbon electrodes filled with the salt. The carbons used varied from 6 to 9 mm. in diameter, the holes being from 1.4 to 2.5 mm. A direct current of 15 amp. from a 104-volt circuit was used. The radiometer slit was reduced

to 0.1 mm. in width, nevertheless the radiation at 2 μ, which at the most gave a deflection of only a few millimeters was not resolved into individual lines. This is in marked contrast with the strong emission lines at 1 μ, and as will be noticed later on, the continuous radiation at 2 μ would blot out any weak emission lines, as far as a radiometer or a bolometer is concerned. Here a photographic process would be better since the effect upon the plate is cumulative, and one would have dark lines superposed upon a dark background, just as Abney and Festing [1] found for their absorption spectra at 1 μ.

Carbon Arc.

In Fig. 1 is given the emission spectrum of the carbon electrodes, curve *a*, and that of the violet vapor of the arc, curve *b*. It will be noticed that there is but little radiation from the vapor except a

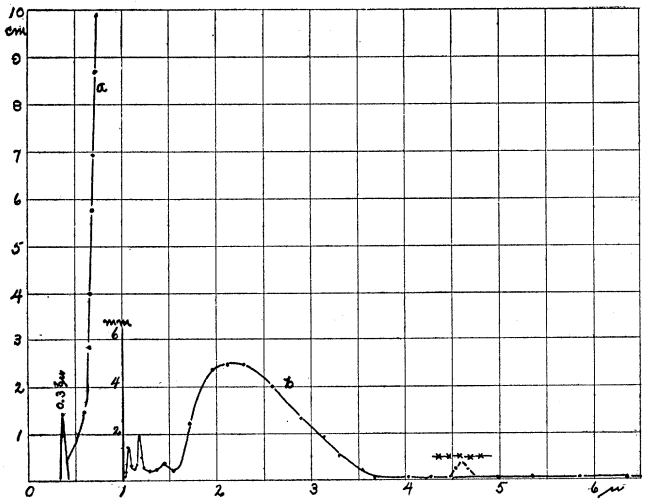

Fig. 1. Carbon arc ; *a* = electrodes, *b* = vapor.

slight amount from 2 μ to 3 μ. On the other hand the deflection was thrown off the scale for the radiation from the electrodes, just beyond the red. Snow [2] found the radiation from the arc vapors concentrated in a single line, in the violet, at 0.385 μ. This line is four times as intense as the one at 1.09 μ. In the present work

[1] Abney and Festing, Phil. Trans., 177, p. 887, 1882.
[2] Snow, PHYS. REV., 1, p. 35, 1893.

the lines are of about equal intensity, due in part to the loss of intensity of the violet line, caused by the radiometer window. A new line occurs at 1.2 μ, while on a thorough reëxamination no line was found at 4.52 μ. This is of considerable interest since it shows that no CO_2 is formed, and that the electrodes are consumed in a different manner. They do not disappear in the ordinary form of combustion. There is but little residue from mechanical disintegration; they disappear chiefly in the form of vapor. The absence of radiation from the carbon vapors is in marked contrast with the radiation from the electrodes, any trace of which, as already mentioned, was sufficient to cause large deflections. The black body radiation is not very intense at a low temperature and the maximum lies beyond 3 μ. The oxides in the arc have a high temperature; the maximum lies at 2 μ and the weak radiation in this region is to be attributed to the low density of the vapors.

Sodium, Na.

Snow (*loc. cit.*) found that the salts of the metals gave the same emission lines as the metal itself, and that the chlorides were well adapted for emission spectra work, using hollow carbon electrodes.

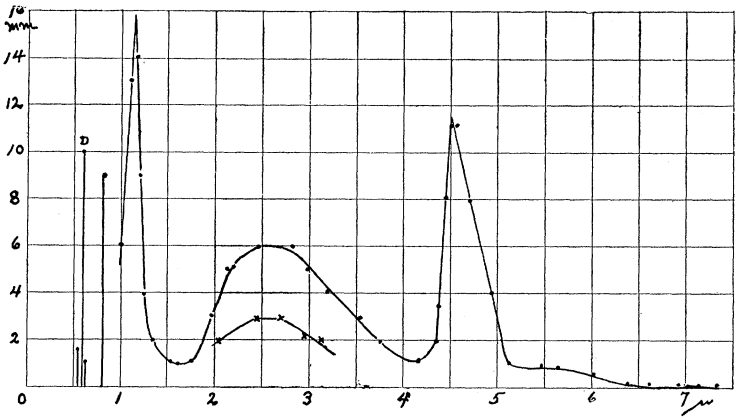

Fig. 2. Na.

For this reason only the chlorides of the metals were used. The present work was not concerned with the verification of his results, which were used only in comparing the relative intensity of the lines

investigated. He used a quartz prism, which on account of its larger dispersion permits a greater accuracy in determining wave-lengths. In the present work the question was whether there are lines beyond the region investigated by him. The distribution of the energy in the vapor of Na is shown in Fig. 2.

Snow found the intensities of the lines at 0.589 μ, 0.818 μ and 1.13 μ to have a ratio of 87 : 66 : 42. In other words the energy in 0.589 μ is more than twice that of the line at 1.132 μ. In the present work the intensities of these two lines are exactly reversed, and in the same proportion. Since the dispersion is smaller this may be due to the impurity of the spectrum.

From 2 μ to 3 μ there is a weak continuous radiation, which appears to be due to the oxides of the metals in the arc.

For Li this is not so intense, and, since the solid material (dust) coming from the arc is also less, the evidence is strengthened in favor of the emission at 2 μ to 3 μ being due to oxides. The emission band at 4.52 μ is also to be noticed. Since it occurs only

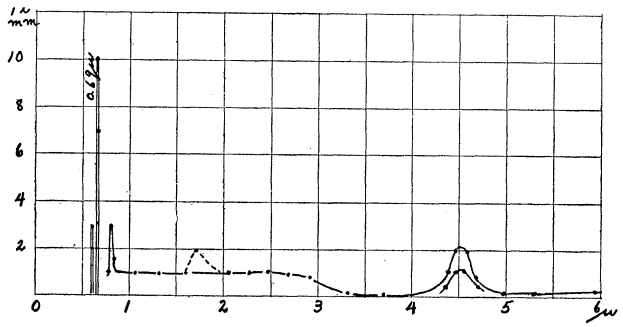

Fig. 3. Li.

when the salts of the metals are in the arc, and is *not* to be found in the carbon arc its source remains undetermined. If it be due to CO_2, from the air, then from the shifting of the maximum to the longer wave-lengths (found by Paschen, *loc. cit.*, being at 4.40 μ for the bunsen flame) it would appear that the temperature of the arc is about 4,000° absolute.

Lithium, Li.

The chloride of lithium vaporizes so easily that no true measure of the radiation from the dense vapor could be obtained. In like

manner the radiation from the oxides at 2 μ to 3 μ is also weak. The bands at 0.67 μ and 0.811 μ (Fig. 3) have the same ratio of intensity as found by Snow. Beyond this point no lines could be detected, except a slight band at 4.52 μ.

