

Temperatures Indicated by Intensity Distributions in Band Spectra

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It is generally supposed that the intensity of any particular line in a band spectrum may be calculated from the Maxwell-Boltzmann law, assuming the gas to be in temperature equilibrium. From the results of this experimental work, it appears that under some conditions of excitation other factors than the temperature of the gas govern the intensity distribution. Measurements on the negative bands of N_2^+ excited in low voltage arcs in the pure gas show that at 1100°K and 2800°K the distribution of intensities among the rotational lines is exactly the same, whilst the admixture of helium with nitrogen alters the distribution completely and gives a much lower indicated temperature. Similar results are found with the first negative bands of CO^+ . The differences are accounted for

by the conversion of translational energy of the electrons into rotational energy of the molecules when the bands are excited by electron impacts in the pure gas. When the bands are excited by impacts of the second kind in gas mixtures, no change in rotational energy occurs and thus the indicated temperature is much lower. The distribution of intensity among the vibrational states of the molecules has been examined for the complete system of negative bands of N_2^+ . While almost all of the energy is concentrated in the low vibration states when the bands are excited by electron impacts, the energy is spread out towards the higher vibration states when the excitation is by collisions of the second kind with metastable helium atoms.

INTENSITY DISTRIBUTION AMONG THE ROTATIONAL LINES

A NUMBER of investigations have been made on the relation between the distribution of intensity among the rotational lines of a band and the temperature of the gas in which the molecules are excited. The general conclusion has almost universally been that the temperature of the gas is correctly revealed by the distribution of intensity among the rotational lines. Thus in 1922, Birge¹ came to this conclusion for various absorption and emission bands and applied this method in estimating the temperature of the sun. More recently Ornstein² and his pupils have estimated the temperatures of various types of electric arcs by similar methods, and Vegard³ drew some conclusions relative to the temperature of the upper regions of the atmosphere from observations on the distribution of intensity in the negative bands of nitrogen.

While the weight of evidence points to the correctness of the assumption that temperatures

can be ascertained by this means, certain cases have been noted of distributions of intensity among the rotational and vibrational states of molecules other than that expected from the temperature of the gas. In cases of thermal excitation, there is no doubt that the distribution will accord with that expected, but in other types of excitation, it is not so obvious that the distribution will accord with that predicted from the temperature of the gas. One such case is that of the distribution of intensity among the vibrational states in the B band system of BO excited by active nitrogen as reported in 1931 by Elliott.⁴ Very recently Johnson and Turner⁵ found from studies of the distribution of intensity in the helium bands that, while the intensity distribution was Maxwellian, the indicated temperature was much higher than the temperature of the gas. Duffendack and Smith⁶ in 1929 reported a significant difference in the appearance of the first negative bands of CO^+ when excited in low voltage arcs in the pure gas and in a mixture of 10 percent CO and 90 percent He. The present investigation is an outgrowth of this observation and it will be shown that in

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¹ Birge, *Astrophysical J.* **55**, 273 (1922).

² Ornstein and v. Wijk: *Zeits. f. Physik* **49**, 315 (1928); *Proc. Amst. Acad.* **33**, 44 (1930). v. Wijk, *Zeits. f. Physik* **59**, 313 (1930).

³ Vegard, *Ter. Mag. and Atmos. Elec.* p. 389, Sept., 1932.

⁴ Elliott, *Zeits. f. Physik* **67**, 75 (1931).

⁵ Johnson and Turner, *Proc. Roy. Soc.* **A142**, 574 (1933).

⁶ Duffendack and Smith, *Phys. Rev.* **34**, 77 (1929).

some instances the temperature indicated by the intensity distribution is not related to the temperature of the gas.

