Temperature Parameters from Negative Bands of Nitrogen under Excitation by Electron Impact

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In a field-free space, temperature determations along the axis of the discharge tube have been carried out from measurements on the intensity distribution of the negative bands of nitrogen under different excitation conditions. The indicated temperatures were compared with the true gas temperatures directly measured by a thermoelement and found to be the same. From a heat conduction consideration, a theoretical formula has been derived in terms of Bessel functions, which gives calculated values in good agreement with the experimental results. The variation of temperature with gas pressure was determined and it was found that the change of the thermal conductivity of the gas within the experimental range could account for the results. The temperature variation with current under different positions of the tube was ascribed to the effect of convection currents. The indicated temperature was experimentally proved to be independent of the accelerating potentials from 20 volts to 800 volts. The non-transference of energy between electrons and molecular rotation was attributed to the large difference of the masses of the electrons and nitrogen molecules.

The temperature distribution between the electrodes in a low voltage arc has been investigated. The fact that in this case, the temperature increases with potential applied to the arc was explained by the fact that the energy of the positive ions, which increases with field, is readily transferred to the gas molecules. When the negative bands were excited by collisions of the second kind, it was concluded that some of the surplus energy goes into molecular rotation during the process of the collisions. In a cold cathode glow discharge, gas temperatures as well as electron temperatures were measured. The results showed that both these temperatures were higher near the cathode fall space.

INTRODUCTION

THE intensity measurements of individual lines in a band will lead to information of the relative populations of the rotational energy states of the radiating molecules. The collective description of the distribution of the molecular energy states is made possible by means of a so-called temperature parameter or effective temperature. It is worthy of note that under various excitation conditions, the distribution is such that it can be described by a temperature parameter. Any variation of the temperature parameter will correspond to a new distribution of the molecules among the energy states. If there exists a thermal equilibrium between the excited molecules and those in the ground states, the temperature parameter will be equal to the true temperature of the source. But in cases where conditions are far from thermal equilibrium, temperature determinations from the intensity distribution of bands will yield results which are still significant to an interpretation of the excitation conditions.

A wide range of temperature variations has been found by many investigators[1–4] employing the negative bands of nitrogen which are particularly suitable for this investigation because of the numerous lines in the bands and the sufficient width of the line separations for complete resolution by a prism spectrograph. Duffendack, Revans and Roy[5] have measured the temperature parameter in a low voltage arc where positive ions and electrons can gain considerable energy from the field and so the determined temperature, which represents the mean kinetic energy of the various particles in the source, is not the true temperature of the gas. It is interesting to see how the temperature behaves in a source where the field is comparatively negligible. It is the purpose of the present work to study the temperature distribution along a beam in a field free space and to compare the temperature directly measured by a thermoelement with that indicated from intensities of bands produced under various excitation conditions. Such studies

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[1] L. S. Ornstein and W. R. van Wijk, Zeits. f. Physik **49**, 315 (1928).
[2] W. R. van Wijk, Zeits. f. Physik **59**, 313 (1930).
[3] A. E. Lindh, Zeits. f. Physik **67**, 67 (1931).
[4] N. Thompson, Proc. Phys. Soc. **46**, 436 (1934); **47**, 413 (1935).
[5] Duffendack, Revans and Roy, Phys. Rev. **45**, 807 (1934).

are important in the investigation of the transfer of energy from electrons to molecules and also in the explanation of the development of heat in electric discharges.

The intensity of a spectral line emitted from an assemblage of radiating systems depends on the number of particles in the initial state, the transition probability, and the emitted frequency associated with two states in the radiating particles. By the extension of Einstein's theory[6] and through the correspondence principle, the intensity expression can be shown to be