Potassium, K.

In Fig. 4 is shown the emission curve of potassium. The KCl does not vaporize so easily as LiCl and is readily adapted to the arc. Snow found strong lines at 0.768 μ, 1.155 μ and 1.22 μ, the first one being four times that of the band at 1.15 μ. In the present work the last two lines were not not quite resolved and no comparison can be made. The band at 1.47 μ was also found by Snow. The usual region of continuous radiation is found from 2 μ to 3 μ. The 4.52 μ emission band is strong. The emission band of CO_2 at

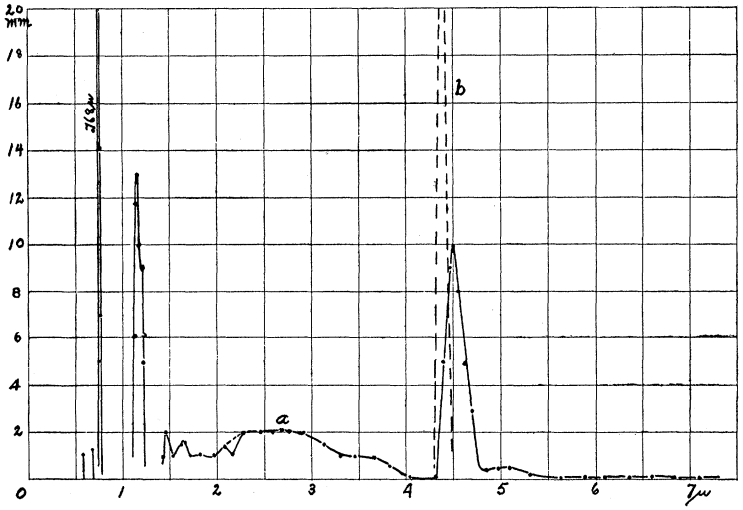

Fig. 4. Potassium; b = Bunsen flame.

4.40 μ, using a bunsen burner, is also given, curve b, — the latter is three times (deflection equals 3.2 cm.) as strong as the band at 4.52 μ.

As a whole from these curves it will be noticed that no emission lines occur beyond 2 μ, which is entirely unexpected. Beyond this point a weak emission line would be obliterated by the continuous spectrum. The band at 4.52 μ will be noticed shifted to 4.75 μ

in the vacuum tube radiation. The intensity of the emission lines found depends upon the density of the metallic vapor in the arc. From the fact that no lines were observed beyond those found by Snow it is not to be inferred that no lines lie beyond $2\,\mu$. The work simply shows that, for the conditions which produce the lines at the end of the red, no lines of measurable intensity are to be found beyond this point. It is true that Lehmann[1] has just shown that Rb and Cs have lines at $1.7\,\mu$; but the emission curves of these two elements, found by Snow, also show *weak* lines in this region, and it is only the cumulative effect upon the phosphor-photographic plate that has enabled Lehmann to map them.

II. INFRA-RED EMISSION SPECTRA OF GASES IN VACUUM TUBES.

Since the incandescent oxides in the arc and spark emit a continuous spectrum of sufficient intensity to obliterate any weak emission lines, beyond 2μ, it is impossible to detect them. The vacuum tube lacks these defects, and is adapted to this work provided one has sensitive apparatus to detect the radiation emitted.

The dispersed infra-red radiation from gases in a vacuum tube is of considerable interest in comparison with the radiation of gases in a flame. The work of Julius[2] and of Paschen[3] shows that by mere temperature elevation gases emit characteristic discontinuous spectra. From a theoretical standpoint such an investigation is also of importance, since all the infra-red lines predicted by our spectral series formulæ end in the short wave-lengths just beyond the red. This presents the interesting question whether emission lines are to be found beyond the region of $2\,\mu$. In this connection a recent theoretical paper by Garbasso[4] is to be noticed in which he maintains that the series of Kayser and Runge have a real existence.

In the preliminary part of this work the vacuum tube used by Drew[5] was employed. In this tube the electrodes were at right angles to and at a short distance from the main part which formed the positive column. Several rubber joints were in series with the

[1] Lehmann, Phys. Zeit., 5, 823, 1904.
[2] Julius, Licht u. Wärmestrahlung verbrannter Gase, Berlin, 1890.
[3] Paschen, Ann. der Physik., 3, 53, p. 334, 1894.
[4] Garbasso, Nuovo Cimento, 9, p. 113, 1905.
[5] Drew, PHYS. REV., 17, p. 321, 1903.

mercury pump, McLeod gauge and the vacuum tube. Several gases were examined, all of which, except hydrogen, showed an emission band in common at 4.75 μ. Hoping to gain intensity of the radiation, a tube was made similar to one used by Runge and Paschen.[1] The aluminum electrodes were 2.5 cm. long, and 2.8 cm. diameter, through which the radiation passed axially into the spectrometer slit of 8 mm. length and 1 mm. width. The radiometer slit was 0.7 mm. The internal diameter of the main portion of the vacuum tube was 1 cm. and its length was from 15 to 18 cm. The window was of rock salt secured on the outside by means of bees-wax covered with shellac varnish. The window was also secured by means of shellac which had been boiled until it thickened. To avoid rubber joints the vacuum tube was sealed to the pump and the gases introduced through a barometric column of mercury. The tube was air tight but, at a low pressure, it would become so hot that vapors would be given off and the cathode luminescence would disappear. This luminescence would reappear after the tube had cooled. According to Travers (Study of Gases), this is due to gases absorbed by the electrodes. At any rate it did not interfere with the work, since the tube was used at such a pressure that it did not become heated. All evidence indicated that the impurity band at 4.75μ, which was found in all the gases in the preliminary work was due to something that entered with the gas ; and it was finally shown to be due to contamination with CO_2 while making the gas. The problem then was to make a gas which was free from even slight traces of CO_2. Previous experience showed that to bubble a gas through several purifying solutions in series with the pump was not sufficient. Hence, in preparing such a gas like CO, an ordinary mercury gas pipette was used. The gas was washed back and forth from the mercury pipette, through a tube containing P_2O_5 into a pipette of KOH, for about half an hour, to free it from CO_2 and to dry it. After such a treatment nitrogen and oxygen did not show the impurity band at 4.75 μ.

The residual gas in the pump and glass connecting tubes was swept out by passing a discharge through it and heating it from the outside.

[1] Runge and Paschen, Astrophys. Jour., 3, p. 4, 1896.

A large Charpintier and also a Max Kohl No. 4 induction coil were used to excite the vacuum tube. For convenience, for most of this work, the primary was connected directly through a rheostat to a 104 volt, 60 or 120 cycle, alternating current.

An ammeter was placed in the primary circuit, while an a. c. millivoltmeter having a resistance of 21,760 ohms was used to measure the current in the secondary.