If the molecules of a gas are in thermal equilibrium at a temperature of $T^\circ\text{K}$, then the number of molecules that possess an amount of energy E is proportional to the Boltzmann factor, $\exp(-E/kT)$, where k is the Boltzmann constant. If this energy E consists partly of energy of electronic excitation E_e , partly of atomic vibration E_v , and partly of molecular rotation E_r , this temperature factor may be written

$$\exp[-(E_e + E_v + E_r)/kT].$$

For molecules of the same gas and the same electronic and vibrational energies, i.e., for molecules whose transitions give rise to a particular band, E_e and E_v are constant, and so the temperature factor becomes $\exp(-E_r/kT)$. The intensity of an emission line in a band may thus be written

$$I = Ci \exp(-E_r/kT),$$

where i is an intensity factor proportional to the probability of the transition and to the statistical weight $2j+1$ of the initial level, where j is the rotational quantum number. The factor C is a constant, or very nearly a constant, for a given band and must be calculated for the particular state in question. In the case of the negative bands of nitrogen, the intensities of the rotation lines, after inserting the appropriate intensity factor, reduces to

$$I_i = Cj \exp(-j(j+1)h^2/8\pi^2IkT).$$

If, then, we plot the values of $\ln I_i/j$ against $j(j+1)$, the slope of the line is given by $-B/kT$, where $B = h^2/8\pi^2I$.

The value of the parameter T may also be obtained from the quantum number of the line of maximum intensity, for

$$T = j_m(j_m+1)h^2/4\pi^2Ik,$$

where j_m is the rotational quantum number of the line of maximum intensity in the band. Both methods were used to determine the temperature parameter in this investigation.

APPARATUS

A low voltage arc excited in a Pyrex bulb 12 cm in diameter was the source of radiation in most of the experiments. The space between the filament and the anode was about 15 mm. The anode was a disk of nickel 15 mm in diameter, and the gas was at a pressure of 2 mm of Hg. At 100 m.a. current, the discharge confined itself to a bright glow between the anode and filament. At higher currents, the gases, especially CO, cleaned up very rapidly. The filament was either of six turns of 12 mil tungsten wire, run white hot, or an oxide coated strip of nickel. To start the discharge with the oxide coated filament, it was necessary to employ sufficient current to heat one spot bright red, but once the discharge started, the glow remained bright and steady without extraneous heating of the filament. It was just possible to see the dull red glow of the oxide coating and so the temperature of the filament could hardly have been more than 1000°K.

The spectrographs employed were a Hilger E-1 with a quartz prism, used in the third region for the ultraviolet bands of CO^+ , and the 21 ft. grating of the department for the negative bands of nitrogen. The photographic plate used was the Eastman Polychrome, the contrast of which is well known from its extensive use in this laboratory. In the first experiments, the temperature parameters were determined from the position in the band of the line of maximum intensity and the relative intensities of the lines were not measured. If a Maxwellian distribution exists, this method gives the correct temperature parameter. In order to avoid making this assumption, the relative intensities of the lines were measured⁷ in the later work and the temperatures determined both from the position of the line of maximum intensity and from the slope of the $\ln(I_i/j)$ vs. $j(j+1)$ plot. Excellent agreement was had between the values obtained from the two methods.

EXPERIMENTAL PROCEDURE

The discharge tube was baked out thoroughly and the metal parts thoroughly degassed in order to remove all traces of CO especially as this

⁷ Thomson and Duffendack, J.O.S.A. 23, 101 (1933).

affects the distribution of intensity in the negative bands of nitrogen. The tube was then filled with nitrogen, or nitrogen and helium, to a total pressure of 2 mm. The discharge current was kept at 100 m.a., and some part of the discharge placed to form an image on the slit of the spectrograph. Four positions in the glow were photographed. In the first case, the end-on image of the filament was thrown on the slit, and, in the case of the tungsten filament, the temperature of the gas inside the helix was about 2600°C. The other parts of the discharge investigated were at 5 mm, 10 mm and 15 mm from the filament. In the last case, the image of the cold anode was thrown close to the slit, and the layer of gas next to that was photographed. The object of this experiment was to photograph gas at various temperatures and determine the effect on the temperature parameter in the intensity formula.