$$I=\frac{64\pi^4\nu_{jj'}{}^4N}{3C^3\sigma}g_jP^2(jj')e^{-E_j/kT}, \qquad (1)$$

in which $\nu_{jj'}$ is the radiating frequency for the transition $j\rightarrow j'$, N the total number of molecules present, g_j the statistical weight, and $P(jj')$ the electric moment for the transition. σ is the Zustandssumme $\Sigma g_je^{-E_j/kT}$, where k is Boltzmann's constant and E_j the energy of the particle in the initial level j. For molecules of given electronic and vibrational transition, the Boltzmann factor in the above expression can be replaced by $\exp[-J'(J'+1)h^2/8\pi^2I'kT]$, where J' is the rotational quantum number in the initial state, I' the moment of inertia of the molecule in the initial state, and T the temperature parameter corresponding to a thermal equilibrium. For the negative bands of nitrogen, the product of g_j and $P^2(jj')$ was shown by Mullikan[7] to be proportional to J' for the R branch and to $J'+1$ for the P branch. As the spread of the lines within a band covers only a very short region of wave-lengths, the correction factor $\nu_{jj'}{}^4$, in this case may be considered constant. Hence the intensity relation for the R branch becomes then

$$I=CT'\exp[-J'(J'+1)h^2/8\pi^2I'kT], \qquad (2)$$

in which C is a constant or nearly so in a given band.

If the distribution of energies of molecules amongst the initial rotational levels for an emission band is Maxwellian, the temperature parameter can be determined from the slope of a log (I/J') *vs.* $J'(J'+1)$ plot. The temperature determined in this way can be checked by estimating the position of the most intense line in the band. The latter method is not so accurate, because the envelope of the intensity distribution curve usually has a broad maximum. Very recently, Knauss and McCay[8] developed a new method for temperature determinations, which makes use of the intersection of the envelopes of the microphotometer records for the different branches of a given band. The temperature is obtained by locating the place in a band, where the simultaneous requirements of equality of intensity and equality of frequency are satisfied.

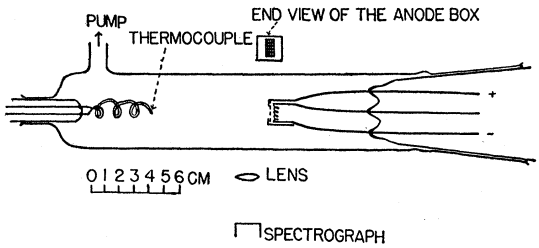

FIG. 1. Discharge tube.

APPARATUS

The discharge tube used in the experiments was of the ordinary type frequently employed in investigating collision problems. In Fig. 1 is given a diagrammatic sketch of the tube. The cathode consisted either of a bare tungsten wire of 15 mil diameter and 8 cm long coiled into 15 turns, or of a molybdenum strip about 2 cm long and 2 mm wide coated with barium and strontium oxides. The anode was in the form of a cubic box ($17\times17\times17$ mm) made of thin nickel sheets. On one side of the box an opening about 4×10 mm was cut and a piece of fine nickel gauze was put inside. The box and gauze were at equal potentials. The filament was mounted inside the box at a distance of about 3 mm from the gauze. At a gas pressure of a few tenths mm Hg, only a few collisions could be made between electrons and gas molecules inside the box. For a potential of 800 volts, the glow extended about 8 cm outward from the gauze. The box entirely enclosed the filament so that a practically field-free space was obtained outside the box. The whole electrode system could be

[6] A. Einstein, Physik. Zeits. **18**, 121 (1917).
[7] R. S. Mullikan, Phys. Rev. **30**, 138 (1927).
[8] H. P. Knauss and M. S. McCay, Phys. Rev. **52**, 1143 (1937).

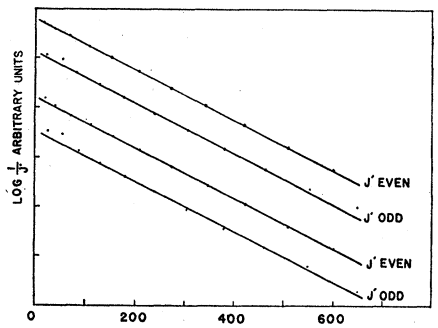

FIG. 2. Log I/J' *vs.* $J'(J'+1)$ plot for λ4278 band.

easily taken out of the tube through a glass joint for adjustment and filament renewal.