The primary current varied from 3 to 6 amp., and the secondary from 0.012 to 0.028 ampere.

Since the spectrometer arm was movable, the vacuum tube had to be adjusted before the slit, by hand. The points on the curves given are usually the mean of several readings.

Observations were made for constant current in secondary and variable pressure, and also for constant pressure and variable current.

The method of observation consisted in obtaining the radiometer deflection for the gas when the discharge was passing and then, after stopping the discharge, allowing the deflection to return towards its original zero reading. The hot cell would prevent the deflection from returning to the original zero in 50 seconds (radiometer period) and the difference in the two zero readings gave approximately the deflection due to the hot cell. Another method for finding the deflection due to the hot cell consisted in passing the discharge for 50 seconds, then on stopping the discharge and raising the shutter reading the deflection. Of course the cell cools somewhat while obtaining the deflection, but it is not a great amount in comparison with the total deflection. Since the cell became heated the least at 0.6 to 1 mm., it was used at this pressure. In the region up to 1.5 μ *no* radiation from the hot cell could be detected. Beyond 3 μ, for a pressure of 0.6 to 1 mm., the deflections often amounted to several centimeters. On the other hand nitrogen shows strong lines at 1 μ which would indicate that if nitrogen emits bands on account of its thermal condition, then it must be at a *higher temperature* than the cell.

Water Vapor, H_2O.

After finding the impurity band at 4.75 μ in all the gases except hydrogen, and knowing that water has an absorption band at this

point, a special attachment was provided to introduce water into the previously exhausted pump and vacuum tube.

The emission spectrum was found for various pressures, up to 3 mm., but no emission bands were found. On the contrary, the hot cell, after stopping the discharge, gave deflections which were as large as those for the vapor. With water vapor the cell became much hotter than for the other gases.

A slight trace of water vapor has a great effect in depressing the intensity of the emission lines as was found on allowing air to enter the tube; and only after filling the tube several times with air and exhausting it did the air lines, at 0.9 μ, 1.05 μ and 4.75 μ, appear in their usual intensity.

It will be noticed that the water vapor has *no* emission lines, which is true of the vapor in a bunsen or oxyhydrogen flame. On the the other hand alcohol vapor shows quite a strong emission spectrum from 2 μ to 3 μ. This is probably due to the difference in density of the two vapors.

Hydrogen, H.

This sample of hydrogen was generated from Zn + HCl and dried in H_2SO_4 and in P_2SO_5.

In the region of 1 μ energy is radiated which may be due to slight traces of nitrogen. *No* emission band is to be found at 4.75 μ. The radiation curve for the hot cell (observations plotted in circles) coincides with that of the gas.

Oxygen, O.

The first sample of oxygen, made by heating $KClO_3 + MnO_2$, showed the impurity band at 4.75 μ and no further examination was made of it.

A sample of electrolytic oxygen was then taken from the large generator and washed in KOH and dried over P_2O_5 on glass wool. Two examinations were made, on different days, but *no* emission band could be detected at 4.75 μ. In the region of 1 μ no deflections, greater than 1.5 mm. were recorded. As a whole the gas showed *no* emission lines for the region examined, which was to 5 μ, This is of considerable interest in what follows on CO and CO_2, where there is a strong emission line at 4.75 μ.

Carbon Dioxide, CO_2.

This gas was made from $KClO_3 + H_2SO_4$ and dried in P_2O_5. It was found that there are *no* emission lines until we arrive at 4.75 μ.

The current through the gas varies with the pressure. An examination of the 4.75 μ band was made for constant current and variable pressure, the current being 0.02 ampère. The results are shown in Fig. 6, which will be discussed in connection with CO, and it will be sufficient to add that the gas was first put into a pipette of phosphorus to remove the oxygen which was present. Starting with a sample of this gas at 1 mm. pressure, and adding oxygen until the pressure was 3.7 mm., no change could be detected in intensity of 4.75 μ the band which would indicate that if the band be due to CO then the CO_2 is already dissociated when starting. Occasionally a dark ring or dark patches would appear on the inside of the constricted portion of the vacuum tube. It would suddenly disappear and then reappear elsewhere. Whether it was due to carbon in the tube or to the dissociation of CO_2 remains undetermined.

Warburg's work[1] shows that the temperature of the axis of the tube is much higher for nitrogen than for hydrogen, so that traces of CO_2 in nitrogen ought to become the hotter. It was noticed that the 4.75 μ band occurring as an impurity, was most intense in nitrogen, which, if the same amount of CO_2 was present in each gas, would indicate that the N was the hotter.

Carbon Monoxide, CO.

The CO was made by heating oxalic acid, $C_2H_4O_2$, and conc. H_2SO_4 and passed through a KOH solution into a pipette of KOH. The generating flask was then replaced by a mercury gas pipette and a tube of P_2O_5 on glass wool, and the gas was then washed back and forth through the P_2O_5 for a long time. This sample showed no water vapor lines at low pressures. The emission curves of CO are in Fig. 5, where curve *a* is for a pressure of 0.3 mm. and *b* for a pressure of 0.8 mm. There seems to be a slight trace of radiation throughout the spectrum but *no* strong emission lines are to be found except the one at 4.75 μ.

An examination of this band was made for a constant current of

[1] Warburg, Ann. der Physik. (3), 34, p. 265, 1895.

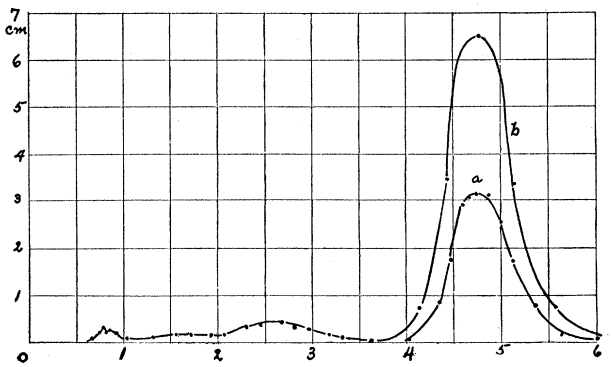

Fig. 5. CO ; $a = 0.3$ mm. pressure, $b = 0.8$ mm. pressure.