The time of exposure necessary to obtain a mean plate blackening, the same in all cases, increased enormously in the four successive positions. The intensity probably fell off exponentially with the distance from the filament. The results show that it was not stray light from the intense glow around the filament which was forming the photographic image. Were that the case, the variation of exposure time would not be expected to be so marked. The actual times necessary were from one minute at the filament to four hours at the anode. This point was further tested by welding small nickel shields to the filament leads, so placed that no light from regions near the filament could fall upon the condensing lens.

Photographs of the negative bands of nitrogen at 3914Å and 4278Å were taken in pure nitrogen and in mixtures of nitrogen with helium, carbon monoxide, argon and neon, respectively, each containing various percentages of nitrogen. Photographs of the first negative bands of CO⁺ were taken in mixtures with nitrogen, helium and argon. The negative bands of oxygen were also examined in the pure gas and in mixtures with helium. Both for O₂ and for CO, the first negative bands lie in the ultraviolet, and, although the experimental procedure is more difficult and less weight is to be placed on the

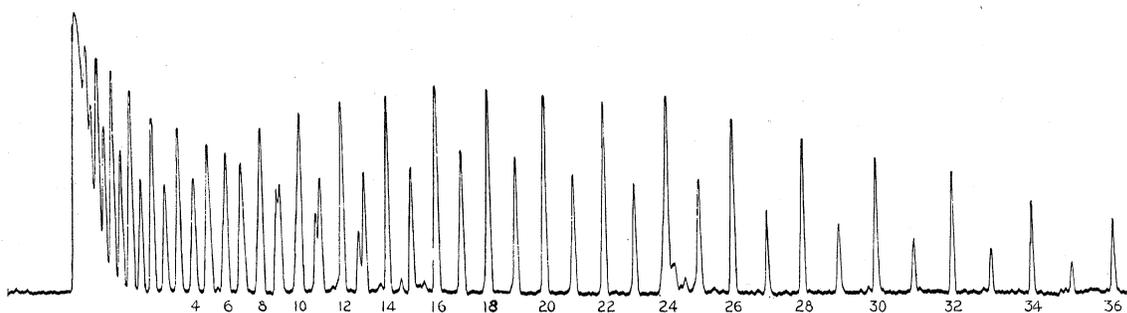
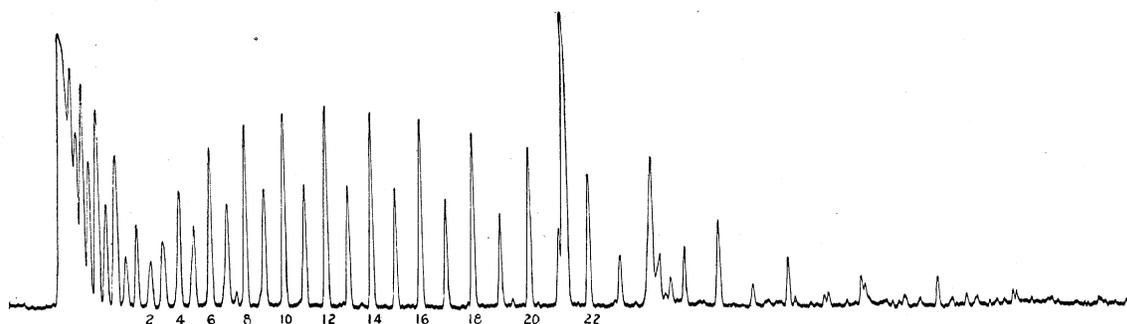
observations, they do confirm the conclusions arrived at for nitrogen.

In addition to the low voltage arc two other sources were used: an electrodeless discharge, and the glow discharge excited by a sixty cycle neon sign transformer giving a potential difference of 14,000 volts on open circuit. The lengths of exposure needed for the 21 foot grating with these sources were forty hours and eight hours, respectively.

