By substituting the experimental values of $x_e\omega_e$, ω_e, B_e, and α into (13) and (14), k_{111} and k_{1111} were found and are given in Table IV. The corresponding k_{111}' and k_{1111}' were then found from Eqs. (12) and are also listed in Table IV. By substituting the values of k_{111}', B_e', ω_e into (14), the value of α' was found to be 0.0168 cm^{-1} as compared with the experimental value of 0.0169 cm^{-1}. $(x_e\omega_e)'$ found in Table IV was computed by substituting k_{111}' and k_{1111}' and ω_e' into Eq. (13). This is equivalent to the relation

$$(x_e\omega_e)'/(x_e\omega_e)=(\omega_e'/\omega_e)^2. \qquad (15)$$

The equilibrium value ω_e' was computed from the ratio of the reduced masses and ω_e, Eq. (12). All the constants computed have been tabulated in Table IV.

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Negative Corona in Freon-Air Mixtures

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(Received April 7, 1947)

In order to gain information as to the importance of negative space charges in coronas, studies of negative corona in freon-air mixtures were undertaken. The mixtures used ranged from 10^{-4} to 10^2 percent of freon-12 in dry air. The onset potentials of the intermittent corona region were constant in all mixtures, approximately 6 to 7 kv with X/p about 100; only in pure freon it changed to 12,600 volts with X/p about 200. Concentrations of freon up to one percent revealed corona characteristics very similar to those of air. From one to 20 percent mixtures showed rapidly decaying Trichel pulses. Upon analysis this seems due to the formation of Cl^- and F^-, which are shown to be still stable at values of $X/p\geqq 200$. As a consequence, negative space charges will be stable in regions much closer to the corona point than in air and will, therefore, be more efficient in suppressing the discharge as is indicated by decaying pulse sizes. At still higher concentrations the more stable Cl^- and F^- formed heavier space charges, inhibiting the formation of large electron avalanches to such an extent that only incipient Trichel bursts were produced. Thus the range of potential of the intermittent corona region was extended to higher values, and the corona current *vs.* potential curves showed rapidly decreasing slopes with increasing amounts of freon.

INTRODUCTION

THIS investigation was undertaken for two reasons: to explain in more detail the mechanism that is active in the suppression of sparks because of the presence of gases which form very stable negative ions; and to investigate the character of space-charge pulses in such coronas in order to further our understanding of the more general mechanisms active in spark breakdown in any gas. It is essential to state the reasons for utilizing corona studies for this purpose rather than studies of sparking potentials with plane parallel electrodes. The propagation of a discharge at or near atmospheric pressure is mainly based on the formation of streamers proceeding from the anode or the mid-gap region. This occurs only near a threshold value. A plane parallel gap does not lend itself easily to a detailed study of the mechanisms involved because of the rapidity of events succeeding the initiating streamer. In a corona, however, the range of potentials from onset to spark breakdown is wide. In addition, there are the inherent advantages of strongly divergent electric fields and differences in mechanisms between positive and negative coronas. The proper choice of the geometry of corona gaps, i.e., confocal paraboloids or a hyperboloid point electrode opposite a plane enables one to make field calculations and to observe space-charge phenomena which are obscured in experiments on plane parallel gaps.

The characteristic curves of any point-to-plane corona, plotting the gap current against the applied potential, are made up of three ranges of specific interest. The "dark-current" range occurs well below the onset of any visible corona, and the sharper the point the narrower this range will be. It depends most strongly on the first Townsend coefficient α and to a lesser degree on the secondary mechanism near the point. The latter is caused chiefly by the efficiency of liberation of electrons from the point surface by positive ion bombardment and also to some photoelectric liberation from the cathode. The currents in this range vary from 10^{-14} ampere to about 10^{-8} ampere. Photo-ionization and excitation in the gas as well as space-charge distortion of the static electric fields are negligible.

