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MASS SPECTROGRAPH ANALYSES, AND CRITICAL POTENTIALS FOR THE PRODUCTION OF IONS BY ELECTRON IMPACT, IN NITROGEN AND CARBON MONOXIDE

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Abstract

The dissociation products formed by bombarding nitrogen and carbon monoxide with electrons of a definite velocity have been studied with a mass spectrograph.

Nitrogen.—N_2^+ and N^+ ions appear at 15.8 ± 0.1 and 24.5 ± 0.1 volts respectively. The N^+ ion has kinetic energy and is attributed to $N_2\rightarrow N^+ + N + e$. Increases in the efficiency of production of the N^+ ion appear at 40.0 ± 1.0 and 47.0 ± 1.0 volts. The largest percentage of the total positive ion current carried by kinetic energy ions is approximately 28 percent at 140–160 volts. Efficiency curves of total ionization and of N_2^+ exhibit maxima at 100.0 ± 5.0 and 60.0 ± 5.0 volts respectively.

Carbon monoxide.—CO^+, C^+ and CO^{++} ions appear at 13.9 ± 0.2, 22.5 ± 0.2, and 43.0 ± 1.0 volts respectively. Maximum numbers of CO^+, C^+, and CO^{++} ions formed per electron per cm path per mm pressure at 0°C are 10.13, 0.50, and 0.14 at 102, 105, and 125 volts respectively. The C^+ ion possesses kinetic energy and is probably due to $CO\rightarrow C^+ + O + e$. Assuming that the CO^{++} ion would dissociate into $C^{++}+O$ the energy of dissociation cannot be less than from 2 to 3 volts. O^- ions are formed between 9.5 ± 1.0 and 16.5 ± 1.0 volts, and again beginning at 22.5 ± 1.0 volts and reach a maximum at 33 volts. The first group is evidently due to the attachment of an electron to the CO molecule followed by a dissociation $CO^-\rightarrow C+O^-$. The second group may be due to $CO\rightarrow C^+ + O^-$. O^- ions are only 2.7 percent as numerous as C^+ ions at 30 volts.

Introduction

THE material presented in this paper is an extension of the work done by Bleakney[1] on multiply charged ions produced by electron impact in gases at low pressures. The purpose of this paper is to describe the results of a similar study of the ionization products in the diatomic molecular gases—nitrogen and carbon monoxide. Smyth[2] and Hogness and Lunn[3] have made mass spectrograph analyses of the ions produced in nitrogen by electron impact while Hogness and Harkness[4] have made a similar study of carbon monoxide. The present method confirms some of the results of these previous investigations and presents some new data, particularly in the experiments on carbon monoxide.

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[1] W. Bleakney, Phys. Rev. **34,** 157 (1929); **35,** 139 (1930); **35,** 1180 (1930); **36,** 1303 (1930)

[2] H. D. Smyth, Proc. Roy. Soc. **104A,** 121 (1923).

[3] T. R. Hogness and E. G. Lunn, Phys. Rev. **26,** 786 (1925).

[4] T. R. Hogness and R. W. Harkness, Phys. Rev. **32,** 936 (1928).

APPARATUS AND PROCEDURE

The apparatus employed in this experiment was the same as that used by Bleakney[1] in the study of helium, neon, and argon. The nitrogen and carbon monoxide used were prepared by Smith.[5] The gases were admitted to the apparatus through a fine capillary at the end of the tube opposite the electron gun and were pumped through the ionization chamber and out past the filament. Effects of dissociation by the filament were thus reduced to a minimum. The pressures used were from 5 to 10×10^{-5} mm Hg. The gases used were found to be very pure. Water vapor and a trace of carbon monoxide existed as impurities in the tube before the gas to be studied was admitted. If liquid oxygen were kept on the mercury trap continuously for about 80 hours the water vapor impurity was so reduced as not to interfere appreciably. The carbon monoxide impurity was never large enough to be troublesome except in determining ionization potentials.

RESULTS

Nitrogen

A typical *e/m* analysis curve of the products obtained by bombarding nitrogen with electrons of definite velocity is shown in Fig. 1. The positive ion current to the analyzer is plotted as a function of the analyzing field, E, in volts. This curve shows the N_2^+ and the N^+ ions. A background of H_2O^+ shows between the two peaks. The trailing off to the right of the N^+ ion may be attributed to those N^+ ions which have considerable kinetic energy.

