COLLISIONS OF THE SECOND KIND AND THEIR EFFECT ON THE FIELD IN THE POSITIVE COLUMN OF A GLOW DISCHARGE IN MIXTURES OF THE RARE GASES

By L. B. Headrick and O. S. Duffendack
University of Michigan

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Abstract

A study was made of the collision processes in the uniform positive column of a glow discharge in mixtures composed of two of the rare gases, helium, neon and argon and a mixture of each of these gases with mercury vapor, by means of measurements of the electric field and by spectroscopic observations. The discharge tube was of cylindrical form, 4.4 cm in diameter, with plane parallel electrodes The electrode distance could be varied from zero to 32 cm by means of an external electromagnet. The phenomena were studied with currents from 20 to 40 m.a. and pressures from 5 to 30 mm of mercury. The mixtures were circulated through the discharge tube and a purifying system during the entire time that observations were being made. It was very important to maintain extreme purity of the gases. The results show that the electrical and spectral characteristics of the uniform positive column in mixtures of monatomic gases can be explained principally in terms of collisions of the second kind between the ions or metastable atoms of one gas and the neutral atoms of the other. The effect of limitation of electron velocities is insufficient to explain the results, and its effect is shown to be negligible as compared with collisions of the second kind when the concentration of one gas is very small. The necessary condition for a large effect to be produced in the electrical and spectral characteristics of the positive column by a small percentage of one gas added to another is that a close resonance exists between the metastable states of the main gas and the ionization potential or excited states of the added gas atom or ion. By the introduction of as little as 0.4 percent neon or argon into helium, a marked increase in the electric field is produced, and the spectrum emitted is changed almost completely from the arc spectrum of helium to that of neon or argon respectively. The addition of mercury vapor at room temperature to neon caused a decrease of 45 percent in the field while the addition of mercury to either argon or helium produced a small increase. In the cases where the excitation and ionization potentials of the added gas were above the metastable states of the main gas, no reactions between the two gases could occur to affect the concentration of metastable atoms. In these cases practically no change in either the spectral or electrical characteristics were observed upon adding a small amount of one gas to another. However, in larger proportions the change produced in the field was proportional to the amounts of the two gases and the difference between the field in each of the pure gases. This result is accounted for mainly by the difference in the energy of the ionization processes in the two gases by electron impact.

Introduction

THE phenomena occurring when electricity passes through a gas are many and complicated. The various phenomena have been the subject of many investigations and a great deal is known about the electrical and spectral characteristics of the different types of electrical discharges. Until the development of the Bohr theory of the atom, the beginning of the classification of spectroscopic data, and the measurements of critical potentials by means of

electrons of controlled velocity, very little was known about the mechanism of the elementary processes involved in the discharge of electricity through gases. With the information obtained from the classification of spectroscopic data, the spectroscopic study coupled with measurements of the electrical characteristics of a discharge gives a very powerful means of studying the elementary processes taking place. This method has been used by the writers to study the collision phenomena occurring in the positive column of a glow discharge in mixtures of the rare gases.

Klein and Rosseland[1] suggested that since a collision between an electron and a molecule may result in the excitation of the molecule, due to its absorption of the kinetic energy of the moving electron, the reverse of this process should also take place; that is, the change of excitation energy of a molecule to kinetic energy of an electron at a collision between an excited atom and a slowly moving electron. This type of collision is called a collision of the *second kind*. The former process is called a collision of the *first kind*. Franck[2] has shown that the theory of Klein and Rosseland may be extended to include impacts of the second kind between excited atoms and neutral atoms.

Nearly all gases, unless very carefully purified, contain small amounts of other gases as impurities. It has been observed from spectroscopic studies that, in certain regions of a discharge and for certain gases as impurities, the spectra of the impurities were often stronger than that of the main gas. These observations led to spectroscopic investigations of discharges in mixtures of gases.

Duffendack[3,4,5,6] and a number of his pupils have made spectroscopic studies on the excitation in a low voltage arc in mixtures of the rare gases with nitrogen, carbon monoxide, and various metal vapors in a tungsten furnace. The limits and maxima of excitation observed were explained on the basis of collisions of the second kind between the excited atoms or rare gas ions and the neutral gas or metal molecules.

Sawyer,[7] Takahashi,[8] Naudé,[9] Kruger,[10] Frerichs[11] and others have used the hollow cathode discharge with the rare gases to excite the spectra of various metals and have explained the observed maxima and limits of excitation on the basis of collisions of the second kind.

Penning[12,13] has shown that certain phenomena regarding the sparking potentials of mixtures of the rare gases and also other gases can be explained by means of collisions of the second kind.

[1] Klein and Rosseland, Zeits f. Physik **4,** 46 (1921)
[2] J Franck, Zeits. f. Physik **9,** 259 (1922).
[3] O S. Duffendack and H. L. Smith, Phys. Rev. **34,** 68 (1929).
[4] O. S. Duffendack and R. A. Wolfe, Phys. Rev. **34,** 409 (1929).
[5] O. S. Duffendack and J. G. Black, Phys. Rev. **34,** 35 (1929).
[6] O. S. Duffendack, C. L. Henshaw and Marie Goyer, Phys. Rev. **34,** 1132 (1929).
[7] R. A. Sawyer, Phys. Rev. **36,** 44 (1930).
[8] Y. Takahashi, Ann. d. Physik **3,** 49 (1929).
[9] S. M. Naudé, Ann. d. Physik **3,** 1 (1929).
[10] G. Kruger, Phys. Rev. **34,** 1122 (1929).
[11] R. Frerichs, Ann. d. Physik **85,** 376 (1928).
[12] F. M. Penning, Zeits. f. Physik **46,** 335 (1928).
[13] F. M. Penning, Zeits. f. Physik **57,** 723 (1929).

In the present investigation the study of the effect of collisions of the second kind on discharge characteristics has been extended to the positive column of a glow discharge. Mixtures of the three rare gases, helium, neon and argon and mixtures of each of these with mercury vapor were used. The study of collision phenomena and the processes of production of ions was made by observing simultaneously the changes in excitation and in the electric field in the positive column with the change in the proportion of the two gases in a mixture.