In the "intermittent-corona" range the currents vary from 10^{-8} to about 10^{-6} ampere, and the corona becomes visible. In addition to the coefficient α, the secondary actions at the cathode point become more prominent. The most characteristic aspect of this range is the flickering or intermittent, visible corona. Associated with it are large current fluctuations at any fixed potential and transient space-charge pulses in the immediate vicinity of the point. Space-charge distortion of the electric field occurs intermittently. The corona is not self-sustaining and requires electrons from external ionizing sources to re-initiate it.

The third range is that of the "continuous corona" where the currents for a given potential are steady and reproducible and where the visible character is not erratic. The corona is self-sustaining, and the currents vary smoothly from about 10^{-5} ampere until this form of discharge is finally terminated by a disruptive spark or arc.

It should be noted that the transitions from the first to the second, and from the second to the third range do not always occur at a fixed and reproducible potential for a given gap geometry and gas, since the mechanisms active in the second range are subject to strong statistical fluctuations. We have tried to minimize these by providing external ionization from a weak Ra source placed in the vicinity of the gap. The results discussed here are mainly concerned with the second range and partly with the third.

APPARATUS AND TECHNIQUE

These experiments were carried out in freon-dry-air mixtures near atmospheric pressure (745 mm Hg) in a closed Pyrex system described elsewhere.[1] A 3.1-cm point-to-plane gap was used, employing a hemispherically-capped, smoothly polished Pt point (0.5-mm in diameter) opposite a circular Pt plane of 4-cm diameter with rounded edges. A 70-kv transformer supplied the high voltage through a half-wave rectifier and a one mfd filter condenser. The potential was determined with a 50 megohm, corona-shielded, Taylor resistor in series with an accurate micro-ammeter. Freon-12, dichloro-difluoro-methane, obtained from commercial tanks, was used without further purification since the manufacturer's[2] specifications of purity seemed adequate for this work. The freon-air mixtures ranged 10^{-4} to 10^{2} percent by volume of freon and were obtained by successive dilutions. Test observations with room air, dried over a CO_2 snow-alcohol mixture, were made before and after the work on freon-air mixtures. By the use of liquid air traps, mercury vapor from the diffusion pump and manometer was carefully excluded from the discharge chamber.

Potential *versus* current characteristics were taken up to voltages which were safely below the breakdown limit. Constant gap geometry was thus maintained throughout. A tele-microscope (30×) enabled good visual observation of the discharge, and the transient space-charge pulses at the point were observed with an oscilloscope[3] which was connected across a 3×10^{4} ohms resistor between the plate electrode and ground. A weak radium source was placed 6 inches from the gap in order to facilitate the observation of pulse formation preceding onset of the steady corona.

EXPERIMENTAL RESULTS

One hundred percent dry air and mixtures up to 0.1 percent of freon showed similar results. The first space-charge pulses (termed by Loeb[4] "Trichel" pulses and explained subsequently in the discussion) were observed in the oscillograph at about 6000 volts and were accompanied by faintly visible light flashes at currents of approximately 10^{-8} ampere. These pulses never attained the regularity of frequency nor the uniformity of amplitude observed by Trichel[5] in an open air

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[1] G. L. Weissler, Phys. Rev. **63**, 96 (1942).

[2] Kinetic Chemicals, Inc., 10th and Market Streets, Wilmington, Delaware, Technical Paper No. 6 on Freon-12 (Underwriter's Report), and Technical Paper No. 8.

[3] A. F. Kip, Phys. Rev. **55**, 549 (1939), Fig. 1B.

[4] L. B. Loeb, A. F. Kip, G. G. Hudson, and W. H. Bennett, Phys. Rev. **60**, 714 (1941).