EXPERIMENTAL PROCEDURE

The electrodes and the discharge tube were thoroughly outgassed. Care was taken to exclude mercury vapor and vapors from stopcock grease during the admission of nitrogen, because it was found that the temperature parameter was affected by these vapors. A Hilger E-1 spectrograph with a glass prism was used in the experiments. The fine structure of the negative bands at λλ4278 and 4709 was well resolved with this instrument. By means of a condensing lens, an image was formed on the slit of the spectrograph of a part of the discharge. Eastman Polychrome photographic plates were used throughout. Intensity marks were put on each plate by means of a step slit.[9] The microphotometer traces of the bands showed that the lines were sharp and symmetric, therefore the peak intensities were used instead of the integrated values.

In most cases in the experiments, the log (I/J') *vs.* $J'(J'+1)$ plot gave straight lines. Hence a Boltzmann distribution among the rotational levels existed. Fig. 2 is the plot of two spectra under the same discharge conditions. Since the bands show alternate intensities, two straight lines will be obtained by treating separately the even and odd values of the quantum numbers for the R branch of the bands. The temperature parameter is determined from the slopes of these lines and it will be seen from the graphs that good agreement is obtained in the results from the different lines. Sometimes two or three points at low J' values did not fall on the straight line. This deviation from linearity may be due to the inhomogeneity of temperature in the discharge tube as pointed out by Lochte-Holtgreven and Maecker.[10] The pressure in the tube was low and so no self-absorption or self-reversal was observed to affect the intensity graphs appreciably.

The true temperature of the gas was measured by means of an iron-constantan thermocouple mounted in the tube as shown in Fig. 1. In order to see how much the measured temperature was affected by the radiation of the filament, since the thermocouple was subjected to the radiation in the experiments, two tests were made. One was to heat up the filament until it reached the equilibrium temperature and then the filament was suddenly cut off. The thermocouple showed that the gas temperature fell down in accordance with Newton's law of cooling. Were radiation affecting the thermocouple, its temperature would show an abrupt change. The other test was to measure the variation of temperature along a radius of the tube by moving the thermocouple. The temperature decreased as one moved

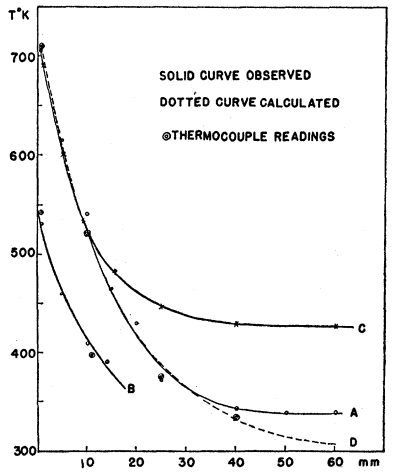

FIG. 3. Temperature distributions along the axis of the tube. Curve A, excitation by electron impact with tungsten filament, pressure 0.3 mm, 800 volts, 20 ma. Curve B, excitation by electron impact with oxide-coated filament, pressure 0.3 mm, 100 volts, 20 ma. Curve C, excitation by collision of the second kind, total pressure 1.6 mm, 800 volts, 20 ma. Curve D calculated.

[9] K. B. Thomson and O. S. Duffendack, J. Opt. Soc. Am. **23**, 101 (1933).

[10] W. Lochte-Holtgreven and H. Maecker, Zeits. f. Physik **105**, 1 (1937).

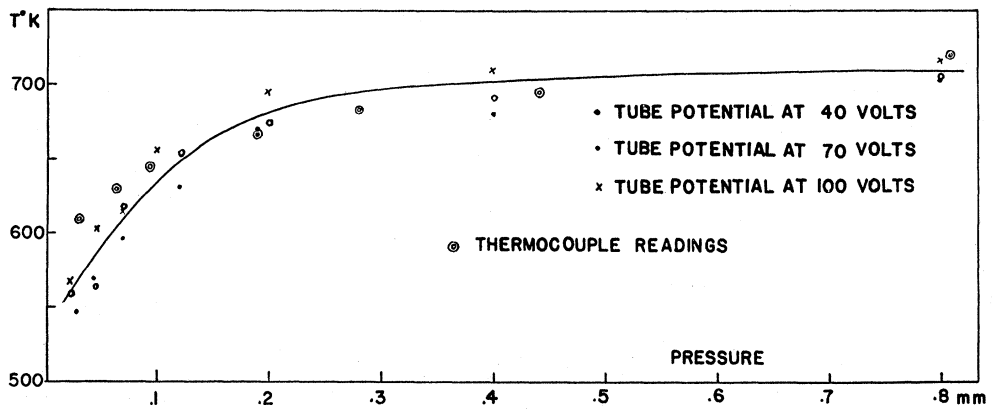

FIG. 4. Temperature variation as a function of pressure.

away from the axis of the tube. But no sudden drop was observed when the thermocouple passed the point where it received no direct light from the filament.