0.02 amp. and variable pressure. The results are given in Fig. 6, in which the abscissæ are pressures in millimeters of mercury, and the ordinates are deflections in centimeters. It is to be noticed that

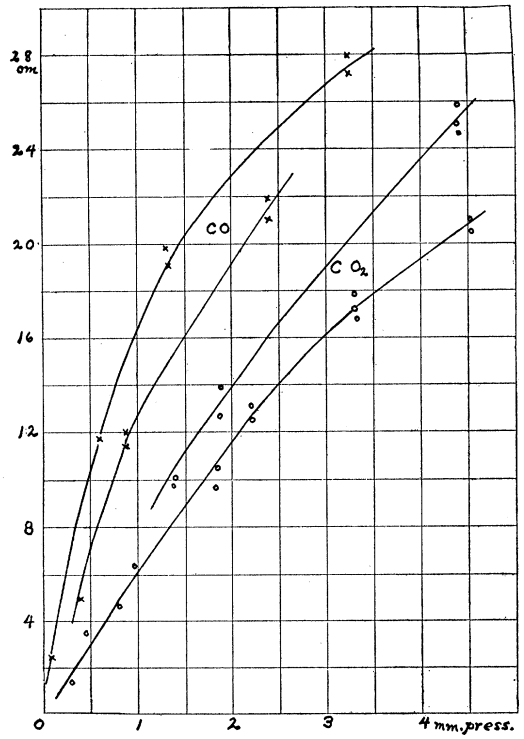

Fig. 6. CO and CO_2 band at 4.75 μ. Variation in intensity with pressure.

the intensity of the CO band is much greater than that of CO_2 for *all* pressures, the current of 0.02 amp. being the same for both gases. Moreover the intensity does not pass through a maximum as is true of the H and N lines lying near the visible spectrum. The greater intensity of the CO would make it appear as though the 4.75 μ band were due to this gas.

Ethyl Alcohol, C_2H_5OH.

Ordinary absolute ethyl alcohol was used. It was introduced into the previously exhausted pump, through an especially provided bulb and stopcock. The emission curve, Fig. 7, is very un-

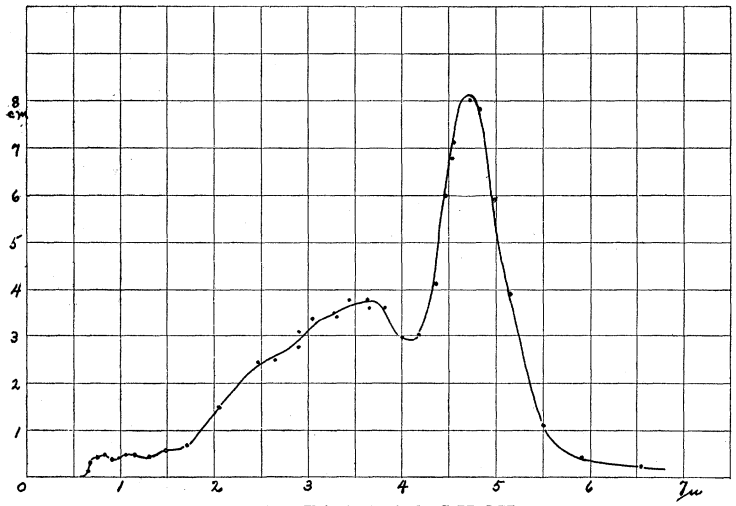

Fig. 7. Ethyl alcohol, C_2H_5OH.

usual. It shows no distinct lines except the strong band at 4.75 μ which is to be found only in CO and CO_2. The continuous spectrum from 2 to 4 μ is difficult of explanation. Possibly it is a composite of bands of alcohol vapor equivalent to the water vapor bands found in the bunsen flame. In the latter, however, the bands are in groups with regions of zero radiation. The bands at 4.75 μ indicate a dissociation of the alcohol vapor into H (red line) and CO_2 or CO, just as ammonia shows the nitrogen bands.

Nitrogen, N.

The first sample of nitrogen examined was made by heating a saturated solution of equal parts of sodium nitrite, $NaNO_2$, and ammonium chloride, NH_4Cl, washed in KOH and dried in H_2SO_4 and in P_2O_5.

The emission spectrum of this sample of N is given in Fig. 8, curve *b*. In addition to strong lines just at the end of the red we have the usual band at 4.75 μ which is unusually intense. In fact,

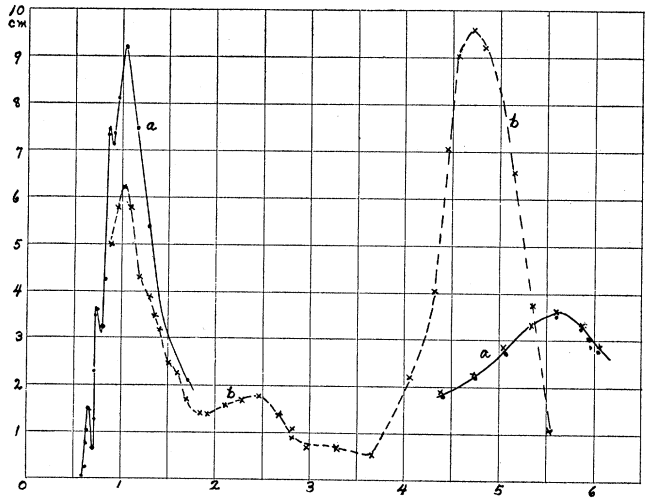

Fig. 8. Nitrogen ; a = atmospheric nitrogen.

for a pressure of 5 mm. the deflections from this band were from 30 to 35 centimeters.

One difficulty in making nitrogen by this method is that the oxides are also formed. The presence of the 4.75 μ band showed that it is due to CO_2 or traces of N in CO or CO_2. The problem then was to prepare a small quantity of nitrogen which was free from oxides of nitrogen, and also free from O and CO_2. The presence of a trace of an inert gas like helium did not enter the question of the origin of the 4.75 μ band. Hence atmospheric nitrogen was most serviceable. To this end a glass tube containing P_2O_5 on glass wool was connected in series with a gas pipette containing a strong KOH solution and a pipette containing sticks of red phosphorus under water. The phosphorus of course was used to re-

move the O, while the KOH removed the CO_2. The air was washed back and forth for some time. The KOH pipette was then replaced by a mercury gas pipette, and the gas was washed back and forth for about half an hour to dry it and remove the last traces of oxygen.

The result is shown in curve *a* of Fig. 8, which is of no small significance, especially in the region of 4.75 μ where *no band* is to be found. The curve (dots and crosses) shows that the radiation from the gas and from the hot cell is of equal intensity. The decrease in the intensity, thus forming an apparent maximum at 5.5 μ is due to the fact that in moving the spectrometer arm the vacuum tube was not adjusted before the slit, hence the last two readings are for the radiation from the side of the tube instead of its axis.

In the final work the gases were not studied in the order given here, the CO_2 and CO coming last. The absence of the 4.75 μ

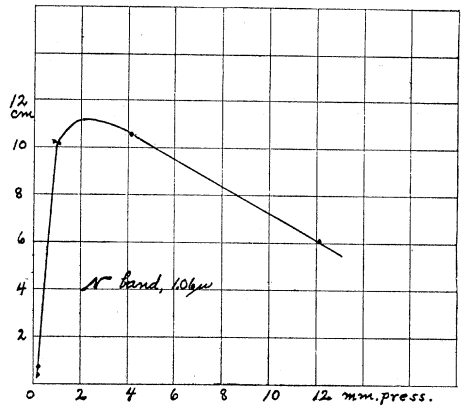

Fig. 9. Variation in intensity with pressure of the nitrogen band at 1.06 μ.

band in N and NH_3 excluded the possibility of its being due to nitrogen. Several drops of water were introduced into the gas, but no change could be detected in the radiation at 4.75 μ showing that this band is not due to water vapor. Hence it remained to be shown whether it is due to CO_2 or CO.