[5] G. W. Trichel, Phys. Rev. **54**, 1078 (1938), Figs. 2, b–f.

gap, but showed the same irregular characteristics that Hudson[4] found with an enclosed gap using clean, dry air free from dust particles, and other sources of triggering electrons which were found essential in the production of regular Trichel pulses. The irregular Trichel-pulse bursts were of varying duration, from 10^{-3} to 10^{-2} second. The amplitude and number of individual peaks in each burst varied, but in general they are represented in Fig. 2A. At higher potentials the number of bursts and the frequency of pulses in each burst increased. Since no "single-sweep" mechanism was available, a detailed study of the pattern, i.e., the exact frequency and shape, was impossible, but the general trends were the same as those reported previously.[4, 5]

At about 12,500 volts and a current of 12 microamperes the transition to the continuous corona occurred, showing the same visual characteristics observed previously.[5] The current *versus* potential curve of dry air and mixtures of less than 0.1 percent of freon for the continuous corona is shown in Fig. 1. Although the current was continuous, fluctuations and irregular Trichel pulses were observed in the oscilloscope throughout this third region, and they decreased in amplitude with increasing currents.

With mixtures of from 0.1 to one percent of freon in dry air the only notable difference occurred with the appearance in the intermittent corona region of what might be termed a hysteresis effect. After several minutes at relatively high currents in the continuous corona region, a decrease of the potential below 12.5 kv produced average current values in the intermittent corona region which were much lower than those during the upward run. A few minutes after the first run, with the voltage off during the interval, a second run was started. The first Trichel pulses and faint light flashes then were observed at 9 to 10 kv at a current of about 10^{-8} ampere rather than at 6 kv as in the first run. This hysteresis effect became more pronounced with a larger amount of charge passing across the gap and with a shorter time interval between the first and second runs. An interval of 30 minutes or more gave results duplicating those of the first run.

As the freon content was increased from one to 20 percent, the shape of the Trichel bursts changed from that of Fig. 2A to the decaying ones of Figs. 2B and 2C. This may be caused by the production of increasing amounts of Cl^- and F^- by the discharge. Mixtures of over 20 percent freon showed similar pulses with reduced amplitudes. At concentrations of 60 percent freon and above it was difficult to distinguish the bursts because of their reduced size. These incipient Trichel pulses showed the same regularity as the original Trichel pulses, and they also disappeared at higher potentials.

With mixtures of freon of one to 100 percent the current *versus* potential curves showed successively decreasing slopes with increasing amounts of freon (Fig. 1). Similar results were found for

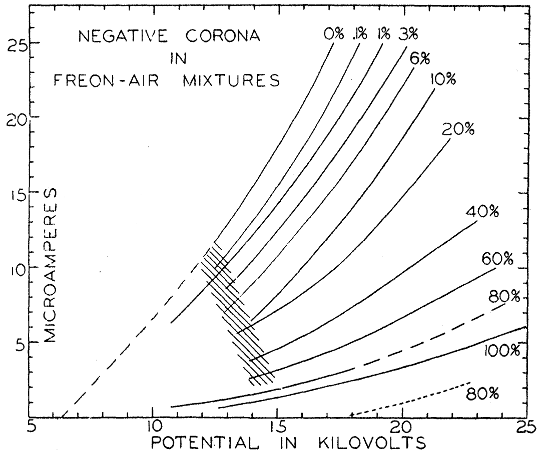

FIG. 1. Current *vs.* potential curves for negative corona in freon-air mixtures. The percentage number indicates the amount of freon by volume in dry, clean air. Total gas pressure: 745 mm of Hg. To the left of the shaded area and below the dotted continuation of the pure air curve (0 percent), the current values for all mixtures fluctuate violently. The dotted 80 percent curve below the 100 percent one is due to the formation of several secondary corona spots 1 to 2 cm from the tip of the point electrode on the stem.

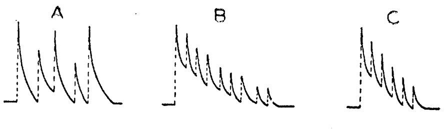

FIG. 2. A: Irregular Trichel-pulse burst in dry, clean air near onset of negative corona (7000 volts). B: The same in 6 percent freon in air, $p=745$ mm of Hg. C: The same in 10 percent freon in air, $p=745$ mm of Hg. It is possible that the individual pulses in B and C return to the zero line. Because of the high speed of pulse formation (less than one microsecond) the details of this oscillograph trace must be instrumental, but the general decay of the pulses seems to be real.