In order to determine whether there was any relation between the electron temperature in the plasma of the low voltage arc and the temperature parameter of the intensity distribution, measurements were made on the electron temperatures by the usual Langmuir probe method. The collector consisted of a molybdenum wire 0.2 mm in diameter and was mounted about 2 mm from the filament. The currents collected gave very nice straight-line semi-logarithmic plots indicating two groups of electrons. The primary group had the temperature corresponding to the accelerating potential of the electrons from the filament. The large group of plasma electrons in a 100 m.a. arc at 50 volts had temperatures of about 20,000°K and the results were the same for pure nitrogen and for mixtures of 10 percent nitrogen and 90 percent helium. The electron temperatures were enormously greater than the temperatures indicated by the intensity distribution in the bands and had no relation to them.

RESULTS

Typical microphotometer traces are shown in Fig. 1 (a) and (b). The upper is a trace of the N₂⁺ band at 3914Å taken in the pure gas. The source was a 100 m.a. low voltage arc at 200 volts. The gas pressure was 2 mm and the light was taken from a point 5 mm from the tungsten filament. The lower trace is of the same band taken under the same conditions of arc current and voltage, gas pressure and position in the discharge, but this time the nitrogen formed but 5 percent of the total gas mixture, the balance being helium. The high peak next to the line corresponding to $j=21$ in the *R* branch is the helium line at 3888Å. It is readily seen that the intensity distribution is entirely different and

FIG. 1(a). 3914 N₂ in pure nitrogen.FIG. 1(b). 3914 N₂ in helium; 0.1 mm nitrogen, 1.9 mm helium.

that in the excitation with helium a lower value of the parameter T must be taken. The temperatures indicated by the intensity distributions are 1425°K for the pure gas and 500°K for the mixture. This procedure was repeated for various percentages of nitrogen in helium, and the variation of T with the nitrogen content of the mixture is shown in Fig. 2.

Traces identical with those of Fig. 1 were obtained when the much cooler oxide coated

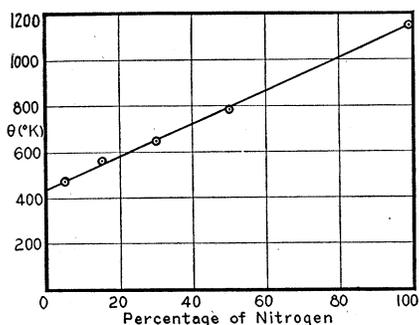


FIG. 2. Showing the relation between θ and the percentage of N₂ in the nitrogen—helium mixture. This relation is independent of the filament temperature.

filament was used and show that the intensity distribution among the lines of the bands is independent of the temperature of the filament. Furthermore the indicated temperatures in a given arc were the same for all positions in the arc between the filament and the anode, and therefore the temperature parameter is also independent of the temperature of the gas. Except for a small change in the indicated temperature with a change in the arc voltage, to be discussed later, the parameter T depends only on the composition of the gas. The results are the same in the case of the first negative bands of CO⁺ in the pure gas and in mixtures with helium. Microphotometer traces of some of these bands are shown in Fig. 3.

In the spectra of the same bands excited in the electrodeless discharge and in the glow discharge produced by the neon sign transformer, the indicated temperatures were much lower. The values obtained from the positions of the lines of maximum intensity were 330°K and 430°K, respectively, both of which must have been close to the true temperatures of the gas in the discharges. Furthermore, in these cases when

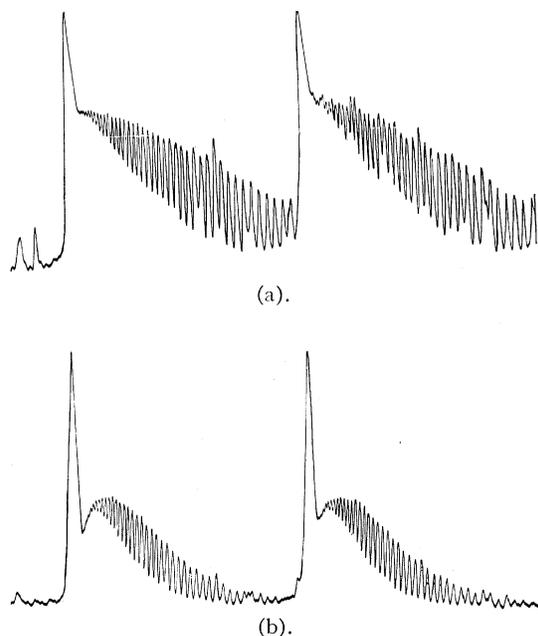


FIG. 3. Negative bands of CO⁺ excited (a) by electron impacts (b) by metastable helium atoms.

the current density was small, the intensity distribution was the same in the helium mixture as in the pure gases.