In discussing those two gases it was shown that the radiation from CO is much stronger than for CO_2 at 4.75 μ.

The presence of strong emission bands just beyond the red hav-

ing maxima at 0.66 μ, 0.75 μ, 0.90 μ and 1.06 μ was found only in nitrogen. Helium [1] is the only other gas known which has strong lines (bands) in this region, and from the scanty data at hand it appears as though this property were confined to the inert gases.

A study was then made of these emission bands under constant current and variable pressure and *vice versa*. In Fig. 9, is given the curve of the 1.06 μ band for variable pressure (current const. 0.02 amp.) which is the ordinary gas conduction curve of the visible spectrum. Ordinates are deflections in centimeters, abscissæ are

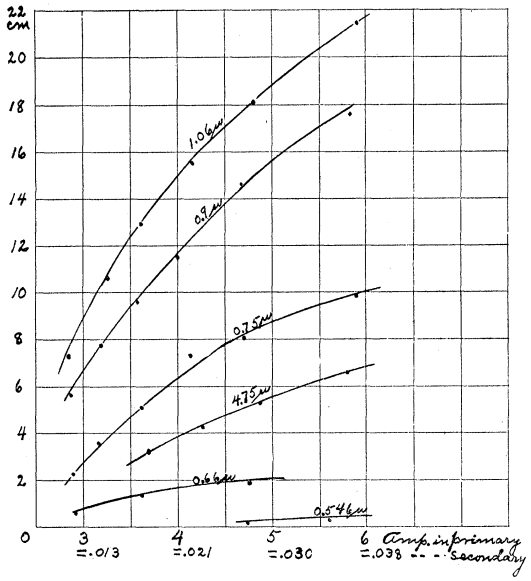

Fig. 10. Variation in intensity of the nitrogen bands with current.

pressures in millimeters. The maximum lies at about 2 mm. which agrees well with observations in the visible spectrum.

In Fig. 10 are given the emission curves of the bands at 0.546 μ, 0.667 μ, 0.75 μ, 0.90 μ, 1.06 μ and 4.75 μ, keeping the pressure constant at 1.4 mm. and varying the current.

All the curves agree in showing that the intensity (plotted as ordinates) increases with increase in current in the secondary, which agrees with Langenbach,[2] and with Ferry [3] for the visible spectrum.

[1] Runge and Paschen, Astrophys Jour., 3, p. 4, 1896.
[2] Langenbach, Ann. der Phys. (4), 10, p. 789, 1903.
[3] Ferry, PHYS. REV., 7, 1, 1898.

Several large Leyden jars were used in parallel with the vacuum tube when the intensity of the radiation increased due to an increase in the current through the tube.

Ammonia, NH_3.

The ammonia used was made by heating $NH_4Cl + KOH$ (solid) and passing the gas through tubes of CaO which had been heated for several hours. These tubes were heated while starting, to expel the air. The first sample was examined just after the C_2H_5OH, and from the appearance of the curve, Fig. 11, some of

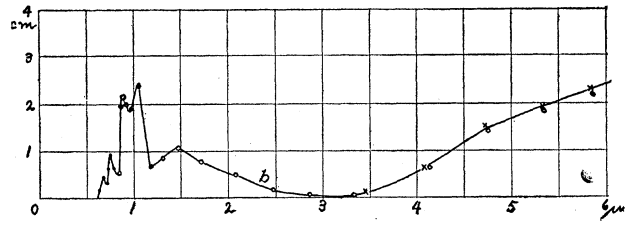

Fig. 11. Ammonia, NH_3.

the latter vapor must have been present. The second sample, made with greater precautions, did not show any radiation beyond 2.5 μ. In the region of 4.75 μ, the observations for the radiation from the hot cell and the gas (indicated by crosses) coincide. The nitrogren bands at 0.75 μ, 0.9 μ and 1.06 μ are due to the dissociated NH_3.

Radiation From a Vacuum Tube When Heated Externally.

The very different behavior of the 4.75 μ band from those at the end of the red made it highly desirable to learn whether it can be due to the mere rise in temperature of the gas. If it obeys Kirchoff's law, it cannot be more intense than the black body radiation at the same temperature. The radiation of the hot glass cell beyond 3 μ, when hot (at cathode-ray pressure) gave deflections that were comparable with that of the 4.75 μ band. This would lead one to think that the 4.75 μ band is due simply to rise in temperature of the gas. On the other hand, in the region of 1 μ the hot cell gave *no* appreciable deflections, while the gas, nitrogen, gave *strong* emission bands, which would indicate that if these emission bands

be due to a pure thermal excitation, following Kirchoff's law then the temperature of the gas must be very high as compared with that of the cell walls. The problem then was to find the radiation from the vacuum tube when heated externally to the temperature it had during the electrical discharge, which is really the black body radiation; also to find the radiation from a black body, *e. g.*, a Leslie cube, whose temperature can be quite accurately determined.

In order to determine the radiation from the vacuum tube when externally heated, the part between the electrodes was wound with an iron wire through which an electric current was passed. The walls of the tube were heated to the temperature they generally had during the electrical discharge at very low pressure. The tube was filled with air and with CO_2, and the radiation was found for *all pressures* up to atmospheric. The deflections were thrown entirely off the scale for *all* pressures for the region of 4.75 μ, hence this region of the spectrum was not explored for emission bands. This indicates an intensity of radiation several times that from the vacuum tube during the passage of the discharge. Although the ends of the tube were not hot, when heated externally, the tube is analogous to the black body. Whether or not it is entirely analogous is not of the chief importance. Its radiation was several times as intense as that from the electrically excited tube, which was the question to be answered. Whether or not the emission band at 4.75 μ is due to thermal excitation, due merely to a rise in temperature, or to electrical excitation is undetermined. The experiment shows that since its intensity is less than that of a black body, it is not untenable to consider it to be due to a rise in temperature of the gas.

But this is not a sufficient criterion for udging the quality of the radiation. One objection is that the selective emission at 4.75 μ ceases immediately after the electrical discharge ceases, which is not true of the externally heated tube. Warburg (*loc. cit.*) has shown from theoretical considerations that after the discharge ceases it requires only a small fraction of a second for the gas to assume its original temperature.

In this connection it is well to notice Paschen's[1] work on the emission of CO_2, when heated in a metal tube, also when passed

[1] Paschen, Ann. der Physik. (3), 53, p. 26, 1894.

through a coil of sheet platinum 4 cm. long, 3 mm. internal diameter, heated electrically.