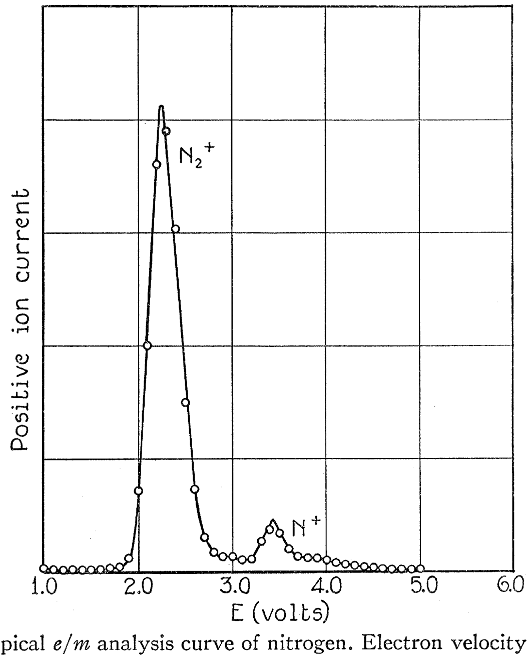

Fig. 1. A typical *e/m* analysis curve of nitrogen. Electron velocity = 100 volts.

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[5] John T. Tate and P. T. Smith, unpublished.

The ionization potentials of the N_2^+ and N^+ ions were determined by plotting the maximum heights of the peaks as a function of the electron velocity in volts. When the liquid oxygen on the mercury trap was replaced by solid carbon dioxide there was a sufficient amount of mercury vapor present in the tube for calibration purposes. The results are shown in Fig. 2 (a). The impurity under the curve for N_2^+ is CO^+ whereas that under the N^+ curve is

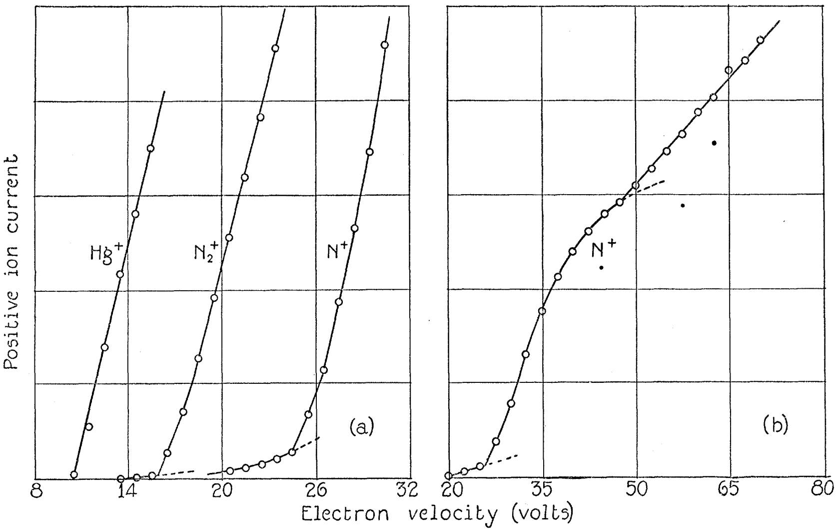

Fig. 2. (a) Curves showing the ionization potentials in nitrogen. (b) Ionization potential curves of N^+ showing a break at 47 volts.

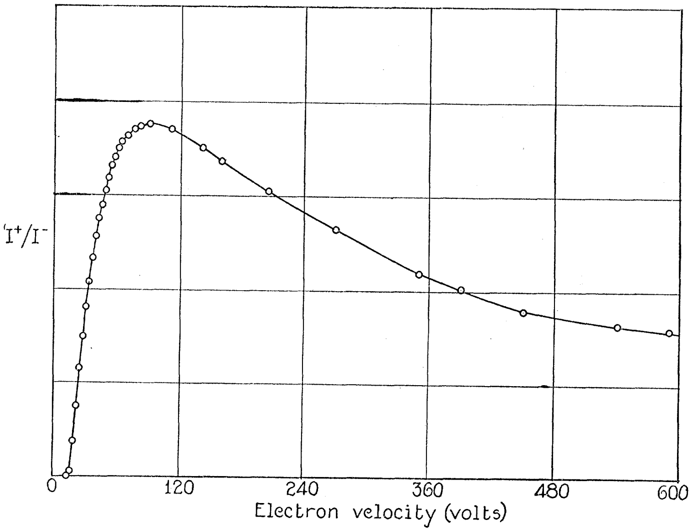

Fig. 3. Efficiency curve for nitrogen.