EXPERIMENTAL RESULTS

The discharge tube was mounted in the horizontal position. For a given voltage applied between the filament and the anode of the tube and at a fixed tube current and gas pressure, a series of exposures was made on the same plate. For these exposures, light was focused from different positions along the axis of the tube. The exposure times necessary to obtain a measurable blackening varied from 15 minutes just outside the opening of the box to 6 hours at 6 cm away. The intensity fell off rapidly with distance from the opening. In the case of higher voltages, it was necessary to admit gas during a run through an adjustable leak to the discharge tube to compensate for the disappearance of traces of gas during the exposure. The results are presented in Fig. 3*A*. When a lower accelerating potential was employed, the glow contracted toward the opening. The temperature distribution, however, remained the same.

In order to see how much the determined temperature was affected by the temperature of the filament, an oxide-coated filament was used, which gave sufficient emission when heated barely to incandescence, so that its temperature was much lower than that of bare tungsten. In the case of the cooler filament, it was found that the determined temperatures were lower, but distributed along the axis of the tube in the same manner as will be noted in Fig. 3*B*.

It was thought that the determined temperatures from bands may be equal to the true temperatures of the gas in the discharge tube. The gas temperatures were then measured by a thermocouple along the tube. The results were in good agreement with those from band intensities as shown by the graph. It may be concluded from these experiments that the temperature at any point along the tube depends on the temperature of the gas, as determined mainly by the temperature of the filament, and not on the energy of the electrons.

The variation of temperature as a function of pressure was obtained with different accelerating potentials. Fig. 4 is the plot of the results obtained when one focused on the slit of the spectrograph a portion in the discharge just outside of the opening; the discharge current is 20 ma. The plot shows that the determined temperatures were independent of the accelerating potentials, and that at the lower pressures the temperatures increased linearly with pressure and then came to a constant at higher pressures, in agreement with temperatures of the gas as determined by the thermocouple. During exposure, the pressure of the gas in the tube continually decreased, and admission of gas was made intermittently. The fluctuation of pressure in the tube may explain the scattering of the points on the plot.

When the tube was mounted horizontally, a nearly constant temperature was obtained as the tube current was changed from 10 ma to 100 ma,

and the temperature indicated by the thermocouple was in good agreement with that from the bands. When the tube was mounted vertically, with the filament in the lower end, it was found that both the band temperatures and thermocouple readings increased linearly with tube current as shown in Fig. 5. It is concluded that the temperature variation with current must be a heat effect. In the case of a vertical tube, convection currents become appreciable. It will be noted from the graph that the temperature of the gas at a point 2 mm above the box increased about 175°K, when the tube current was increased from 20 ma to 100 ma.

As we have already seen, the temperatures determined by a thermocouple and from intensity distributions of the rotational lines of a band were independent of the potential applied between the filament and anode, when the pressure and current as well as distance from the opening of the anode was varied. So far as the present experimental arrangement is concerned, it was definitely found experimentally that the band temperature is constant at various accelerating potentials up to 800 volts. However, a temperature variation was observed at very low potentials as shown in Fig. 6. Below 20 volts the negative bands did not come out but the positive bands were very strong. On increasing the potential, the intensity of the negative bands increased also. Under the same discharge conditions, the thermocouple gave a constant gas temperature, which was equal to the band temperature at the higher potentials. When the potential had a value less than 28 volts, the band temperature was lower than the gas temperature. This discrepancy between the temperatures was thought to be due to the contraction of glow.

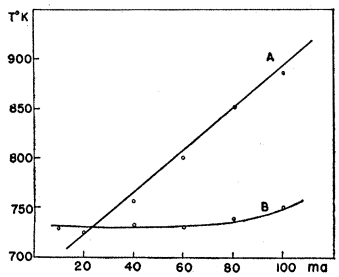

FIG. 5. Temperature variation as a function of current. *A*, tube in the vertical position. *B*, tube in the horizontal position.