Theory of the Uniform Positive Column

The phenomena occurring in the positive column are independent of the material and form of the electrodes and depend only on the properties of the gas, the current density, and the tube diameter. For pure monatomic gases the positive column is uniform under almost all conditions. In diatomic gases or in mixtures, for certain limits of current and pressure, the positive column is striated. The electric field in the uniform positive column is uniform. In the striated positive column a slight sinusoidal variation is superimposed upon the uniform field. This variation has a wave-length equal to the distance between striations. The field reaches a maximum value at the cathode end of the luminous region of each striation. The theory of the uniform positive column will be discussed in detail since practically all of the work in this investigation was done with a uniform column. While most of the data on this part of the discharge are qualitative, some approximate empirical relations have been worked out for a considerable range of the variables. For a tube of cylindrical form, the field is directly proportional to the pressure and inversely proportional to the radius of the discharge tube. At a small current density, for which the positive column does not completely fill the tube, the field increases with an increase in current. The field reaches a maximum value when the column just fills the tube and then decreases slowly until the current density reaches a high value, corresponding to nearly one hundred percent ionization of the gas, after which the field increases quite sharply and rapidly with further increase in current. This condition of practically complete ionization has never been attained in large discharge tubes. It has been studied by Langmuir[14] in capillary tubes with a current density of the order of 40 amp/cm^2.

Schottky[15] has made a study of diffusion currents to the tube walls in the positive column and has developed a theory on the basis of the results obtained. The assumptions made for a cylindrical discharge tube are the following:

(1) The field in the positive column is the source of the energy necessary to maintain a certain degree of ionization which is required for a given discharge condition. (2) Ions are lost by diffusion to the walls where recombination occurs. (3) The current density and concentration of positive ions and electrons is constant throughout the length of the column. (4) The

[14] I. Langmuir, G. E. Rev. **27,** 762 (1924).

[15] Schottky, Phys. Zeits. **25,** 342 and 635 (1924).

radial component of the positive ion current is equal to the radial component of the electron current. (5) The concentration of positive ions and electrons is zero at the walls and reaches a maximum at the tube axis. (6) The dimensions of the tube are large compared to the mean free path of the molecules. (7) Sufficient collisions occur to give both the positive ions and electrons a Maxwellian distribution of velocity.

The equation obtained from these assumptions without the use of Poisson's equation is given below.

$$G = \frac{2.4}{R}\left(\frac{V_i}{H}(B^+ + B^-)\frac{K^+ \cdot K^-}{(K^+ + K^-)^2}\right)^{1/2}.$$

Where G is electric field in volts per cm; R is tube radius in cm; V_i is ionization potential of the gas in volts; H is an efficiency factor of ionization; B^+ is energy of random motion of positive ions in volts; B^- is energy of random motion of negative ions in volts; K^+ is mobility of positive ions; and K^- is mobility of negative ions.

This expression for the dependence of the field on the tube radius checks the empirical relation. The field will however not be equal to zero for R increased indefinitely but will reach a minimum value. The above form of the equations results from the assumption that ions are lost only by diffusion to the tube walls and therefore does not hold for large values of R where recombination in the body of the gas becomes important. This theory does not give the dependence of the field on current density or on pressure.

Morse[16] has developed an equation for the electric field in the positive column, giving its dependence on both the tube radius and the pressure, but not on the current density. He assumes that the relations for mobility and average number of ions produced by an electron under given conditions are known and uses the results of Schottky to determine the diffusion currents to the tube walls. The calculations are based on three general differential equations which represent the conditions for a stable discharge in a tube of unit cross section. The following result is obtained.

$$E = 5.76\epsilon V_r \frac{Gp}{r}.$$

Where E is field in the positive column in volts/cm; G is a constant inversely proportional to the mobilities of positive ions and electrons; p is gas pressure in mm of mercury; r is tube radius in cm; and V_r is ionization potential of the gas, or if metastable states are formed, the first critical potential.

The value of the field given by this equation satisfied the empirical relation for its dependence on both the tube radius and the pressure, but still leaves the dependence on current density to be explained qualitatively. The field increases with the current for small current densities where an increase in current increases the diffusion to the tube walls, but the field decreases slowly for large current densities where the increase in current decreases the

[16] P. M. Morse, Phys. Rev. **31**, 1003 (1928).

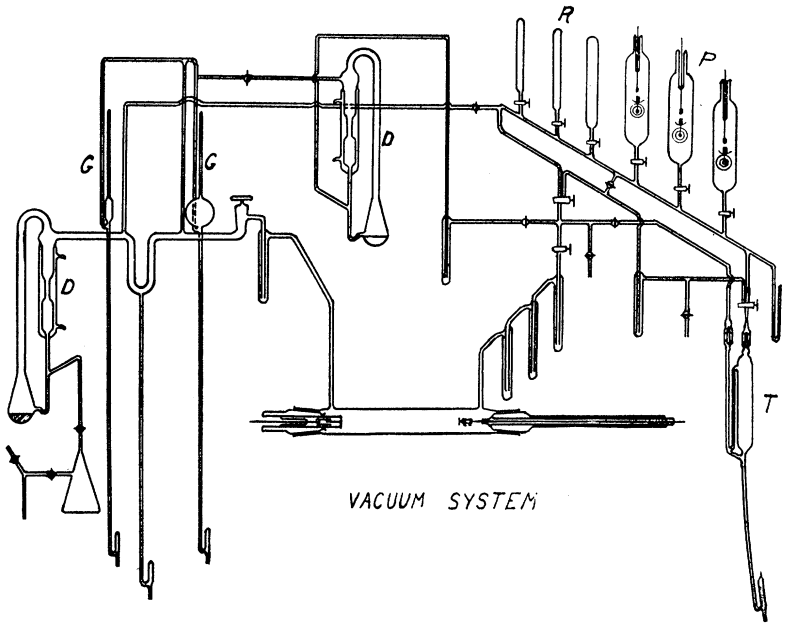

Fig. 1. Diagram of vacuum system.

percent of diffusion to the tube walls. In order to obtain an expression for the field as a function of the current it would be necessary to determine the diffusion current to the tube walls as a function of the current density in the tube.