H_2O^+. This method shows N_2^+ and N^+ appearing at an electron velocity of 15.8 and 24.5 volts respectively with an estimated probable error of ±0.1 volts. Fig. 2 (b) shows an increase in the efficiency of production of the N^+ ion at 47.0 ± 1.0 volts. A similar but considerably smaller increase was noticed at 40.0 ± 1.0 volts. These breaks have also been found by Lozier.[6]

By plotting the ratios of the areas under the N_2^+ peak to the electron current as a function of the electron velocity in volts the maximum efficiency of formation of the N_2^+ ion was found to occur at an electron velocity of 60.0 ± 5.0 volts. The total efficiency of ionization as plotted in Fig. 3 shows a maximum at 100.0 ± 5.0 volts. This curve was obtained by plotting the ratio of the total positive ion current collected at the upper plate of the ionization chamber to the electron current as a function of the electron velocity in volts. The efficiency curve of total ionization in N_2 given in Fig. 3 is almost identical with the one obtained by Smith.[5]

A rough measure of the percentage of the current carried by those ions possessing kinetic energy was obtained by the method outlined by Bleakney,[7] and was shown to reach a maximum of 28 percent at 140–160 volts electron velocity. The assumptions made in obtaining this result make it impossible to consider it as other than an indication of the order of magnitude.

Discussion of results in nitrogen.

The value given in this paper of 15.8 ± 0.1 volts as the ionization potential of N_2, although lower than the generally accepted value, agrees with that given by Samson and Turner[8] and the earlier results obtained by Boucher[9] and by Found.[10] The appearance of N^+ at 24.5 ± 0.1 volts has been attributed to a single impact resulting in $N_2 \rightarrow N^+ + N + e$. The value given is in good agreement with that of 24.6 volts given by Hogness and Lunn[3] who, however, attributed the formation to a different process. According to data given by Samson and Turner[8] together with a correction by Birge[11] the minimum value at which N^+ can appear from the above process is 22.7 ± 0.1 volts. From this the N^+ ion should have at least 0.9 volts kinetic energy. These conclusions have been verified by Lozier.[6] There was no means of determining whether or not any N_2^{++} ions were formed since their m/e is the same as that of the N^+ ion. No N^{++} ions were found below 400 volts. No search was made for negative ions.

Carbon monoxide

Fig. 4 is a typcial e/m analysis curve of the positive ions formed by bombarding CO with electrons. Ions having an m/e of 28, 14, and 12 were found which correspond to CO^+, CO^{++}, and C^+ and have ionization potentials of 13.9 ± 0.2, 43 ± 1.0, and 22.5 ± 0.2 volts respectively as obtained from Fig. 5.

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[6] W. W. Lozier, unpublished.

[7] W. Bleakney, Phys. Rev. **35**, 1185 (1930).

[8] L. A. Turner and E. W. Samson, Phys. Rev. **34**, 747 (1929).

[9] P. E. Boucher, Phys. Rev. **19**, 189 (1922).

[10] C. G. Found, Phys. Rev. **16**, 41 (1920).

[11] R. T. Birge, Phys. Rev. **34**, 1062 (1929).

The second peak from the left in Fig. 4 is due to an ion having an *m/e* of 18 and an ionization potential of 13.2 volts and so has been attributed to H_2O^+. Solid carbon dioxide instead of liquid oxygen was used on the mercury trap in this experiment. The O^+ ion, if formed, was entirely masked by the H_2O^+ ion.