At very low potentials, the glow extended out of the opening only 2 or 3 mm at a gas pressure of 0.3 mm Hg. The band intensity indicated a mean value of the temperature in a certain volume of the glow, while the thermocouple measured the temperature of a point, where its junction was placed; consequently a higher temperature resulted from the thermocouple. If this explanation is correct, at a comparatively lower pressure this discrepancy would disappear on account of the expansion of the glow. An experiment was made at a gas pressure of 0.1 mm Hg and a constant band temperature of 650°K was gained even at the lower potentials. It should be pointed out here that when electrons accelerated by 150 volts and 175 volts were projected into a field-free enclosure, Lindh[3] observed a temperature difference of about 45°K in these two cases. This, however, was not reproduced in the present work.

TEMPERATURE VARIATIONS IN A LOW VOLTAGE ARC

In this experiment, the same discharge tube, with some modifications, was employed. The metal box used as anode was replaced with a nickel plate about 15×15 mm. The electron emission was supplied from a heated platinum wire coated with barium oxide. The distance between the electrodes was about 1 cm. When a low voltage arc ran at 40 ma and light was taken from a point 4 mm from the cathode, it was found that the band temperature increased at first linearly with the potential, then came to a constant value. The rate of increase depended upon the gas pressure. Fig. 7 is a plot of the observed results at two different gas pressures. The increase of temperature with potential is in agreement with the observations of Duffendack, Revans and Roy.[5] These authors proposed some possible ways to account for this phenomenon. One was the transference of a fraction of the electron energy into molecular rotation during an electron impact. As the experimental fact shows that in a field-free space the accelerating potential cannot change the temperature of the gas in a wide range of potential variation, this explanation does not seem to be correct. However, the ions contribute more to the heating

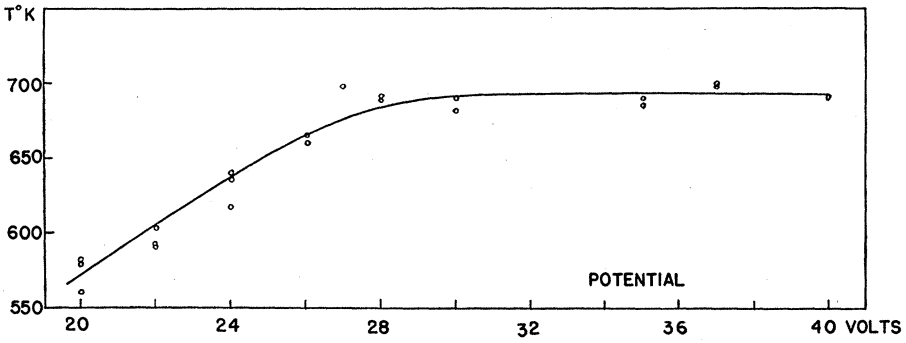

FIG. 6. Temperature variation as a function of potential. Tube pressure 0.3 mm, current 20 ma.

of the gas than electrons because of their larger masses. In a source where the field gradient is not too small, the energy of ions, and therefore their temperature, increases with field strength. In a low voltage arc due to the development of space charges, the field between the electrodes will be differently distributed when different potentials are impressed upon the electrodes. The constant temperature may correspond to a stage of distribution, where further rise of potential will not change the field, that is to the case of a normal low voltage arc in which the cathode fall of potential constitutes practically the entire potential difference of the electrodes. The concentration of ions increases with gas pressure. For a higher pressure, the temperature variation with potential will be more marked. Hence in Fig. 7 the rate of increase of temperature with potential at 1.1 mm Hg is greater than at 0.8 mm Hg.

The temperature distribution along the axis of the tube in a low voltage arc was measured from the intensity distribution of the rotational energy states. Curve *A* in Fig. 8 gives the values observed when the arc was running at 50 volts, 40 ma in a gas pressure of 0.3 mm Hg. Curve *B* is the temperature given by the thermoelement when there was no discharge between the electrodes and indicates roughly the effect on temperature due to radiation and positive ions. It is to be noted that in a low voltage arc, the effect of radiation on temperature should be more pronounced than in the case of the field-free space. The intensity of radiation was very much greater here.