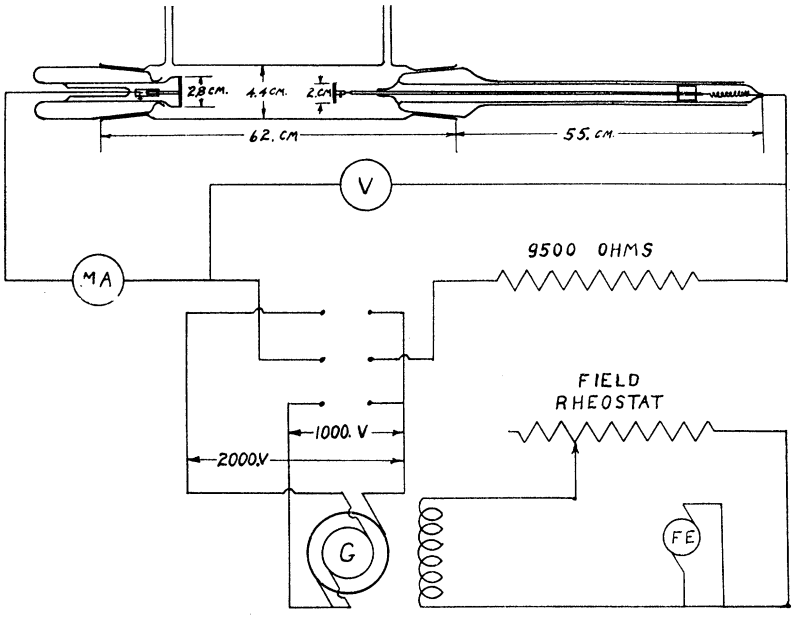

Fig. 2. Diagram of apparatus.

Apparatus

A detailed diagram of the entire vacuum system is shown in Fig. 1. *R* represents the gas storage reservoirs, *P* the gas purifying tubes, *D* diffusion pumps, *G* the McLeod guage and *T* a Toepler pump. Fig. 2 shows a drawing of the discharge tube and a diagram of the electrical circuit used.

Purification of the Gases

Since the results of this investigation depended largely on the purity of the gases used, each gas was very carefully purified before being admitted to the discharge tube. The helium, free from neon, was obtained from the Ohio Chemical Company in a steel bomb under high pressure and was purified by circulating it with a Toepler pump through a charcoal trap immersed in liquid air. The pure gas was stored at a little less than atmospheric pressure in a liter glass reservoir which had been well baked and evacuated.

The neon, of spectroscopic purity, was obtained from Linde Air Products Co., Buffalo, N. Y., in liter glass bulbs. It was further purified in the same manner as described above for helium and stored in a liter glass reservoir. In most cases both of these gases were purified again just before being admitted to the tube by circulating slowly through charcoal in liquid air for about one hour. However, no difference could be found by spectroscopic means or by changes in the electrical characteristics of the discharge when the gases were admitted to the tube directly from the storage reservoirs.

The argon, of commercial grade, was obtained in small metal bombs at high pressure. It contained more impurities than either the helium or the neon, and was the most difficult of the three gases to purify, since, because of its absorption of argon, charcoal in liquid air could not be used. The argon was purified by maintaining an arc of about 2 amperes between a mischmetal and an iron electrode in the gas at a pressure of 10 to 15 cm. The arc was run continuously for from one to two days with the argon in one purifier, then the gas was transferred to another purifier and run under the same conditions for about a week. After this treatment it was still found to contain a very small trace of nitrogen. It was then stored in a reservoir containing well-degassed charcoal where it was allowed to stand for several days at room temperature. When admitted to the tube from this reservoir it was found to be very pure with the exception of a small trace of hydrogen. Most of this hydrogen was removed from the argon by admitting a very small amount of oxygen, generated by heating potassium permanganate, to the gas and circulating the mixture through the discharge tube and liquid air traps. The argon was again stored over well-degassed charcoal for several days, after which time it was found to be very pure.

Preparation of the Tube

The electrodes were well-outgassed by heating with an induction furnace before being mounted in the tube. Before each set of experiments with mixtures of two of the gases the whole system was pumped for several hours and allowed to stand over night, evacuated and with liquid air on the traps, to

test for leaks. In case the system was tight the tube was baked at from 300 to 350°C for four hours while being pumped. At the same time the charcoal trap and the mischmetal getter trap, in the circulating system, were baked at 400°C. This part of the system, including the tube, was then pumped for about 4 hours while the tube and traps cooled. The whole system was allowed to stand over night, evacuated and with liquid air on the traps, to test again for leaks. After pumping again for about two hours the system was ready for use.

Procedure

After the gases were purified and the tube prepared as described above, one of the gases to be used was admitted to the tube very slowly by means of a slow leak grooved stopcock, through the system of traps, Fig. 1, until the desired pressure was obtained and was then circulated for about 20 minutes through the discharge tube and traps with a discharge running at the desired current. The rate of circulation was then decreased to a very low value and the pressure adjusted accurately to the value desired. The current was kept constant, and voltage readings were taken at short time intervals in order to determine when conditions were constant for the taking of data as described below. Pressure measurements were taken at various intervals to see that the pressure and rate of circulation remained constant.

If a very small amount of another gas was to be mixed with the gas already in the tube, the gas in the tube was pumped out with the mercury circulating pump backed by a Toepler pump and stored in an empty reservoir or in a charcoal trap in liquid air. The tube was well pumped out with the mercury pump and a small amount of the other gas admitted to the tube to the pressure necessary to give the percentage mixture desired. The gas previously used was readmitted to the tube slowly in the same manner as before. The process described above of circulating the gases was repeated to insure a homogeneous mixture of the gases and the data were taken as described in the next section. For adding larger amounts of one gas to another, a separate system including a guage with its volume calibrated with respect to the tube volume was used. In this way by starting with one pure gas, mixtures with another gas could be studied in any proportions from very small percentages up to a 50 percent mixture. The results obtained were found to be repeatable within a few percent at any time. For each gas mixture studied a spectrogram of the light emitted from the positive column was taken in order to observe the change in excitation produced with changes of the gas mixture and to check the purity of the gas.

Method Used in Measuring the Potential Gradient in the Positive Column

The method consisted in measuring the total drop in potential across the tube at various electrode distances, while the current was kept constant by varying the e.m.f. in the circuit. The anode was moved by magnetic control from outside the tube. Before any measurements were taken, the discharge was run with the maximum electrode distance for from one to two hours at

constant current until the maintaining voltage across the tube remained constant. The maximum electrode distance was 32 cm. The anode was moved from this point, 2 cm at a time, to within 10 cm of the cathode and back to 32 cm again. Readings of the total voltage across the tube were taken every two cm at intervals of one minute as the electrode distance was decreased and then increased again. The voltage readings for increasing electrode distance checked those for decreasing electrode distance to within less than one percent.

This method of measuring the field is applicable since a uniform cylindrical tube was used, and only the uniform positive column was studied. Since the current density and the concentration of ions and electrons remain constant throughout the length of the uniform positive column, the anode drop in potential does not change with the anode position along the column. The tube was run long enough before any data were taken so that the cathode drop in potential remained constant while observations were being made. The time required to take a complete set of observations was 24 minutes. The voltage readings, taken with decreasing electrode distance, when plotted against electrode distance, gave a straight line very accurately. The slope of this line gave the potential gradient or electric field in the positive column in volts/cm.