He found the radiation of the 4.4 μ band of CO_2 for columns 7 cm. and 33 cm. long. The 7 cm. column behaved like a layer of infinite thickness, *i. e.*, the intensity of the emission of this wave-length is proportional to the intensity of radiation of a black body for the same wave-length and temperature. In Fig. 12, curve *b* represents the emission of the 4.4 μ band of CO_2, for a tube 7 cm. long when heated by means of a bunsen burner from 100 to 500°. In this same figure curve *c*, also due to Paschen, shows the emission

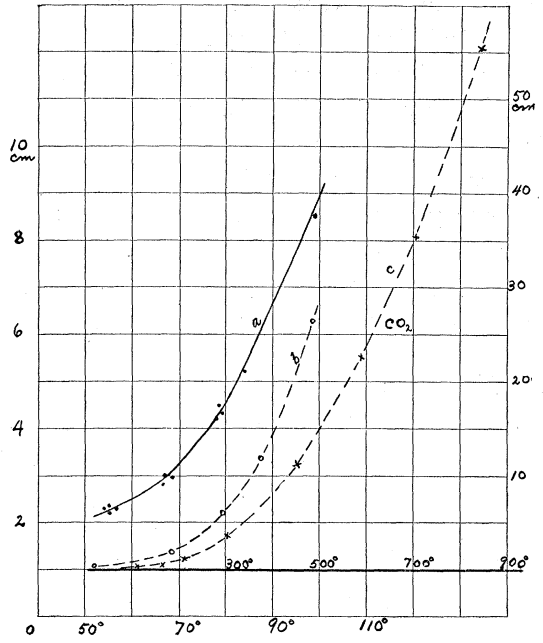

Fig. 12. Radiation from a black body at 100° C., curve *a*; curves *b* and *c* = radiation from CO_2. (Paschen.)

of the 4.4 μ band of CO_2 when heated by passing the gas through a coil of platinum which was heated electrically.

The temperature of the gas was observed by means of two thermopiles, the first one being placed at the point where the gas issued from the orifice; the second one being placed about one centimeter above this point. Both curves show the very rapid increase in intensity of the emission lines with rise in temperature.

RADIATION FROM A BLACK BODY WHEN HEATED TO 100° C.

Since the temperature of the cell could not be determined accurately it was highly desirable to compare its radiation with that of a solid whose temperature could be varied and determined more accurately. To this end the radiation from a thin-walled, blackened copper vessel was found when filled with water which was heated electrically. The escaping vapors from the hot water caused such a variation in the temperature of the room that the radiometer became very unsteady, hence only the region of 4.75 μ was examined. In Fig 12, curve *a* gives the emission curve of this vessel for different temperatures of the water. The curve is very similar to those found by Paschen. Of course, the temperature of the outside of the vessel is less than that of the water, but not sufficient to debar a comparison with the hot vacuum tube. Mention has already been made of the fact that the constricted part of the vacuum tube is the hotter at high pressures, while the regions surrounding the electrodes are the hotter at low cathode-ray pressures. At the latter pressure the deflections for the hot cell were from 8 to 10 cm. The vessel of hot water, under similar conditions gave a deflection of 8.5 cm. for a temperature of about 96°.

At a temperature of 70° the deflection is about 3 cm.

As a whole the results show that the radiation from the cell walls is due to a rise in temperature which is not much, if any, greater than that of the vessel containing water. The temperature of the gas in the vacuum tube is an entirely different question which must be considered separately.

The fact must not be overlooked that the radiation from the vacuum tube gave large deflections simply because of the great sensitiveness of the instrument and not on account of the actual intensity as compared with the deflections from gases in a Bunsen flame. In the latter the deflections for the 4.4 μ CO_2 band were some 60 to 70 cm. for the old instrument, so that in the present work the deflections would be 50 times as great, viz., 3,000 cm. In other words, in the vacuum tube curves the deflections are only from $\frac{1}{250}$ to $\frac{1}{3000}$ as great as from the bunsen flame, and the Nernst heater.

TEMPERATURE OF GAS IN THE VACUUM TUBE.

Warburg's theoretical work (*loc. cit.*) on the temperature of the vacuum tube has already been mentioned. He showed that the temperature of nitrogen is much higher than that of hydrogen.

The intensity of the 4.75 μ impurity band in nitrogen, for all pressures, was so much greater than for all the other gases that one is led to think that it is due to the higher temperature of the gas.

Wood [1] gives data from the observed mean temperature of gases in a vacuum tube for different pressures, and currents of 0.001 to 0.003 ampere. In all cases the computed and observed temperatures are in fair agreement, the observed values being slightly less than Warburg's values, as one would expect, from the use of a thermopile which cannot be made infinitely thin. The observed values fall upon a straight line, which shows the accuracy of the observations. Using these values and extrapolating to a current of 0.02 ampere, in the present work, for a pressure of 1.8 mm. of nitrogen this would indicate a temperature of about 250° C. while for a pressure of 3 mm. the temperature of the axis would be about 325°. For a current of 0.025 ampere the temperature would be 300° and 400° respectively.

The whole shows that for the large currents used in the present work (0.02 to 0.028 amp.) it is not unthinkable that the 4.75 μ band is due to the heating of the residual gas. On the other hand, the black body at 325° C. does not emit a very perceptible radiation at 1 μ while the emission lines of N in this region are very intense. They indicate a very much higher temperature, some 4000° abs., if we consider the maximum of the envelope of the curve, drawn through the highest points of these emission lines, which maximum lies just beyond the red. This reasoning leads to the result that the gas is at two distinct temperatures, which is hardly the case. If the gas had this high temperature then one would expect the cell walls to grow hotter. Electrical excitation suggests itself, which brings us to a theoretical consideration of the phenomena of vacuum tube radiation.

THEORETICAL.

It remains for us to consider the theoretical side of this subject. Experimental observations always have some value. This is not

[1] Wood, Ann. der Physik. (3), 59, p. 238, 1896.

always true of theories which are built, more or less, upon hypotheses and must stand or fall with them. For example, nowadays one no longer considers spectra to be due to molecular or atomic vibrations; the divisibility of the atom into smaller electrically charged particles, called "ions" or "corpuscles", must be assumed to account for observed facts. The foremost and most conservative in propounding such a theory is J. J. Thomson.[1] J. Stark[2] is more daring in that he classifies these "ions," and gives the functions that each class has to perform.