sparking potentials by Skilling, Trump, Nonken, and others.[6] Although larger amounts of freon reduced currents, the onset potentials of the intermittent coronas were roughly 6 kv for all mixtures except for pure freon, where about 12.65 kv were required. Onset potentials of around 13 kv were observed for the continuous corona for air and low percentage mixtures. For larger percentages of freon, onset for the continuous corona region could not be clearly established since both the current and the visual discharge were changing erratically. (This may be caused by fluctuating Cl^- and F^- concentrations caused by the electrical wind.) When plotting these data as in Fig. 1, however, it was possible to obtain current *versus* potential curves for the higher concentrations by using average values except for the region to the left of the shaded line (Fig. 1). In the intermittent corona region the potential range became progressively larger with increasing amounts of freon.

The visual appearance of the discharge gradually changed with increasing amounts of freon from the glow-discharge type in air,[4] with negative glow, Faraday dark space, and narrow positive column, to a larger, diffuse discharge with no dark space. (Loeb[7] gives an excellent analysis of the glow-discharge characteristics of the negative corona and the active ionizing function, contrasting Townsend's α with Morton's[8] proposal.) Intermediate concentrations of freon, 40 to 80 percent, showed alternately at the same potential the wide, diffuse-discharge characteristic of freon, and the narrow type observed in air. A change from the first to the second form was accompanied by an increase in current with a corresponding decrease on changing back to the first type. In the second, more concentrated form, an active cathode spot was formed, and therefore the discharge moved less readily over the point surface than did the diffuse type.

DISCUSSION

In a gas in which electrons attach readily, Trichel pulses represent the major space-charge phenomena of the negative point corona. (In pure, free electron gases such as A, H_2, and N_2, however, it has been found[1] that the Trichel-pulse mechanism is not applicable.) In order to understand the observations in freon it is necessary to discuss first the mechanism in air. When a sufficient negative potential is applied to a point in air at atmospheric pressure, an electron, generated in the high field region, travels away from the point and by cumulative ionization by collision produces $\exp[\int_0^{x_0}\alpha dx]$ new electrons and positive ions. At a distance x_0 from the point surface the electric field X is decreased to such a low value that ionization by electron impact becomes negligible ($\alpha < 1$). In this region ($X/p = 90$) electrons attach readily and form relatively slow negative ions. During the development of the first avalanche new ones are generated by the liberation of triggering electrons from the point surface by three processes: (a) positive ion bombardment; (b) the photoelectric effect at the cathode; and (c) electron emission from rough spots and dust specks. When the electrons in these avalanches have traveled beyond x_0, they enhance the negative-ion space-charge cloud so much that the field in the immediate vicinity of the point is insufficient to permit effective ionization by collision about the point, and the discharge is suppressed. After 10^{-3} to 10^{-4} second the negative ions have traveled sufficiently far into the gap toward the anode to diffuse the limiting negative space charge. The original field is then restored, and if sufficient triggering electrons are furnished by field emission or by the Paetow-Malter effects[9] the process will be repeated. Since it depends only on the clearing time required for the negative ions, it produces regular Trichel pulses in the oscillograph.[5] If, however, the corona point is carefully polished, and dust-free air is used, field emission will be absent. For re-ignition the discharge then depends on triggering electrons liberated from the point by those few positive ions which are still available. (The majority of positive ions are drawn into the point and

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[6] J. G. Trump, F. J. Safford, and R. W. Cloud; Trans. A.I.E.E. **60**, 132 (March 1941); G. C. Nonken, Trans. A.I.E.E. **60**, 1017 (Dec. 1941); H. H. Skilling and W. C. Brenner, Trans. A.I.E.E. **61**, 191 (April, 1942).

[7] L. B. Loeb, "The mechanism of the negative corona at atmospheric pressure in relation to the first Townsend coefficients," Phys. Rev. **71**, 712 (1947),

[8] P. L. Morton, Phys. Rev. **70**, 358 (1946); G. W. Johnson, Phys. Rev. **71**, 278A (1947).