RESULTS

The results of the investigation are shown by the data given in Tables I and II and by the curves in Figs. 3 to 8 inclusive. The values of the electric field in the positive columns are given in Table I for the pure gases, helium, neon, argon and for mixtures of each of these gases with mercury vapor at

TABLE I. *Electric field in the positive column for the rare gases and mixtures of each with mercury vapor.* Current, 40.0 m.a. Pressure, 14.0 mm. Tube diameter, 4.4 cm.

Gas	pure He	He-Hg	pure Ne	Ne-Hg	pure A	A-Hg
Positive column (Field in volts/cm)	17.0	18.4	4.0	2.2	3.8	4.5

about 0.005 mm pressure. It can be seen from this table that mercury vapor added to neon causes a large decrease in the field but when added to either helium or argon causes a slight increase.

Table II gives the results of spectrograms taken from the positive column of the discharge in the various gas mixtures studied. It will be noted that a very small amount of argon added to either helium or neon completely subdues the helium or neon spectrum and only the argon is excited. Mercury has the same effect on either argon or neon; while with mixtures of small amounts of neon or of mercury with helium, the spectra of both gases appear. When argon, containing a trace of nitrogen, is added to neon in amounts up to 2.0 percent the neon spectrum disappears and the argon spectrum appears strong with the nitrogen spectrum weak. As more of the argon, containing a trace of nitrogen, is added to the neon the argon spectrum becomes weak and the nitrogen spectrum strong until with more then 5.0 percent only the nitrogen spectrum appears.

TABLE II. *Results of spectrograms taken of radiation from the positive column of a glow discharge in the various mixtures of the rare gases and mercury vapor studied.*

Gas mixtures	Percentage of added gas greater than the amount given below		Spectrum obtained
Helium—Neon	0.4%	Neon	Helium and Neon
Helium—Argon	0.2%	Argon	Argon only
Neon—Argon	0.15%	Argon	Argon only
Neon—{Argon with a trace of nitrogen}	0.5% 2.0%	{Argon with a trace of nitrogen}	Argon and Nitrogen
Neon—{Argon with a trace of nitrogen}	5.0%	{Argon with a trace of nitrogen}	Nitrogen only
Helium—Mercury	0.03%	Mercury	Helium and Mercury
Neon—Mercury	0.03%	Mercury	Mercury only
Argon—Mercury	0.03%	Mercury	Mercury only

Fig. 3 shows the variation with pressure of the electric field in the positive column for pure helium and for a mixture of neon with helium. These curves show that the field varies directly as the pressure for both the pure gas and the mixture. They also show that the effect on the field produced by adding a small percentage of neon to helium does not change appreciably with the total pressure over a considerable range of pressure.

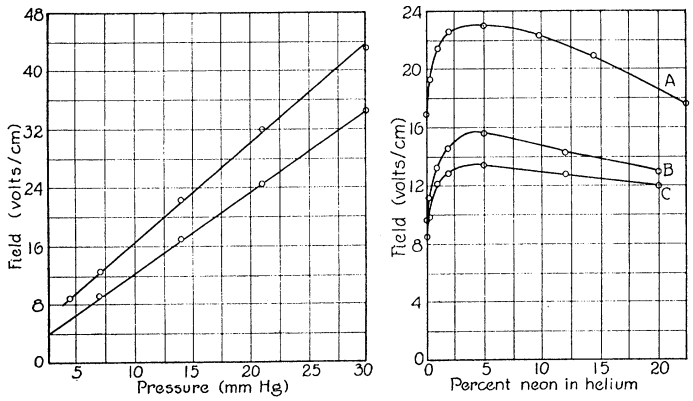

Fig. 3. Variation of electric field with pressure for pure helium A and a mixture of 99.0 percent helium and 1.0 percent of neon B. Current, 40 m.a.

Fig. 4. Variation of electric field with percent of neon added to helium. A, current 40 m.a., pressure 14 mm; B, 20 m.a., 7 mm; C, 40 m.a. 7 mm.

These curves of Fig. 4 show the variation of the electric field in the positive column with small amounts of neon added to helium under different conditions of pressure and current. The interesting point to note here is that the maximum field is a function only of the percent of neon in the helium and is independent of the pressure or of the current density. These curves also show that a large change in the field is produced by a very small amount of neon in helium.

Fig. 5, 6, and 7 show the variation of the field in the positive column with all possible mixtures of the three gases helium, neon, and argon taken only two together.

The curve of Fig. 5 shows that a small amount of neon in helium has a large effect on the field while a small amount of helium added to neon has very little effect on the field.

It can be seen from the curve of Fig. 6 that argon-helium mixtures have about the same characteristics as those of neon-helium except that a smaller amount of argon is more effective in helium than in neon in changing the field. The discontinuity in the curve is probably due to the difference in mobility and large difference in ionization potential of the two gases. For pure argon

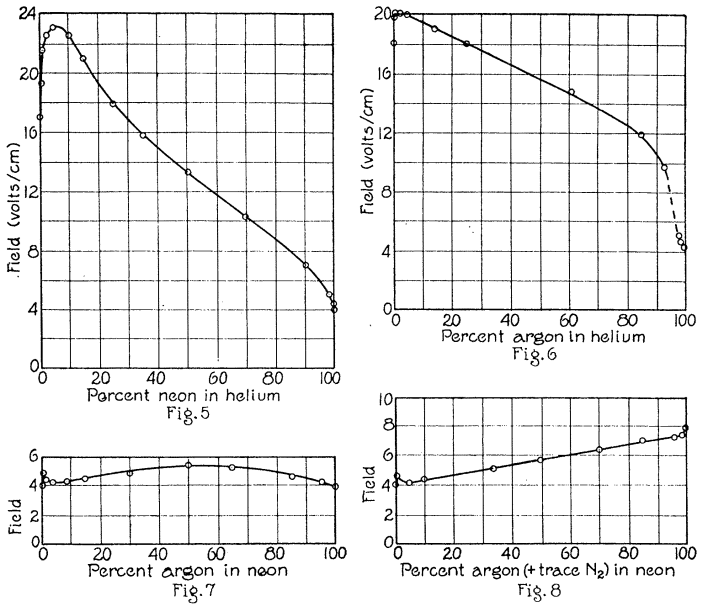

Fig. 5. Variation of electric field with percent of neon in helium. Current 40 m.a., pressure 14 mm.

Fig. 6. Variation of electric field with percent of argon in helium. Current 40 m.a., pressure 14 mm.

Fig. 7. Variation of electric field with percent of argon in neon. Current 40 m.a., pressure 14 mm.