TEMPERATURE VARIATIONS IN CASE OF EXCITATION BY COLLISION OF THE SECOND KIND

In the same discharge tube as was first used, a mixture of nitrogen and helium gases of total pressure 1.6 mm was employed, and the nitrogen contributed only 10 percent of the total pressure. It was found in this case also that the temperature indicated by the intensities of the bands was independent of the tube current and the impressed accelerating potential just as in the case where the negative bands were excited by electron impacts. But the temperature distribution along the axis of the tube showed some difference at the larger distances from the opening of the anode as is shown in Fig. 3*C*. It is very well known that when a metastable helium atom collides with a nitrogen molecule, the excitation energy may be transferred from one to the other by a resonance phenomenon. The helium atom has an amount of energy of 19.77 volts while a nitrogen molecule requires only 19.6 volts for simultaneous ionization and excitation. It is possible that part of the surplus energy of 0.17 volt goes into the rotation of the N_2^+ molecule. Since the masses of helium atoms and

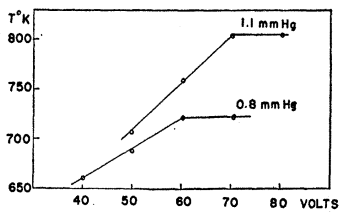

FIG. 7. Temperature variation as a function of potential in a low voltage arc.

nitrogen molecules are comparable, the persistence of molecular rotation[11] will not hold. At nearer distances to the opening where the concentrations of electrons are high (concentration of electrons decreases exponentially with distance), a large fraction of the N_2 molecules is excited by electron impacts, so the temperatures here are close to the temperature of the gas. At larger distances the molecules are excited mainly by collisions of the second kind, consequently a higher temperature is indicated by the bands.

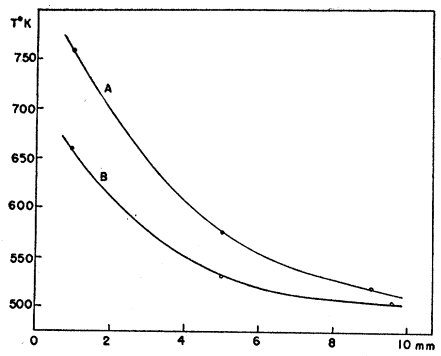

FIG. 8. Temperature distribution between the electrodes in a low voltage arc. *A*, observed from the intensity distribution of bands. *B*, measured by thermocouple when there was no discharge.

TEMPERATURE VARIATIONS IN A COLD CATHODE GLOW DISCHARGE

A cylindrical discharge tube 10 cm long and 8 cm in diameter was employed. At one end of the tube, a circular nickel disk electrode was mounted coaxially and at the other end an aluminum one. A collector made of a 3-mil tungsten wire and 6 mm long with mutually insulated sections as designed by Emeleus[12] was introduced into the tube in such a way that by means of an external electromagnet the collector system could be moved bodily along the axis of the tube. In a glow discharge running at a few hundred volts and about 10 ma in a gas at a pressure of a few tenths mm Hg, both spectroscopic and electrical measurements were made simultaneously. While a portion of the discharge along the tube was thrown upon the slit of the spectrograph with a lens for photographing, electron temperatures were measured by means of a Langmuir probe. The results showed that two groups of electrons existed, each of which was distributed in accordance with Maxwell's law with a characteristic temperature. The higher energy group or fast group had a temperature more than 20 volts and the lower energy group or ultimate group only a few volts. It was found that these two groups existed in any region of the negative glow under different discharge conditions. The fast group had a higher temperature in the cathode fall space where the band temperature was likewise higher. This was expected because we had a strong field in this section of the discharge. The band temperature slowly decreased as the position considered receded from the cathode. Table I shows a typical set of the experimental data, where the space potentials and concentrations of electrons are also included.

[11] O. Oldenberg, Phys. Rev. **37**, 194 (1931).
[12] R. H. Sloane and K. G. Emeleus, Phys. Rev. **44**, 333 (1933).