Before considering these theories it will be well to distinguish between several forms of radiation, since everybody gives out some form of radiation, in the form at least of heat waves of great wavelength. If a body can give out radiation continuously without changing its nature it is called a *pure thermal* radiation. If it cannot continue to give out this radiation indefinitely, without changing its nature, even when the temperature is kept constant (*e. g.*, fluorite which emits light on heating) then the radiation is termed *luminescence.* The vacuum tube is thought to give out light by "*electro-luminescence.*"

The vacuum tube is always quite cool in comparison with the arc. This brings us to the question of "temperature." What do we mean by the temperature of a body, particularly with the two forms of radiation just mentioned. Both emit light, nevertheless, if we were to heat a piece of iron until it felt as hot to the touch, or until the mercury in a thermometer expanded to the same height, as it does for the vacuum tube, we know from ordinary experience that the iron would not emit light. "Temperature" is something we are supposed to measure by ordinary means. The word itself is used carelessly and is an endless source of discussion. To anticipate a little what is to follow — Stark uses the terms "thermal and electrical temperature." The purely "*thermal temperature*" for any one gas is proportional to the mean square of the *molecular* speeds. The "*electrical temperature*" is proportional to the mean square of the *ionic* speeds. In a strong electrical field, *e. g.*, spark electrodes, the ionic velocities will be distributed in a very different

[1] Thomson, Conduction of Electricity Through Gases, Chaps. 13 to 16.
[2] Stark, Elektricität in Gasen.

manner from that prescribed by the Maxwell-Boltzmann Law, and the "electrical temperature" may differ very widely from the "*thermal.*" The arc is a region of high thermal and low electrical temperature; the spark has a low thermal and a high electrical temperature.

To return to the theory, there is considerable evidence for believing that the chemical atom or molecule is composed of positively and negatively charged particles called ions. These oppositely charged particles are equal in amount since the molecule as a whole is electrically neutral. It is possible to separate from the molecule a minute particle which carries a negative charge, and thus leave an equal positive charge on the remainder of the molecule. This state of affairs is brought about whenever an electric field is produced, as for example, the difference of potential between the terminals in the carbon arc, of the spark gap in the secondary of an induction coil, or of the electrodes of a vacuum tube. Under the influence of an electric field these dissociated particles are set in motion. Beside their ordinary gas motion, there will be a component along the length of the tube (in a vacuum tube) produced by the electrical forces. Although the charges are the same, the negative ions, the electrons, on account of their small mass will acquire a great speed, and by collision with neutral molecules will give rise to fresh ions. The energy acquired however will be the same for both since they move through the same difference of potential. The mean free path of the electron will be the greater since it is smaller in size. The mean energy at collision, in any case, will be that acquired by the charged particle in moving through its path under the action of electrical forces. When the electron collides with a molecule several effects will be produced. The first is to increase the kinetic energy of the molecule as a whole, which in turn by colliding with other molecules, will cause a rise in the thermal temperature of the gas. As a result the electrons in the molecules will be thrown out of their positions of equilibrium and will execute a series of vibrations. In so doing they will emit radiation in the form of heat or light, depending upon the intensity of the excitation, which in turn depends upon the temperature.

When an electron collides with a molecule the second effect is an acceleration of the former, which, when properly interpreted, means a wave motion, hence periodicity (Stark, *loc. cit.*). This period will be determined by the time of impact, independently of the chemical nature of the body. Since all possible times of impact are possible, an infinite number of different electromagnetic waves will be emitted, and we have a continuous spectrum. This is for the free electrons. The electrons that remain bound in the molecule will also be set into vibration by the impact of the collision. Since they are thus bound, there will be a relative motion among them, and the period of any one or group of these electrons will be characteristic of the kind of atom. The line and band spectra of the elements are, from this standpoint, due to these electrons within the atom.[1] In a more recent paper on tnis subject by Nutting,[2] the recombination of these dissociated aggregates is emphasized as being the source of line spectra.

For this second effect the energy increases with the potential gradient, since the radiation from the gas is caused by the collisions between molecules and electrons, which latter are moving with high speeds. As already mentioned in the high temperature radiation, where the collision is between molecules, the energy increases with the temperature. The electrical temperature distribution will be different from the thermal, and Kirchoff's law for the relation between emission and absorption will not hold for radiation from a gas in a vacuum tube. The spectral distribution of intensity will be a function of the velocity distribution of the electrons. The greater the number of electrons with high speed in a volume element, the more will the intensity maximum be shifted towards the short wavelengths.

For this reason the cathode glow is blue, since the cathode fall is about 300 volts. On the other hand in the position column, where the fall is only about 30 volts, the light emitted is red for nitrogen. According to Stark's (*loc. cit.*) computations in which the kinetic energy is equated to the temperature, this would indicate an electrical temperature of some 6000° for the cathode glow.

[1] Stark, Ann. der Phys. (4), 14, p. 506, 1904.
[2] Nutting, Astro. Phys. Jour., 21, p. 400, 1905.

The ionic energy[1] (the minimum kinetic energy) necessary to disrupt an atom is in the order, metals, Hg 8 (volts), H, N (27 volts) and O. From this it would follow that if we mix H with N the fall of potential and the electrical temperature of the positive column will be changed. The temperature will be increased if the gas to be added has a higher ionic energy, *e. g.*, N to Hg or N to H (Heuse,[2] Herz). This will be of interest in comparing the relative intensities of the 4.75 μ band of CO_2 when it occurs as an impurity in N (very intense) and in O or NH_3 where it is weak.

These views will now be briefly considered in connection with the results obtained in the present research.

Prior to this investigation on vacuum tube radiation only one type of selective emission of gases in the infra-red had to be accounted for, viz., emission bands of water vapor and CO_2. They were thought to be due to thermal temperature of the gas. However, the data bearing upon this subject are so scarce that writers, in referring to them, generally expressed their opinions rather cautiously. Some have vaguely intimated that it might be something similar to luminescence in the visible spectrum — call it thermalescence.

From the present research on the intensity of the infra-red emission bands of N and CO_2, for constant current and varying pressures, and *vice versa*, it becomes evident that we have to deal with two distinct types of radiation, the one being represented by the 4.75 μ band of CO and CO_2, the other being represented by lines of N at 0.90 μ and 1.06 μ. The 4.75 μ band of CO and CO_2 behaves in an entirely different manner from all the rest. Its intensity increases with increasing pressure (for constant current) of the gas, but never reaches a maximum, becoming asymptotic at 5 to 6 mm. pressure.

On the other hand, the other bands increase in intensity with increase in pressure (for constant current), become a maximum at about 2 mm. pressure, and then decrease in intensity with a further increase in pressure, which agrees with observations in the visible spectrum.

All lines increase in intensity with increase in current, as found in the visible spectrum.

[1] Herz, Ann. der Phys. (3), 54, p. 244, 1893.
[2] Heuse, Verh. d. d. phys. Ges., 1, 269, 1899.

Condensers in parallel with the vacuum tube caused a slight increase in the intensity of the lines, due to an increase in the current through the tube. This is due to the well known fact that on account of the high self-induction of the coil, the discharge of the condenser takes the easier path through the vacuum tube. The whole shows that the bands of N, (He), and H, near the visible spectrum, are related to the visible bands, while the 4.75 μ band is of an entirely different type.

Returning to the theory, it is interesting to recall Ångström's [1] predictions in regard to the mechanism which produces these radiations. As noticed elsewhere, he found that the total radiation *increases*, while the luminous radiation *decreases* with increase in pressure of the gas, and concluded that there is a "regular" and "irregular" radiation present during the electrical discharge. This would tend to change the efficiency of the vacuum tube, as found by Ångström and by Drew.