Fig. 8. Variation of electric field with percent of argon, containing trace of nitrogen, added to neon. Current 40 m.a., pressure 14 mm.

and for mixtures of argon with small amounts of helium the discharge did not fill the tube completely but concentrated toward the axis of the tube. For from 2 to 7 percent helium in argon the discharge was unstable and could not be maintained at the current and pressure desired without changing the resistance of the circuit. For mixtures containing more than 7 percent helium the discharge filled the tube uniformly. The sudden increase in field produced is due to the change in the current density distribution over the cross section of the positive column. Where the current density is large at the tube axis

there is less diffusion of positive ions to the tube walls and therefore a smaller field, than in the case of a more nearly uniform distribution of current over a cross section of the column.

From Fig. 7 it can be seen that small amounts of argon have much less effect on the field in neon than of that in helium and that neon in small amounts has practically no effect on the field in argon.

Fig. 8 shows how the field in neon-argon mixtures is affected by a small trace of nitrogen in the argon.

Discussion and Interpretation of Results

The interpretation of the electrical and spectral characteristics of the positive column in the gas mixtures studied is based principally upon collisions of the second kind between the excited metastable atoms or the ions of one gas and the neutral atoms of the other gas. The effect of limitation of electron velocities observed when a considerable amount of a gas of lower ionization and excitation potentials is added to another gas is insufficient to explain the large effects obtained with the very small percentages of the added gas. With a formula given by K. T. Compton,[17,18] calculations were made of the number of collisions an electron would make with gas atoms in a mixture of helium with 0.1 percent neon under the discharge conditions which obtained. It was found that an electron would make in the order of 1000 collisions with gas atoms and hence, on the average, one collision with a neon atom while gaining the energy represented by the difference between the ionization potential of helium and the lowest excited state of neon. Since the probability of excitation by electron impact under these conditions is far from certainty, an increase in the field of 26 percent could hardly be attributed to limitation of electron velocities by collisions with neon atoms. With the mixture of less than 0.03 percent mercury vapor with neon the field is reduced by 45 percent which is entirely too large an effect to be explained by limitation of electron velocities. Therefore we must turn to collisions of the second kind for a satisfactory explanation of the observed results.

Collisions of the second kind. The following list of reactions, 1 to 6, inclusive, show the possible ways by which collisions of the second kind may take place between two gas atoms X_1 and X_2 where the energy of excitation is transferred from X_1 to X_2. The resultant products of each of the first six reactions may be represented by any one of the expressions 7 to 10, depending upon the relative ionization and excitation potentials of X_1 and X_2.

1. $X_1' + X_2 \rightarrow$
2. $X_1^+ + X_2 \rightarrow$
3. $X_1' + X_2' \rightarrow$
4. $X_1^+ + X_2' \rightarrow$
5. $X_1' + X_2^+ \rightarrow$
6. $X_1^+ + X_2^+ \rightarrow$

7. $X_1 + X_2' + KE$
8. $X_1 + X_2^+ + KE$
9. $X_1 + X_2^{+\prime} + KE$
10. $X_1 + X_2^{++} + KE$

[17] K. T. Compton, Phys. Rev. **32**, 433 (1923).
[18] K. T. Compton, Revs. of Mod. Phys. **2**, 220 (1930).

X' is an excited gas atom, X^+ a gas ion, $X^{+\prime}$ an excited gas ion, X^{++} a doubly ionized ion, and KE is kinetic energy.

The reactions represented by the initial conditions 1 or 2 resulting in 7, 8, or 9 are of most common occurrence in discharges in mixtures and are most important in explaining the effects observed.

Processes of ionization and excitation. The processes of ionization and excitation in the positive column in pure monotomic gases having metastable states can be represented by the following reactions.

Reactions by which ions are produced by electron impact.

$$e_f + X = X^+ + 2e + KE \tag{1}$$

$$e_s + X_m' = X^+ + 2e + KE \tag{2}$$

where e_f is a fast moving electron with sufficient kinetic energy to ionize the neutral gas atom X, and e_s is a slow moving electron with sufficient kinetic energy to ionize an excited metastable atom X_m'.

Reactions by which metastable atoms are produced.

$$e_f + X = X_m' + e + KE \tag{3}$$

$$X' - \text{radiation} = X_m', \tag{4}$$

$$X' + X \rightarrow X_m' + X + KE, \tag{5}$$

where X_m' is an excited metastable atom, and X' is an excited atom in a non-metastable state.

Reactions producing excitation of non-metastable states of atoms.

$$e_{f_1} + X = X' + e + KE. \tag{6}$$

$$e_{s_1} + X_m' = X' + e + KE, \tag{7}$$

where e_{f1} is a fast moving electron with sufficient energy to excite a neutral atom, and e_{s1} is a slow moving electron with sufficient energy to excite a metastable atom.

In gas mixtures composed largely of one gas with a small amount of gas of lower ionization and excitation potentials than those of the main gas, other processes of ionization and excitation take place by collisions of the second kind.

Let X_1 = atoms of the main gas and X_2 = atoms of the gas present in small amounts.

Reactions of the second kind which produce ionization and affect the concentration of metastable atoms in a discharge in gas mixtures are the following.

$$X_{1m}' + X_2 = X_2^+ + e + X_1 + KE \tag{8}$$

$$X_{1m}' + X_2 = X_2^+ + e + X_1 + KE \tag{9}$$

$$X_{1m}' + X_{2m}' = X_2^{+\prime} + e + X_1 + KE. \tag{10}$$

A reaction of the second kind which decreases the concentration of metastable atoms of the main gas and therefore affects the ionization processes in a discharge in a gas mixture is the following

$$X_{1m}' + X_2 = X_2' + X_1 = X_1 + X_2 + \text{radiation}. \tag{11}$$

The reactions involving collisions of the second kind between ions of the main gas and excited or neutral atoms of the mixed gas, do not tend to increase the number of ions. Therefore, they will in general have very little effect on the field in the positive column. Reactions of this type will be discussed only in a few particular cases.

It was shown in the discussion of the theory of the positive column that the electric field gives a measure of the energy necessary to produce the concentration of ions required by the current passed through the tube and includes the energy lost in radiation as well as the heat conducted away by the tube walls. It was also shown that, for a pure gas, the electric field in the positive column is proportional to the ionization or excitation potentials of the gas. It can also be shown that the electric field in the positive column will be a function of the excitation potentials of the gas and proportional to the ratio of the energy emitted as radiation to that producing ionization.