The two *e/m* analysis curves in Fig. 4 were taken at electron velocities of 35 and 210 volts. They show the resolving power of the apparatus as well as the relative magnitudes of the ions formed at those velocities. Attention is called to the complete absence of an ion having an *m/e* of 14 at 35 volts electron velocity. The determination of the ionization potential of CO may not be accurate since the positive ion current due to the Hg^+ ion which was used to calibrate the voltage scale was very small compared to the positive ion current due to the CO^+ ion. The impurity shown under the C^+ curve in Fig. 5 was H_2O^+ while that under the CO^{++} was C^+ and H_2O^+. It was found that by decreasing the drawing out field in the ionization chamber the C^+ peak shown in Fig. 4 decreased considerably in size. This was an indication that the C^+ ion was formed with kinetic energy. This also afforded a means whereby more accurate measurements could be made of the CO^{++} ion inasmuch as decreasing the size of the C^+ peak made the CO^{++} peak stand out more distinctly. An increase in the efficiency of formation of the C^+ ion was consistently evident at about 30 volts.

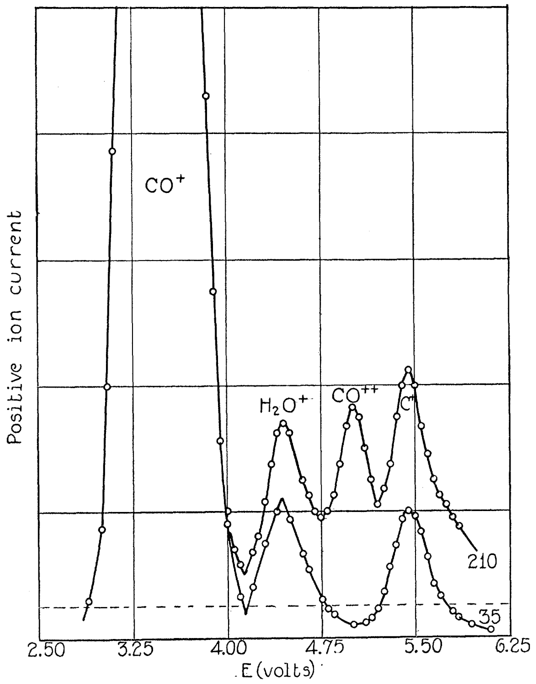

Fig. 4. *e/m* analysis curves of carbon monoxide taken at electron velocities of 35 and 210 volts.

Fig. 6 shows the percent of positive ion current carried by the different ions. These curves were obtained by plotting the ratios of the areas under the peaks to the electron current as a function of the volt velocity of the impinging electrons. Multiplying the total number of ions formed as given by Smith[5] by the percent of current carried by a particular ion and dividing by the charge on the ion gives the number of that type of ion formed per electron per cm path reduced to 1 mm pressure at 0°C. These results are shown in Fig. 7. The numbers of CO^+, C^+, and CO^{++} ions formed reach maxima of 10.13, 0.50, and 0.14 at 102, 105, and 125 volts respectively. An independent determination of the efficiency of formation of the CO^+ ion obtained by plotting the area under the peak yielded a maximum at 100 volts.

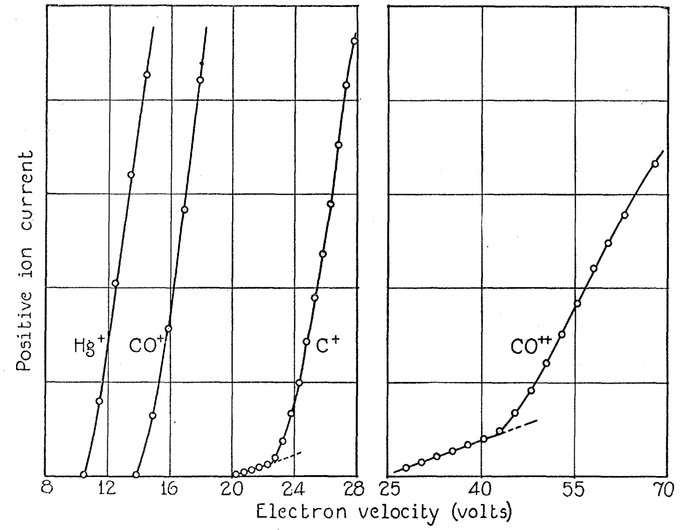

Fig. 5. Curves showing the ionization potentials in carbon monoxide.