INTERPRETATION OF RESULTS

When the bands were excited by electron impacts, it was found that the thermocouple readings were in close agreement with the temperatures determined from intensity measurements on the bands under various excitation conditions. This means that the band temperatures actually represent the true temperatures of the gas. With this experimental fact, the temperature distribution along the beam in a field-free space can be explained by treating the case as a pure heat conduction problem. The source of heat was the heated filament. The total energy supplied to the discharge tube, except the little radiated, was conducted out to the wall of the tube by the gas molecules. The temperature due to radiation was neglected, for it was found that the change of temperature was less than 10 degrees when the discharge was cut off. We also neglected the part of heat conducted away along the leads of the discharge tube as the energy balance was not considered. In the steady state, the differential equation for heat conduction without radiation is

$$\text{div. } (K \text{ grad. } T) = 0, \qquad (3)$$

in which T is the absolute temperature and K the thermal conductivity of the gas considered.

The gas pressure in the tube was not too low and the mean free path was much smaller than the dimensions of the apparatus, hence we may assume that K is proportional to the square root of T. When cylindrical coordinates are introduced, and r is taken along the radius and z along the axis of the tube, the differential equation becomes

$$\frac{1}{r}\frac{\partial}{\partial r}\left(T^{\frac{1}{2}}r\frac{\partial T}{\partial r}\right)+\frac{\partial}{\partial z}\left(T^{\frac{1}{2}}\frac{\partial T}{\partial z}\right)=0. \tag{4}$$

If the substitution $S=T^{\frac{3}{2}}$ is made, the variables can be separated by expressing S as the product of a function of r and a function of z alone. Taking the constant of separation to be n^2, we get the solution of Eq. (4) as

$$S(r, z)=AJ_0(nr)e^{-nz}, \tag{5}$$

where A is a constant to be determined from the boundary conditions.

Since the temperature of the tube wall was constant (301°K), we set the boundary conditions as:

$$T=T_0 \text{ at } r=R,$$

the radius of the tube and $z=$any value; and

$$T=T_0 \text{ at } r=\text{any value and } z\rightarrow\infty. \tag{6}$$

These conditions are all fulfilled if we assume

$$T^{\frac{3}{2}}-T_0^{\frac{3}{2}}=\sum_{s=1}^{\infty}A_sJ_0(n_sr)e^{-n_sz}, \tag{7}$$

provided that n_s is chosen so that

$$J_0(n_sR)=0,$$

where n_s is the root of the Bessel function. The other boundary condition is given by the empirical relation

TABLE I. *Data obtained with Langmuir probe. Pressure 0.7 mm* Hg; *tube current 11 ma; tube voltage 410 volts;* Al *electrode used as cathode.*

Distance between probe and cathode	Space potential from anode	Electron temperature		Concentration per cc $\times 10^{10}$		Band temperature
		Fast	Ultimate	Fast	Ultimate	
3 mm	−12 v	28.0 v	3.3 v	3.36	9.7	503°K
5 mm	− 2.5 v	26.1 v	1.55 v	3.45	14.1	455°K
8 mm	0	23.6 v	1.3 v	3.6	15.3	435°K
11 mm	0	23.6 v	1.23 v	3.64	14.8	430°K

$$T^{\frac{3}{2}}-T_0^{\frac{3}{2}}=6.9(R^2-r^2) \tag{8}$$

at $z=10$ mm, which was obtained experimentally by means of the thermoelement. By means of Eq. (8) and making use of the orthogonal property of the Bessel functions, we obtain

$$A_s=\frac{27.6R^2e^{10n_s}}{(n_sR)^2[J_1(n_sR)]^2}J_2(n_sR). \tag{9}$$

After inserting the numerical values, the solution of our problem becomes

$$\begin{aligned}T^{\frac{3}{2}}=&5200+7500e^{-0.08(z-10)}J_0(0.08r)\\&-728e^{-0.184(z-10)}J_0(0.184r)\\&+254e^{-0.288(z-10)}J_0(0.288r)\\&-129.6e^{-0.393(z-10)}J_0(0.393r)\\&+53.4e^{-0.498(z-10)}J_0(0.498r)+\cdots.\end{aligned} \tag{10}$$

The values calculated from this expression are in good agreement with the observed data at z less than 30 mm as shown in Fig. 3*D*. At larger z values, the observed curve is higher. This deviation may be due to the negligence of some factors in the calculation. Firstly, we did not take into account the radiation part. Secondly, electrons may impart a small amount of energy to a gas molecule even when the collision is elastic. Although the fraction of energy lost by an electron at a collision of this type is only about $2m/M$, where m is the mass of the electron and M that of the molecule, the total energy transfered may become appreciable at the lower temperatures. In addition, positive ions and electrons recombine in the volume of the gas and the energy of recombination appears as heat. All these factors tend to increase the temperature of the gas.