If any process is introduced into the positive column which will change the ratio of the energy expended in radiation to that expended in ionization the field should change. A process which increases the efficiency of ionization will decrease the electric field in the positive column, since for a given current and pressure the concentration of ions remains constant. A process which decreases the efficiency of ionization or increases the energy expended in radiation will cause an increase in the electric field.

By adding a small amount of one gas to another gas the processes of ionization and excitation may be considerably changed. In case the added gas has lower ionization and radiating potentials than the main gas, very large changes in the field may be produced by very small amounts of added gas. When the added gas has higher ionization and excitation potentials than the main gas the field is only changed slightly, the change being proportional to the amount of gas added.

Helium-Neon Mixtures

Consider the case of helium with a small amount of neon added. The variation of electric field in the positive column with the percent of neon added to helium is shown in Fig. 4, for amounts of neon up to 20 percent. The maximum of the field curve comes at 5 percent neon for different values of current and pressure. The amount of increase in the field over that for pure helium caused by the addition of 5 percent neon is 28.3 percent, for curve *A*; 60.8 percent for curve *B*; 61.8 percent for curve *C*. This shows that the effect of the neon on the field of helium is practically independent of the current, but varies with the pressure.

The following table gives the term values of the normal and metastable states, the ionization potentials and excitation potentials of the metastable states of the gases used in this investigation.

To explain the rise in the field produced by adding neon to helium the reactions producing ionization and excitation in the mixture must be considered.

TABLE III. *Metastable states and ionization potentials.*

Atom	Normal state (term in cm^{-1})	Ionization potential (volts)	Metastable (term in cm^{-1})	States excitation potential (Volts)
He	$^1S_0$ 198298.0	24.47	2^3S_1 38454.7	19.73
			2^1S_0 32032.5	20.51
Ne	$^1S_0$ 173930.0	21.47	3^3P_2 39887.0	16.54
			3^3P_0 39110.0	16.64
A	$^1S_0$ 127103.8	15.69	4^3P_2 33996.7	11.50
		15.87	4^3P_0 32557.79	11.67
Hg	$^1S_0$ 84178.5	10.39	6^3P_2 40138.3	5.43
			6^3P_0 46536.2	4.66

First consider the processes for production of ions occurring in pure helium.

$$\underset{>24.47}{e_f} + \text{He} = \underset{24.47}{\text{He}^+} + 2e + KE \tag{1}$$

$$\underset{>4.74}{e_s} + \underset{\substack{20.51\\19.73}}{\text{He}_m'} = \underset{24.47}{\text{He}^+} + 2e + KE. \tag{2}$$

The numbers represent the energy of the state in equivalent volts.
Reactions producing the excitation of the arc spectrum of helium.

$$\underset{>19.73<24.47}{e_f} + \text{He} = \underset{>19.73<24.47}{\text{He}'} + e + KE \tag{3}$$

$$\underset{<4.74}{e_s} + \underset{\substack{20.51\\19.73}}{\text{He}_m'} = \underset{>19.73<24.47}{\text{He}'} + e + KE \tag{4}$$

$$\underset{>19.73<24.47}{\text{He}'} - \text{radiation} = \text{He or} = \underset{\substack{19.73\\20.51}}{\text{He}_m'} \tag{5}$$

When a small amount of neon is added to helium the excitation of the helium arc spectrum is reduced to some extent while the neon arc spectrum is developed very strongly. Therefore the following reaction is considered to take place in the helium-neon mixture.

$$\underset{\substack{20.51\\19.73}}{\text{He}_m'} + \text{Ne} = \underset{19.69 \text{ to } 20.62}{\text{Ne}'} + \text{He} \pm KE \tag{6}$$

These results in Table IV show very close resonance between the metastable levels of helium and a large number of excited states of neon. The excess energy to become kinetic energy is very small for the excitation of a large number of the excited states of neon by impacts with metastable helium. Therefore, this reaction should have quite a high probability of occurrence in helium containing a small amount of neon.

This reaction (6) shows that the presence of a small amount of neon in helium will greatly reduce the concentration of metastable helium atoms, and practically eliminate the reaction (2), one of the processes of producing ions

TABLE IV. *Excitation of neon by metastable helium.*

Helium I Metastable states term (cm^{-1})	excitation potential (Volts)	Neon I Excited states term (cm^{-1})		excitation potential (Volts)	Energy difference in equivalent volts
		$^3P_0$	14395	19.69	0.04
		$^1P_1$	14549	19.67	0.06
2^3S_1 38454.7	19.73	$^3P_0$	20958	18.78	0.95
		$^3P_1$	22891	18.65	1.08
		$^3P_2$	23071	18.62	1.11
		$^1P_1$	23012	18.63	1.10
		8 levels	12419.0	19.91	0.60
			12228.0	19.96	0.55
		10 levels	11520.0	20.05	0.46
			10529.0	20.17	0.34
2^1S_0 32032.5	20.51	$^1P_1$	10272.1	20.20	0.31
		$^3P_2$	10220.8	20.21	0.30
		$^3P_0$	9643.5	20.28	0.23
		8 levels	6961.8	20.61	−0.10
			6880.8	20.62	−0.11

in helium. Therefore, due to the presence of neon, a large amount of energy supplied by the field is transformed into radiation by reaction (6) which would have gone into ionization in the case of pure helium. Thus we see that the presence of a small amount of neon in helium greatly decreases the efficiency of ion production and therefore the field increases. The field decreases again when the concentration of neon atoms becomes large enough so that a considerable amount of the ionization is produced by direct electron impact with neon atoms. After the maximum in the field is reached at 5 percent neon the field gradually decreases to that of pure neon. A small amount of helium has no abnormal effect on the field in neon, as shown by Fig. 5. No collisions of the second kind take place between excited neon and neutral helium because the excited states of helium are all above the metastable states of neon. The spectrum of helium disappears between 10 percent and 5 percent helium in neon, for less than 5 percent helium in neon only the neon spectrum is obtained. This shows that when only a small amount of helium is present in neon, only very few helium atoms are excited by direct electron impact.

The phenomena at this end of the curve show the effect of limitation of electron velocities in mixtures but here the gas of the lower excitation potentials is present in the larger amount. The fact that the helium spectrum is developed quite strongly in mixtures containing as much as 85 percent neon shows that neon is not very effective in limiting the electron velocities even when present in more than 50 percent. Thus limitation of electron velocities sufficient to cause a 20 percent increase in field could not be considered to occur with less than 1 percent neon in helium. Therefore, the effect of the limitation of electron velocities is negligible as compared to collisions of the second kind where neon is present in only a few percent.