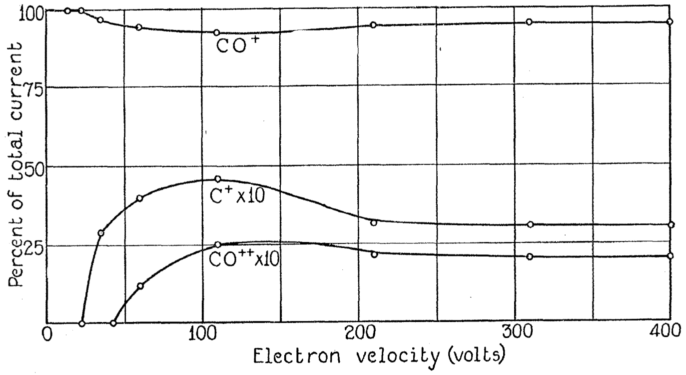

Fig. 6. Percent of total positive ion current carried by CO^+, C^+, and CO^{++} ions.

Negative ions having an m/e of 16 were found in carbon monoxide. These negative ions which are undoubtedly O^- first appeared at 9.5 volts, reached a sharp maximum at 12 volts and had completely disappeared at 16.5 volts as shown in Fig. 8. The same type of negative ions reappeared at 22.5 volts

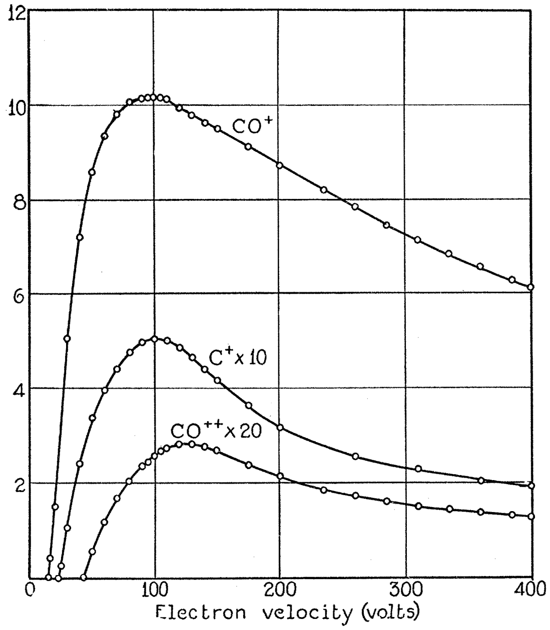

Fig. 7. Number of ions, N, formed per electron per cm path per mm pressure at 0°C.

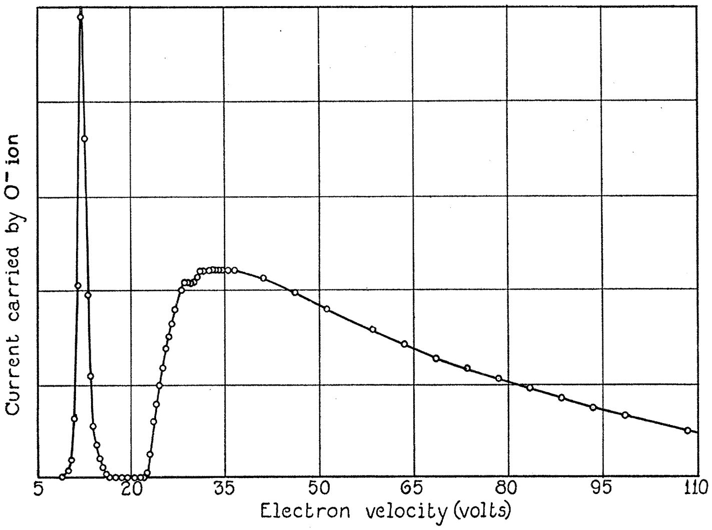

Fig. 8. Current carried by O^- ion in carbon monoxide.

and increased to a maximum at 33 volts and then dropped off gradually as the electron velocity was increased. These voltages given are accurate only to within a volt since the correction had to be calculated rather than determined experimentally. Fig. 8 was obtained by plotting the maximum height of the O^- peak in the analyzer as a function of the electron velocity. If the O^- ion formed at $9.5-16.5$ volts has no kinetic energy and if the one starting in at 22.5 volts does have kinetic energy then the relative heights of the two parts of the curve are not accurate. In this case the second part would be too small. The dip in the curve at 29 volts appeared consistently. This break was also detected by another method[6] in this laboratory. It may be that this dip is associated with the break found at 30 volts in the C^+ ionization potential curve. The O^- ion was found to be only 2.7 percent as numerous as the C^+ ion at an electron velocity of 30 volts.