[9] L. Malter, Phys. Rev. **49**, 478 (1936); **50**, 48 (1936); H. Paetow, Zeits. f. Physik **111**, 770 (1939).

neutralized during or before the choking-off period.) As a result of the low efficiency of secondary emission by positive ions of relatively low energy, this repetitive process will be subjected to strong statistical fluctuations, giving rise to the irregular Trichel pulse-bursts[4] (Fig. 2A).

In flame-decomposition tests performed on freon-12 by the manufacturers,[2] HF, HCl, and other electro-negative gases were produced. A similar and more efficient decomposition process including the production of Cl and F will be initiated by electron impacts. The electron affinity of the oxygen atom is about 2.2. ev, but since O does not exist long in air, most of the attachment is to the O_2 molecules which have an affinity of 0.07 to 0.19 ev. This is markedly lower than the affinities of Cl (3.8 ev) and F (4 ev).

One should, therefore, expect that with freon added in increasing amounts to air, the negative-ion space charges will be formed closer to the point surface. This means a smaller x_0 for avalanche formation, with correspondingly lower currents, and also a greater effectiveness in suppressing the discharge (Fig. 2B, C). The negative ions of chlorine and fluorine must therefore be stable at higher values of the ratio of X/p (field-strength in volts/cm divided by pressure in mm of Hg) than those of oxygen, and efficient electron capture[10] may be possible at values of X/p as high as 200. This value seems to be substantiated by the following calculations:

On the assumption that the corona point was shaped in the form of a hyperboloid of revolution and that the plane electrode was large in diameter compared with the gap, the electric fields at the surface of the point and at different distances from the point were calculated by established methods.[11] (The surface field at the point was calculated to be $X_s = 65$ kv/cm (Fig. 3A) at 5 kv, which is only 54 percent of the value of $X_s' = 120$ found by Kip[12] to be necessary for streamer formation in air. Since he made his observations and calculations with confocal paraboloid electrodes assuring him of much greater accuracy, our values of X and X/p in Fig. 3A indicate only order of magnitudes and relative quantities. Since $X_s = kV_s$ it is possible to replace the calculated factor $k = 13$ by a factor $k' = 120$ (kv/cm)/5 (kv) = 24 obtained from direct comparison with Kip's data. The curves for $X/p = f(x)$ given there must thus be shifted by this fraction, and results shown in Fig. 3B are based on this correction.) Values of $X/p = 200$ at a distance of only 0.3 mm from the point surface for an applied potential of 12 kv were found (Fig. 3B). The very low corona currents in pure freon and the absence of normal size Trichel-pulse bursts appear to be mainly due to the absence of large avalanche formation. It is possible that the triggering electrons have only 6 or 7 ionizing free paths over a distance x_0, say 0.3 mm before attachment occurs, instead of 13 or 14 as in air over the same x_0, and their energy is dissipated in dissociation, vibrational levels, etc. It is interesting that the onset potentials of the intermittent corona region for pure air and freon mixtures up to 80 percent are approximately the same (6 to 7 kv). The corresponding value of X/p at the point surface is about 100 (Fig. 3A), which is close to $X/p = 90$ when the negative O_2 ion sheds its electron.[13] For 100 percent freon,

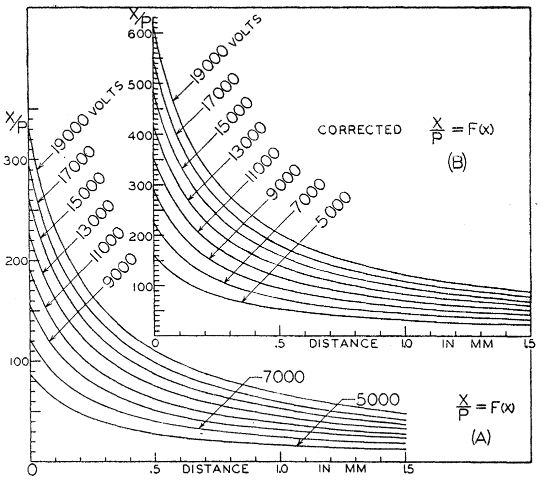

FIG. 3. A: X/p as a function of distance x in mm from the point surface: $X_s = kV_s$ and $X_x = (RX_s)/(R+x)$; $2R = 0.5$-mm diam.; $k = 13$, when hyperboloid point is assumed; $p = 745$ mm of Hg. B: Corrected values of $X/p = f(x)$, using Kip's data; see text.