In the present work, the *decrease* in infra-red radiation (4.75 μ band) and the simultaneous *increase* in the visible radiation, with decrease in pressure, explains very clearly the rise in efficiency of vacuum tubes. It also explains why the total radiation passes through a minimum as observed by Ångström and by Drew (*loc. cit.*).

In connection with the theoretical work just mentioned the behavior of these two types of radiation may be explained in the following manner: Consider the lines in and near the visible spectrum. At high pressures the electrons will not attain a high speed on account of the numerous neutral molecules, and their freedom of motion will be limited. At a lower pressure their freedom of motion will be greater, the number of collisions will be more frequent, the ionization will increase and the electrical temperature [2] which is proportional to the mean square of the ionic speeds will attain a maximum. At a still lower pressure, on account of the scarcity of the molecules, there will be fewer collisions in a given time, the ionization will decrease and the "electrical temperature" will decrease.

On the other hand this explanation will not account for the behavior of the 4.75 μ band which appears to be due to a thermal

[1] Ångström, Ann. der Physik. (3), 48, p. 493, 1893.

[2] Stark, Elektricität in Gasen, from consideration of the kinetic energy of the electron computes an electrical temperature of some 6000°.

radiation, excited by the collision of electrons with the neutral gas molecules. The gas molecule as a whole will suffer an increase in its kinetic energy, and, in colliding with other molecules, will cause a rise in the thermal temperature of the gas. With increase in pressure, *i. e.*, in the number of gas molecules, the number of collisions will increase, the intensity of the thermal radiation will increase but will not pass through a maximum, as is true of the other bands, because a stage will be arrived at where there will be a decrease in the ionization and in the collisions of the molecules. At still higher pressures the gas would cease to conduct the current.

Aside from these theoretical considerations, there is some experimental evidence for believing that the 4.75 μ band is of thermal origin. First, the gas must be hotter than the tube, for during the passage of the current the radiation tangential to the axis of the tube is probably different from the longitudinal, and the cell walls assume the mean temperature of the gas only after the current has passed for some time. It has already been shown under the discussion of the temperature of the gas in the vacuum tube, that the mean thermal temperature is from 300° to 400° C., depending upon the current and the pressure. It was also shown there that the black body at these temperatures did not emit a perceptible radiation at 1 μ, while the emission lines in this region are very intense, indicating a temperature of perhaps 4000° abs. On the other hand the "black body" at 4.75 μ radiated almost as intensely as the vacuum tube. This would indicate two distinct temperatures, which is hardly the case.

Second, the distribution of the heat in the vacuum tube is very different for different pressures. At a high pressure the constricted portion of the vacuum tube is the hotter while at low pressure it is quite cool, and the region surrounding the electrodes is the hotter.

Third, the emission increases with the pressure (equivalent to an increase in the thickness of the emitting layer) and approaches a limiting value. Paschen (*loc. cit.*) has found for CO_2 at atmospheric pressure, in a brass tube heated by a bunsen burner that a column 7 cm. long emitted and absorbed energy just as strong as a column 33 cm. long. In the present case the 15 cm. column of CO_2 at 5 mm. pressure is equivalent to a column 1 mm. long at 760 mm.

pressure. This is not a very long column of the gas as compared with Paschen's, nevertheless, judging from the behavior of the small traces of CO_2 in air, it does seem impossible for it to emit radiation as intense as that observed at 4.75 μ. This would require a very high temperature. If the shifting of the CO_2 band toward the long wave-lengths continues with the rise in temperature for the region beyond 4.4 μ, just as Paschen (*loc. cit.*) found for the region preceding 4.4 μ, then the 4.75 μ band would indicate a temperature of some 6500° to 7000° (found by extrapolating from Paschen's values). This is close to Stark's (*loc. cit.*) "electrical temperature" of 6000° for the cathode glow. Returning to the strong emission lines just at the end of the red, if we consider the maximum of the envelope (the curve) drawn through the highest points on these emission lines, which maximum lies just beyond the red, then, from the "displacement law" $\lambda_{max.} T = \text{const.}$, the thermal temperature appears to be about 4000° abs.

From this line of reasoning it would appear that we can consider the 4.75 μ band and the bands at the end of the red to be due to a high thermal condition in the vacuum tube, without having recourse to an "electrical temperature."

The continuous spectrum of alcohol vapor would indicate a higher temperature than that found by bolometric measurements. But even here the evidence is contradictory when compared with the emission of water vapor which showed no emission spectrum at 2.8 μ, where the bunsen flame has emission lines.

Evidently further investigation is needed to elucidate this subject — and such an investigation is in progress.

Summary.

The present investigation of infra-red emission spectra had for its aim the study of the region of the spectrum lying beyond 2 μ, which heretofore had never been examined. The question of the presence of emission lines beyond this point is chiefly of theoretical interest.

Two classes of radiation have been investigated, viz., the arc between metallic electrodes and the chlorides of the alkali metals in the carbon arc, and the discharge through a vacuum tube using different vapors and gases.

It was found for the arc between metal electrodes, that the oxides emitted a black body spectrum of sufficient intensity to obliterate any emission lines if any were present.

Using the chlorides of the alkali metals, the strong emission lines mapped by Snow were verified, but beyond 2 μ *no* emission lines could be found.

The emission spectra of the following vapors and gases were examined in a vacuum tube; H_2O, C_2H_5OH, H, N, NH_3, CO and CO_2. Of this number the C_2H_5OH, CO_2 and CO have a very strong emission band at 4.75 μ.

Nitrogen is the only gas studied which has strong emission lines in the infra-red. The maxima are at 0.75 μ, 0.90 μ and 1.06 μ. The behavior of these lines is entirely different from the 4.75 μ band found in CO_2 and CO. At a constant current the intensity of the 4.75 μ band increases with the pressure but never reaches a maximum, becoming asymptotic at 5 to 6 mm. pressure. On the other hand the nitrogen bands increase in intensity with increase in pressure, become a maximum at about 2 mm. pressure, then decrease in intensity with a further increase in pressure, which agrees with observations in the visible spectrum.

At a constant pressure all lines increase in intensity with increase in current, as found in the visible spectrum.

Condensers in parallel increased the intensity slightly, due to an increase in the current through the tube.

The aim in using a vacuum tube was to avoid oxides. No lines, however, were found beyond 2 μ, except the 4.75 μ band which seems to be due to the warming of the gas. Since the intensity of the vacuum tube radiation is only from $\frac{1}{250}$ to $\frac{1}{3000}$ as great as that of a black body, if there be weak emission lines beyond 6 μ it would be almost impossible to detect them with our present measuring instruments.

The emission spectrum of C_2H_5OH shows that a vapor in a vacuum tube can emit a continuous spectrum.

BUREAU OF STANDARDS,
WASHINGTON D. C., Aug., 1905