The behavior of the temperature variation with pressure is quite understandable from heat conduction considerations. Soddy and Berry[13] found that the thermal conductivity of gases at extremely low pressures is accurately proportional to the pressure up to a value of about 0.05 mm. Then the departure from the linear relation begins and beyond 1.5 mm the conductivity does not sensibly increase with increasing pressure. Knudsen[14] investigated the problem theo-

[13] F. Soddy and A. J. Berry, Proc. Roy. Soc. **A83**, 254 (1910).

[14] M. Knudsen, Ann. d. Physik **34**, 593 (1911).

retically and found that at very low pressures where the mean free path of molecules becomes comparable with the dimensions of the apparatus, there should be a linear relation between the rate of dissipation of energy and gas pressure. The pressure range employed in the present work lies between the two extreme cases, so the observation that the temperature increases with pressure corresponds to the transition region. A quantitative explanation is very difficult and was not attempted.

The independence of temperature and the accelerating potential has been found to hold over a wide range. This result is in agreement with the observations of Ornstein and Langstroth,[15] who reported that the development of the rotational structure of the N_2^+ band at λ3914 did not change appreciably by increasing the accelerating potential up to 26 volts. When the negative bands are excited by electron impacts, the N_2 molecule preserves its angular momentum on account of the large difference of masses of the impacting particles. This persistence of molecular rotation is possible, because the moment of inertia of N_2^+ molecules in the excited state is very little different from that of the N_2 molecule in the ground state (the moment of inertia of $N_2^{+\prime}$ is 1.34×10^{-39} g cm^2 and that of N_2 1.39×10^{-39}) as was first noticed by van Wijk.[16] In view of this fact, the distribution of the molecules among the rotational states will not be changed during the process of excitation.

[15] L. S. Ornstein and G. O. Langstroth, Proc. Akad. Amst. **36**, 384 (1933); G. O. Langstroth, Proc. Roy. Soc. **A146**, 166 (1934).

[16] W. R. van Wijk, Zeits. f. Physik **75**, 584 (1932).

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A Search for an Electrostatic Analog to the Gravitational Red Shift*

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The possibility of an effect of electrostatic difference of potential upon the frequency of light, analogous to the gravitational red shift, has been investigated. Light of wave-length λ5461A was made to pass from a region of alternately zero, 300 kilovolts positive, and 300 kilovolts negative potential, established by means of a Van de Graaff generator, to a sensitive interferometer in vacuum at zero potential, where a frequency shift was sought. The results indicate a shift of about 0.9 ± 1.0 part in 10^{15} per volt, which is interpreted as a definite null result.

INTRODUCTION

GUIDED solely by analogy with the gravitational red shift, Kennedy and Thorndike undertook in 1930 a search for a frequency shift due to electrostatic difference of potential.[1] The data quoted by them indicated a shift of 1.1 ± 0.8 part in 10^{14} per volt for the source at positive potential with respect to the interferometer, and of 3.1 ± 1.6 parts in 10^{14} per volt for the source at negative potential. They interpreted these values as indicating a null result.

The fact that the indicated shifts were in both cases in excess of the probable error suggested the possibility that an investigation with increase of sensitivity might exhibit those differences as genuine excesses over the probable error and so reveal the existence of an effect of the kind sought.

APPARATUS AND METHOD

The experiment consists essentially in comparing the frequency of a spectral line in a suitable source at zero potential with that of the same source under identical conditions except that the potential of the source is raised or lowered. The source of light was a low voltage

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[1] R. J. Kennedy and E. M. Thorndike, Proc. Nat. Acad. **17**, 620 (1931).