Helium-Argon Mixtures

Fig. 6 shows that the maximum value of the field for the mixture is produced with 1.5 percent argon which is less than the amount of neon required to produce the maximum effect in helium. However, the maximum increase in the field for the mixture over that of pure helium is only 17.6 percent for argon, as compared with an increase of 28.3 percent caused by the addition of 5 percent neon to helium. The results of spectrograms given in Table II show that with 0.2 percent argon in helium the arc spectrum of helium is completely surpressed and only the argon arc spectrum is developed. These facts would indicate that argon is more effective in removing metastable helium atoms than neon but that part of the energy of these metastable helium atoms is converted into ionization of argon and not entirely lost in radiation, as was the case of neon. These results are particularly interesting because neither the helium ion nor the metastable states of the helium atom are in close resonance with any of the known excited states of neutral argon or of the argon ion. The lowest excited state of argon II is the term ^2s 108730 cm^{-1} or 13.41 volts above the normal state of argon II. The first ionization potential of argon is 15.69 volts. Thus to ionize and excite argon would require at least $15.69+13.41=29.10$ volts. The highest metastable state of helium is 2^1S_0 32032.5 cm^{-1} or 20.51 volts above the normal state, which is 8.59 volts too low to ionize and excite argon. The ionization potential of helium is 24.47 volts, which is 4.63 volts too low to ionize and excite argon.

Spectrograms taken of the positive column in mixtures of a small amount of argon in helium show that the spark spectrum of argon is not excited in mixtures with helium. The spectrogram of argon alone shows only the arc spectrum of argon. The spectrograms of helium-argon mixtures also show only the arc lines of argon and the strongest arc line of helium. However, there are a large number of strong argon spark lines in the region photographed which would have appeared if an appreciable amount of excitation of the argon ion had occurred. Therefore, the only possible reactions between metastable helium and neutral argon are the following:

$$\underset{19.73\ \text{or}\ 20.51}{He_m'} + A = \underset{15.69\ \text{or}\ 15.87}{A^+} + He + \underset{3.86\ \text{to}\ 4.82}{KE} + e \qquad (1)$$

$$\underset{19.73\ \text{or}\ 20.51}{He_m'} + A = \underset{19.0\ \text{to}\ 20.5}{A'} + He + KE. \qquad (2)$$

TABLE V. *Table for reaction* (1).

Helium Term (cm^{-1})	Excitation potential of metastable state	Argon Term	Ionization potential (volts)	Energy difference in equivalent (volts)
2^3S_1 38454.7	19.73	$4^2P_0$0	15.69	4.04
2^1S_0 32032.5	20.51	$4^2P_0$0	15.69	4.82
2^1S_0 32032.5	20.51	4^2P_1 1430.	15.87	4.64
2^3S_1 38454.7	19.73	4^2P_1 1430.	15.87	3.86

The amount of energy going into kinetic energy is too large to make reaction (1) very probable. However, the results indicate that this reaction does occur to some extent in helium-argon mixtures.

From the results obtained with mixtures of a small amount of argon with helium it would appear that reaction (2) has a high probability of occurrence. The outer electron configuration of argon is $3s^2$, $3p^6$. It seems probable that two of the p electrons could be excited simultaneously by a collision of an argon atom with a metastable helium atom, which would excite negative terms in argon I. Negative terms have not been observed in the argon I spectrum, but there is no reason to expect negative terms to be excited under normal discharge conditions in argon when practically all of the excitation is by electron impact, However, if negative terms exist which are in close resonance with the metastable states of helium, reaction (2) should be highly probable in mixtures of a small amount of argon with helium. Reaction (2) will account for the strong excitation of the arc spectrum of argon in helium-argon mixtures and also will account for the increase of the field in helium produced by the addition of small amounts of argon. The negative terms which could be excited by reaction (2) would lie between three and four volts above the ionization potential of argon I. It would be interesting to make an extended spectroscopic study of the excitation of argon by metastable helium in the positive column to see if such negative terms could be observed.

Neon-Argon Mixtures

In this case the field in the positive column is small and nearly the same for each pure gas. Under the existing conditions of current, pressure, and tube diameter, the field in neon was 4.0 volts/cm; in argon 3.8 volts/cm. However, the curve in Fig. 7 shows that a small amount of argon added to neon causes a small increase in the field while neon in small amounts has practically no effect on the field in argon.

The possible reactions for argon mixtures are the following

$$\underset{\substack{16.64\\16.54}}{\mathrm{Ne}_m'} + \mathrm{A} = \underset{\substack{15.69\\15.87}}{\mathrm{A}^+} + \mathrm{Ne} + e + \underset{0.67 \text{ to } 0.95 \text{ volts}}{KE} \qquad (1)$$

$$\underset{\substack{16.64\\16.54}}{\mathrm{Ne}_m'} + \mathrm{A} = \underset{16.54 \text{ to } 16.64 \text{ volts}}{\mathrm{A}'} + \mathrm{Ne} + KE. \qquad (2)$$

Reaction (1) tends to decrease the field and (2) tends to increase the field. Reaction (1) would not have a high probility due to the large residual energy to be transformed to kinetic energy. The probability of transitions to the negative term states demanded by reaction (2) is also small. This is in agreement with the fact that argon has only a small effect on the field when added to neon.

The curve Fig. 7 shows that a maximum field is reached at about equal proportions of argon and neon due to the fact that there are more possible excited states in a mixture of the two gases than in either gas separately. Therefore, a greater part of the total energy of the field is expended in radia-

tion than would be the case for either gas separately. The fact that the field in pure argon is only slightly less than that in pure neon even though the ionization potential of argon is much less than that of neon must be due to a proportionally greater amount of the total energy supplied by the field going into radiation and heat in argon than in neon.

Helium-Mercury Mixtures

TABLE VI. *Excited states of mercury I and II which result from reactions with helium, neon and argon.*

Mercury II		Mercury I	
Term from normal state of Hg II (cm^{-1})	Equivalent volts from normal state of Hg II	Term from ionized state of Hg I (cm^{-1})	Equivalent volts from normal state of Hg I
$^2D_3$ 119695	14.75	6^3P_0 −7860	11.36
$^2D_3$ 134732	16.62	6^3P_1 −9798	11.60
2^2P_1 135666	16.71	6^3P_1 −9798	11.60
2^2P_2 144789	17.85	Ionization Potential	10.39
3^2P_2 196151	24.20	6^1S_0 84178.5	normal state
Hg^{++} 235461	29.06		

The possible reactions which can occur in helium-mercury mixtures are the following:

$$\underset{\substack{20.51\\19.73}}{He_m'} + Hg = \underset{17.85}{Hg^{+\prime}} + He + e + \underset{\substack{1.88\text{ volts}\\2.66}}{K.E.} \quad (1)$$

$$\underset{24.47}{He^+} + Hg = \underset{24.20}{Hg^{+\prime}} + He + e + \underset{0.27\text{ volts}}{K.E.} \quad (2)$$

The probability of reaction (1) occurring is low since the residual kinetic energy is too high for close resonance. Reaction (2) has a higher probability of occurrence but will have very little effect on the ion concentration.