DISTRIBUTION OF INTENSITY AMONG THE VIBRATIONAL STATES OF NITROGEN

Ornstein and Brinkman⁸ have shown that, in the case of the electric arc, the vibrational energy distribution in the violet cyanogen band system obeys the Maxwell-Boltzmann law and that the temperature derived from this distribution is the same as that derived from the distribution of intensity among the rotational lines of one of the bands. This is very probably always true whenever the excitation is almost completely due to thermal action but may not be true for other modes of excitation.

The complete system of the negative bands of N₂⁺ has been examined when excited in the low voltage arc by means of electron impacts in the pure gas and also when excited by collisions of the second kind with metastable helium atoms in mixtures of helium and nitrogen. In Fig. 4, a

⁸ Ornstein and Brinkman Kon. Akad. van Wet. te Amster. 34, 33 (1931).

TABLE I. Densities of negative bands excited by electron impacts.

v' \ v''	0	1	2	3	4	5
0	3914 40	4278 18	4709 9			
1	3582 10	3884 8	4237 10	4652 4		
2	3308	3564 2*	3858	4199 3	4600 2	
3	3078 †	3299	3549 1*	3835	4166 1	4516 1

* Partially obscured by other bands.
† Not in region of spectrum photographed.

TABLE II. Densities of negative bands excited by metastable atoms of helium.

v' \ v''	0	1	2	3	4	5	6	7	8	9
0	3914 20	4278 15	4709 9							
1	3582 12	3884 10	4237 12	4652 8						
2	3308 5*	3564 10	3858 6	4199 10	4600 7					
3	3078 †	3299 4	3549 10	3835 2*	4166 6	4554 5				
4	2885 †	3076 †	3293 5	3538 6*	3818 2*	4141 4	4516 4			
5					3533 3*			4486 3		
6									4467 2	
7										4459 1

* Partially obscured by other bands.
† Not in region of spectrum photographed.

section of one of the plates is reproduced. The spectrum (a) was excited by electron impacts in the pure gas and (b) was excited by impacts of the second kind with metastable helium atoms. For (a), a low voltage arc of 62 milliamperes at 100 volts was maintained in pure nitrogen at 0.3 mm pressure, and for (b) the arc had the same current and voltage in a mixture of 90 percent helium and 10 percent nitrogen at a total pressure of 2 mm. Tables I and II give a list of the bands observed in each case together with an estimate of the photographic densities of the bands. From the tables it is seen that we get the usual parabolic distribution of intensity among the vibrational states. But when the bands are excited by electron impacts, the intensity is concentrated largely among the bands of low vibration, while,

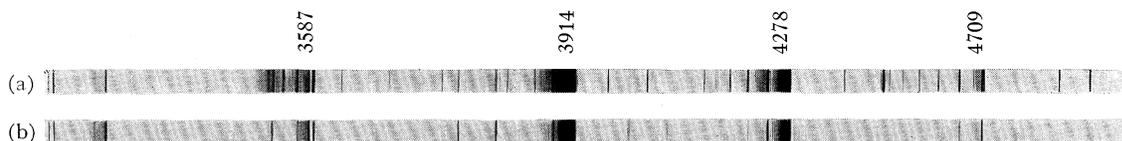


FIG. 4. Low voltage arc. (a) 10 percent N_2 , 90 percent He at total pressure of 2 mm; (b) N_2 at 0.2 mm pressure.

on the other hand, when the bands are excited by collisions of the second kind, the intensity is spread out toward the higher vibration quantum states. Smyth and Arnott⁹ found a similar distribution when these bands were excited by canal rays.