Discussion of results in carbon monoxide.

The value of 13.9 ± 0.2 volts as given in this paper as the ionization potential of CO agrees with that given by Hogness and Harkness[4] but may be in error as mentioned before. Birge[12] gives a calculated value of 14.2 volts. In a private communication Mulliken gives the most probable value of the heat of dissociation of CO as 9.8 volts. With the value given by Hopfield[13] of 11.2 volts as the ionization potential of the carbon atom the minimum electron velocity at which the C^+ ion could appear by the single process $CO \rightarrow C^+ + O + e$ is 21 volts. The appearance of C^+ at 22.5 ± 0.2 volts indicates 1.5 volts kinetic energy to be divided between the dissociation products. The value of 22.5 ± 0.2 volts is also in good agreement with the value of 22.8 volts given by Hogness and Harkness.[4]

The CO^{++} ion appearing at 43.0 ± 1.0 volts is, so far as the author knows, the first multiply charged polyatomic molecule whose ionization potential has been determined. J. J. Thomson[14] found a doubly charged molecular ion having an m/e of 28 and attributed it to either N_2^{++} or CO^{++}. R. Conrad[15] has identified several doubly charged molecules in the glow discharge of mixtures of methane, oxygen, and water vapor.

The experimental value of 43.0 ± 1.0 volts for the critical potential of $CO \rightarrow CO^{++} + 2e$ indicates that the dissociation products of the doubly charged ion are most likely to be $C^{++} + O$ rather than $C^+ + O^+$ or $C + O^{++}$. If one combines the energy necessary to dissociate CO into $C + O$ which is 9.8 volts as given above with the ionization potentials of 11.2[12] and 13.5[16] volts for atomic carbon and oxygen respectively 34.5 volts is obtained for an assumed dissociation of CO into $C^+ + O^+$. As this is much less than the observed value of 43 volts it does not seem possible that $C^+ + O^+$ can be the correct dissociation products. In a similar way with the 35[17] volts energy necessary to remove the second electron from atomic oxygen one gets 58.3 volts

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[12] R. T. Birge, Nature **117**, 229 (1926).

[13] J. J. Hopfield, Phys. Rev. **35**, 1586 (1930).

[14] J. J. Thomson, "Rays of Positive Electricity," 2nd Ed., p. 84 (1921).

[15] R. Conrad, Phys. Zeits. **31**, 888 (1930).

[16] J. J. Hopfield, Astrophys. J. **59**, 114 (1924).

[17] R. A. Millikan and I. S. Bowen, Proc. Nat. Acad. Sci. **13**, 531 (1927).

for the energy necessary to dissociate CO into $C+O^{++}$. Since it seems unlikely that the dissociation energy of CO^{++} can be as high as $58.3-43\simeq 15$ volts, and since in the formation of CO^{+} the dissociation products were found to be $C^{+}+O$ and not $C+O^{+}$, the dissociation of CO^{++} into $C+O^{++}$ is very improbable. The dissociation into $C^{++}+O$ requires 9.8 $(CO\rightarrow C+O)+11.2(C+O\rightarrow C^{+}+O+e)$[12] $+24.3(C^{+}+O\rightarrow C^{++}+O+e)$[17] $=45.3$ volts which shows that the heat of dissociation of the CO^{++} ion cannot be less than from 2 to 3 volts.

The only thing to be said about the O^{-} ion at the present time is that its first appearance is probably due to an attachment of an electron to a CO molecule followed by the dissociation $CO^{-}\rightarrow C+O^{-}$. The fact that it appears only over a small range of electron velocities lends support to the above interpretation. The second appearance may be due to a splitting up of $CO\rightarrow C^{+}+O^{-}$. The negative ion will be discussed by Lozier.[6]

It is a pleasure to acknowledge the constant interest and timely suggestions of Professor John T. Tate and the many helpful discussions with Drs. W. W. Lozier and P. T. Smith.