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[10] H. S. W. Massey, *Negative Ions* (Cambridge University Press, New York, 1938), Chapters III and IV.

[11] C. F. Eyring, S. S. Mackeown, and R. A. Millikan, Phys. Rev. **31**, 900 (1928); (see also reference (4) page 715).

[12] A. F. Kip, Phys. Rev. **55**, 551 (1939).

[13] L. B. Loeb, Phys. Rev. **48**, 684 (1935); see also Loeb, *Fundamental Processes of Electrical Discharge in Gases* (John Wiley and Sons, Inc., New York, 1939), pp. 291–293.

the onset potential is 12.65 kv with a value of $X/p=200$ at the point surface. (The same values of X/p are found along a vertical line above 0.3 mm in Fig. 3B for the respective point potentials of 6 and 12 kv.) This indicates the threshold of stability of the negative ions produced in freon. The negative ion formation and the relatively inelastic electron impacts in freon tend to decrease materially the first Townsend coefficient α.

The hysteresis effect of increased onset potentials for the intermittent corona may be explained by the accumulation of decomposition products of freon which are particularly effective in electron capture. Since free atoms like Cl and F will recombine to form molecules, it is not surprising to find that the effect disappears with time. Such reactive gases can also be absorbed by electrode materials and similar substances. In an enclosed, air-filled chamber a transient lowering of the sparking potential was observed as a result of the formation of nitrous oxides after the passage of several sparks,[14] but in freon the reverse is true.

We wish to express our appreciation to Professor L. B. Loeb for the loan of the discharge chamber used in this work and for his assistance in the interpretation of the results in the light of recent data from his research group.

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[14] W. R. Haseltine, Phys. Rev. 58, 188 (A) (1940).

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Positive Corona in Freon-Air Mixtures

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(Received April 7, 1947)

In this investigation of positive corona, streamer pulses increased in frequency and strength to a maximum at one percent of freon in air. The visual characteristic of the corona changed markedly indicating also that the discharge sustained itself largely by the streamer mechanism. The dissociation of freon by the discharge created stable Cl^- and F^- ions which neutralized the positive space charges and therefore stimulated streamers. As the freon content was increased, streamers degenerated until they could not be distinguished from burst pulses. The onset potentials were shifted to higher values and the current *vs.* potential curves showed decreasing slopes with increasing amounts of freon.

EXPERIMENTAL RESULTS

THE data on the positive point-to-plane corona in freon-air mixtures were obtained by using the techniques described previously.[1] In air the intermittent corona region (Geiger-counter regime) began with the onset of streamers[2] at a point potential of 5 kv, and it extended over a range of about 200 volts. Some burst pulses were also observed. At 5.2 kv onset of the continuous corona occurred, and streamers no longer were present. The current was 0.25 microampere, and the visual appearance of the discharge was steady. Further increase in potential resulted in monotonically increasing currents (Fig. 1). At between 20 and 25 kv occasional "breakdown" streamers were observed. Since these only occur close to the sparking potential, the runs were terminated. The visual character of the discharge was that of a uniform glow which extended over a larger surface area of the point as the potential was raised.

It has been pointed out before[3] that the addition of small amounts of impurities to the gas strongly influences streamer formation and thereby sparking potentials. Therefore, after several runs with the same dry air filling, streamers were observed in the continuous corona region. They did not occur in this region after the refilling of the chamber, and the results of

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[1] G. L. Weissler and E. I. Mohr, preceding paper on negative corona.

[2] A. F. Kip, Phys. Rev. 55, 551 (1939).

[3] G. L. Weissler, Phys. Rev. 63, 96 (1943); R. W. Haseltine, Phys. Rev. 58, 188A (1940).