If thermal equilibrium exists, the intensity of a particular band is given by

$$I_{v'} = AP_{v',v''} \exp(-E_{v'}/kT),$$

where $E_{v'}$ is the vibrational energy in the initial state and $P_{v',v''}$ is the transition probability for a transition from v' to v'' . From this formula, it is obvious that the temperature indicated by the intensity distribution in (a) where the excitation was by electron impacts is much lower than that in (b) where the excitation was by collisions of the second kind. This result is in direct contrast with that obtained from the distribution of intensity among the rotational lines of individual bands excited in the same two sources. The intensity distribution among the vibrational states in the second positive band system of nitrogen was found to be the same in pure nitrogen and in mixtures of nitrogen with helium, although the bands are much weaker in the latter case. This agreement of intensity distribution in the positive band system was to be expected as these bands are not excited by collisions of the second kind with metastable helium atoms and are excited by electron impacts in both the pure gas and in the mixture with helium.

DISCUSSION

It is obvious from the results that, under the conditions of excitation prevailing in these experiments, the effective parameter, T , has little to do with the temperature. In the case of excitation by impacts of the second kind, the parameter for the rotational distribution has a value which is

probably close to the real temperature while the parameter for the vibrational distribution is far from it. The close agreement between the value of the parameter for the rotational distribution and the temperature of the gas can be accounted for in the following manner. In such an impact, the exchange of momentum is not different from that in ordinary kinetic theory impacts between gas molecules and the quantum number of the rotational state will not change by more than one unit as a general rule. In fact, the action radius of the metastable helium atom for this impact may be so great that there will be no mechanical reaction at all. In any case, the rotational distribution of the gas molecules will not be greatly disturbed, and so the parameter, T , will have a value close to the temperature of the gas.

On the other hand, the vibrational distribution may be expected to be considerably altered by impacts of the second kind. The force between the nitrogen atoms in an impact of the second kind with metastable helium atoms, for example, will be affected by the field of the metastable atom. As a consequence, the distance between the atoms of the molecule may change markedly during the time the molecules are in proximity of each other and the resulting ion be left in a higher vibrational state. Thus the temperature parameter for the vibrational states may be higher than that for the rotational states of the same molecules and have a value higher than the temperature of the gas.

That the high indicated temperature for the vibrational distribution is a consequence of the impacts of the second kind and is not due to the mere presence of another gas is shown by the fact that the positive bands of nitrogen and of carbon monoxide when excited in mixtures with helium have the same vibrational distribution as well as the same rotational distribution as when they are excited in the pure gas. It was also observed that the negative bands of N_2^+ are

⁹ Smyth and Arnott, Phys. Rev. **36**, 1023 (1930).

strongly excited in a mixture of 10 percent N_2 with 90 percent CO, and the rotational and vibrational distributions are quite like those of the same bands excited by metastable helium atoms. The negative bands of CO^+ are, however, only weakly excited in a similar mixture with nitrogen as the preponderant gas. In this case the rotational and vibrational distributions are quite like those of the same bands excited in a low voltage arc in the pure gas. Thus it would seem that the first negative bands of N_2^+ are excited by impacts of the second kind by excited CO^+ ions whereas the negative bands of CO^+ cannot be excited by impacts of the second kind with excited N_2^+ ions. As the energy level of the initial state of the negative band system of N_2^+ is 19.6 volts while that of the initial state of the first negative system of CO^+ is 19.8 volts, these results are to be expected. The kinetic energy of the ions in the discharge was too low to make up the deficit in energy in the latter case.

The distribution of intensity among the vibrational states when the bands were excited by electron impacts in a low voltage arc in the pure gas is the usual one which has been accounted for by the Franck-Condon theory. The temperature parameter of this distribution was not determined, but it is probably close to the temperature of the gas.

The higher temperature indicated by the rotational distribution under these same conditions should be explained. It is obvious from the experiments that the value of the parameter has nothing to do with the temperature and varies for pure gases very slowly and only with the accelerating potential of the electrons. Several possible explanations have been considered, such as the possibility of the gradual raising of the rotational states of the molecules by successive electron impacts previous to the exciting impact and the action on neutral molecules of the impacts of positive ions moving through the gas. Neither of these seemed adequate and they were rejected in favor of the following proposal based upon the direct effect of an electron impact at the time of the ionization and excitation of the molecule.