From the results of spectrograms of this mixture given in Table II it can be seen that both the spectra of helium and mercury are developed, which indicates that the mercury is not very effective in eliminating the metastable states of helium. The results given in Table I show that mercury has very little effect on the field in the positive column of helium. Both of these facts are in agreement with the low probability of the occurrence of reaction (1) in helium-mercury mixtures.

Neon-Mercury Mixtures

The case is quite different for neon and mercury mixtures. The only possible reaction for neon-mercury mixtures is the following.

$$\underset{\substack{16.64\\16.54}}{Ne_m'} + Hg = \underset{16.62}{\overset{16.71}{Hg^{+\prime}}} + e + \underset{\substack{0.02\text{ or }-0.07\\-0.08\text{ or }-0.17}}{K.E.} + Ne \quad (1)$$

This is the only reaction which can occur in neon-mercury mixtures that will affect the field in the positive column and which has a high enough probability of occurrence to be considered. This reaction has a very high prob-

ability due to the close resonance between the metastable states of neon and the excited states of the mercury ion.

Since most of the energy of the metastable neon atoms goes into ionization of mercury this reaction greatly increases the efficiency of the ionization processes in neon-mercury mixtures over those of pure neon. This is shown by the fact that the field in the positive column of neon is reduced to almost one half of its original value by the addition of less than 0.03 percent mercury vapor. The results of spectrograms of the neon-mercury mixture given in Table III show that the mercury arc spectrum is developed strongly while the neon arc spectrum is completely absent. This would be expected according to the above reaction which would greatly reduce the concentration of metastable neon atoms in the mixture over that for pure neon. If the results were attributed to the effect of limitation of electron velocities, mercury vapor would be expected to have the same effect on helium as it has on neon and possibly to a greater extent, but instead mercury vapor causes a slight increase in the field for helium. This fact is strong evidence that the observed effects, where one gas is present in a small percent of the total volume, are correctly attributed to the action of collisions of the second kind.

Mixture of Argon and Mercury

The possible reactions in argon containing a small amount of mercury are

$$\underset{\substack{11.50\\11.67}}{A_m'} + Hg = \underset{10.39}{Hg^+} + A + \underset{\substack{1.11\\1.28}}{K.E.} + e \qquad (1)$$

$$\underset{\substack{11.50\\11.67}}{A_m'} + Hg = \underset{\substack{11.36\\11.60}}{Hg'} + A + \underset{\substack{0.14,\ -0.10\\0.31,\ \ 0.07}}{K.E.} + e \qquad (2)$$

$$\underset{\substack{15.69\\15.86}}{A^+} + Hg = \underset{14.75}{Hg^{+\prime}} + A + \underset{\substack{0.94\\1.11}}{K.E.} + e. \qquad (3)$$

Reaction (1) has a low probability of occurrence due to the rather high residual kinetic energy. Reaction (2) has a high probability due to the quite close resonance, the residual kinetic energy being small. This reaction corresponds to the excitation of negative terms of the mercury arc spectrum which have been observed with hollow cathode excitation of mercury by impacts of the second kind.[19] Reaction (3) is not very probable and would not have much effect on the electric field in any case.

The results of spectrograms given in Table II show that the mercury spectrum is very much stronger than the argon spectrum in the mixture. This fact is in good agreement with the probability of reaction (2) being much greater than that of reaction (1). The fact that the field in the argon mercury mixture is higher than in pure argon shows that reaction (2) occurs with greater probability than reaction (1).

By comparing curves in Figs. 7 and 8 the effect of a trace of a diatomic gas as an impurity in one of the gases can be seen. Only a trace of nitrogen

[19] F. Paschen, Preuss Akad. p. 3, 1928; also Naudé (reference 9).

was sufficient to more than double the field in pure argon. This large increase was due to the excitation of the nitrogen bands by collisions of the second kind with argon metastable atoms. In diatomic gases also a larger proportion of the energy of electron impacts goes into radiation than in monatomic gases and this causes an increase in the field. The spectrograms taken of these mixtures show that the nitrogen band spectrum begins to be developed strongly where the field in this mixture becomes larger than the corresponding mixture of pure argon and pure neon.

Birge and Hopfield[20] give the energy-level system for the positive bands of nitrogen. There are three states at 8.1, 8.5 and 9.4 volts, respectively. Each of the states have a large number of vibration levels. These vibrational levels extend from 8.1 to 14 volts. The ionization potential of nitrogen is given as 16.7 volts. The metastable states of argon at 11.50 and 11.67 volts will be in very close resonance with a large number of excited states of the nitrogen molecule. The metastable states of neon at 16.58 and 16.67 are in close resonance with the ionization potential of the nitrogen molecule. Therefore one would expect a very strong excitation of the positive bands of nitrogen in a mixture of neon and argon containing a trace of nitrogen, by impacts of the second kind between the metastable states of argon and neon and the neutral nitrogen molecules. From the curves in Figs. 7 and 8, it can be seen that the field in a mixture of neon and argon is greatly increased by the addition of a trace of nitrogen. This result is in good agreement with the fact that the metastable states of argon are in very close resonance with many excited states of the nitrogen molecule. Thus the concentration of metastable argon and neon atoms is very effectively decreased by the presence of only a trace of nitrogen.

Conclusion

The results show that the electrical and spectral characteristics of the uniform positive column in mixtures of monatomic gases can be explained principally in terms of collisions of the second kind between the ions or metastable atoms of one gas and the neutral atoms of the other. The effect of limitation of electron velocities is wholly inadequate to explain the results obtained for mixtures containing a fraction of 1 percent of one gas and is negligible as compared to the effect of collisions of the second kind. The limitation of electron velocities does occur in mixtures where both gases are present in large amounts and produces an appreciable effect.

The necessary condition for a large effect to be produced in the electrical and spectral characteristics of the positive column by a small percentage of one gas added to another is that there exists a close resonance between the metastable states of the main gas and the ionization potential or excited states of the added gas atom or ion.

[20] R. T. Birge and J. J. Hopfield, Astrophys. J. **68**, 257 (1928).