The electrons will be scattered by the impacts with the gas molecules and the angular momenta after impact with respect to the centroid of the

molecule will be different from the angular momenta before impact. One might apply the principle of the conservation of angular momentum if he knew enough about the scattering of electrons under these conditions, but very little is known about this type of scattering. In general, inelastic scattering is at smaller angles than elastic scattering and is nearly all forward so that very small changes in the angular momentum of the molecule would be expected. However, when the molecule is ionized simultaneously so that the ejected electron must be taken into consideration, one can say nothing about a probable change in the angular momentum of the molecule. For this case, Mott and Massey¹⁰ state that the intensity of the scattered electron beam will be greater than for elastic scattering for angles near zero and ninety degrees and less at intermediate angles.

Let us consider the case of excitation by electrons of energy distributed about a mean value of 100 electron-volts. The range of velocities in this distribution will be very small compared with the average velocity, so that the number of electrons will be a sharp-peaked function of the velocity. If, on impact, a small fraction of the electron energy is transformed into energy of rotation of the molecule one will get a new rotational distribution of the molecules about an angular velocity increased by a few quantum units. Before impact, this distribution was Maxwellian and could be characterized by a certain temperature, the gas temperature. The nature of the distribution would be altered very little and so the new distribution could also be characterized by a temperature which would be higher than gas temperature. This is what the experiments seem to show. The position of the line of maximum intensity in the N_2^+ 3914 band was at $j_m=12$ for a low voltage arc at 25 volts, at $j_m \approx 13.5$ for an arc at 100 volts and at $j_m \approx 15.5$ for a 200 volt arc. The temperatures corresponding to these positions are 855°K, 1078°K, and 1425°K, whereas the gas temperature was probably about 550°K. Thus it is seen that the shift of the position of the maximum is very small and increases slowly with the voltage of the exciting electrons. Hence

¹⁰ Mott and Massey, *Atomic Collisions*, p. 174.

only a small fraction of the energy of the electrons need be transformed into increased energy of rotation of the molecule in order to account for the results. For 100 volt electrons the shift would require that approximately 0.009 electron-volt energy be transformed or only 0.009 percent of the kinetic energy of the electron before impact.

In this connection, mention should be made of the observations of Lindh¹¹ who investigated the intensity distribution in the 3914 band excited by electrons projected into a field free enclosure. He found that the distribution was Maxwellian and that the indicated temperatures

¹¹ Lindh, *Zeits. f. Physik* **67**, 67 (1931).

were 551°K and 596°K for electrons accelerated by 150 volts and 175 volts, respectively. These temperatures, while lower than those indicated for the low voltage arcs in pure gases, show that increasing the voltage increases the temperature parameter. The difference in the experimental conditions undoubtedly accounts for the difference in the values of the indicated temperatures in the experiments of Lindh and those of the present investigation.

In conclusion, the authors wish to express their appreciation for the suggestions of Professor G. E. Uhlenbeck and Dr. L. A. Young during discussions of this problem with them.

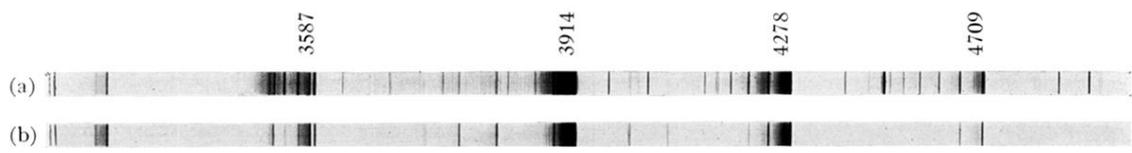


FIG. 4. Low voltage arc. (a) 10 percent N_2 , 90 percent He at total pressure of 2 mm; (b) N_2 at 0.2 mm pressure.