JANUARY 15, 1932 *PHYSICAL REVIEW* *VOLUME 39*

THE DISSOCIATION OF NITROGEN AND CARBON MONOXIDE BY ELECTRON IMPACT

By John T. Tate and W. Wallace Lozier*
University of Minnesota

(Received December 1, 1931)

Abstract

The energies of the dissociation products of N_2 and CO formed by electron impact have been studied. The kinetic energy distributions of C^+ ions from CO and N^+ ions from N_2 have been measured and for both gases the most probable kinetic energy of the ions is about 3 volts. The variation with electron energy of the probability of production of N^+ ions from N_2 and C^+ ions from CO (the ions having specified energies) has been studied. The minimum electron energies necessary to produce C^+ and N^+ ions of specified energy have been determined and they satisfy the requirements of the principle of conservation of energy. From these measurements heats of dissociation as follows have been determined:

Process	Heat of dissociation (volts)
$N_2 \rightarrow N+N$	8.4 ± 0.5
$N_2^+ \rightarrow N^+ + N$	$\geqq 7.1 \pm 0.5$
$CO \rightarrow C+O$	9.3 ± 0.5
$CO^+ \rightarrow C^+ + O$	$\geqq 6.4 \pm 0.5$

The following are probably the dissociation processes detected in the experiments:

Process	Energy of ions (volts)	Energy of impacting electron (volts)
$N_2 \rightarrow N^+ + N + e$	2 to 7	27 to 37
$N_2 \rightarrow N^+ + N^* + e$	1 to 2	35 to 37
$N_2 \rightarrow N^+ + N^+ + 2e$	4 to 8	46 to 54

Negative ions (O^-) were observed and are believed to result from the following processes:

Process	Energy of O^- ions (volts)	Energy of impacting electron (volts)
$CO + e \rightarrow C + O^-$	0 to 1	10 to 14
$CO \rightarrow C^+ + O^-$	0 to 2	22 to 26

Introduction

Collisions between electrons and molecules of a gas produce a number of fascinating phenomena. The results of such collisions are far more complicated than those involved in impact between electrons and atoms, for although the direct action of the projectile electron is doubtless upon the electrons of the molecule just as in atomic impact, the subsequent events are much more varied. Provided the pressure is sufficiently low an atom, once excited by impact, has little choice but to lose the energy of excitation by radiation. An excited molecule, on the other hand, may radiate or it may dissociate in a variety of ways. An interesting feature of the dissociating process is that in general the constituents fly apart with considerable velocity.[1] This results from the fact that the electron's action on the molecule is

---

* National Research Fellow.

[1] E. U. Condon, Phys. Rev. **35**, 658 (1930) abstract; W. Bleakney and J. T. Tate, Phys. Rev. **35**, 658 (1930) abstract; W. Bleakney, Phys. Rev. **35**, 1180 (1930).

completed before the constituent atoms have changed much in position (Franck-Condon principle). Thus when dissociation takes place the act of the projectile electron is so to modify the electron configuration of the molecules that the resultant force between atoms is repulsive while the atoms are still close together. The consequent effect of this is that the atoms fly apart and in doing so attain considerable kinetic energy.

A year ago one of us[2] described a method and apparatus[3] which are suitable for a study of these kinetic energies. The method was applied to the study of the dissociation of hydrogen by electron impact. In the case of hydrogen the forces between atoms for various electron configurations have been calculated by quantum mechanical methods so that a comparison with the experimental results was possible. The theoretical predictions were satisfactorily verified.

Unfortunately, for no gas other than hydrogen are the interatomic forces satisfactorily amenable to computation. On the other hand it seems desirable to extend the experimental study to other gases, for, as will be pointed out in this paper, such studies give some information about molecular binding forces and, in some instances at least, a quantitative measure of the heats of dissociation. We present here the results for nitrogen and carbon monoxide.

RELATION BETWEEN ENERGY OF DISSOCIATING PRODUCTS AND THAT OF PRIMARY ELECTRONS

If the energy communicated to the molecule by the electron impact is V_i and if $U_2 - U_1$ is the change in potential energy of the constituent parts of the molecule before and after dissociation, it is readily seen that the energy which appears as kinetic energy of the products of dissociation is

$$V_i - (U_2 - U_1).$$

If the masses of the products of dissociation are equal, as in the case of H_2 or N_2 the kinetic energy of each atom after dissociation will be

$$\tfrac{1}{2}[V_i - (U_2 - U_1)].$$

In general, however, if the masses of the products are not equal the kinetic energy will be divided in the inverse ratio of the masses. Thus, if the masses are m_1 and m_2 the kinetic energy of constituent 1 is

$$\frac{m_2}{m_1 + m_2}[V_i - (U_2 - U_1)].$$

Experimentally we can measure the minimum energy the electrons need to have (V_i) to produce a dissociating product which has the measured energy, V_F. It is evident that the relation between V_F and V_i should be a

---

[2] W. Wallace Lozier, Phys. Rev. **36**, 1285 (1930).

[3] Acknowledgment should be made that the apparatus used in this work was similar to one which had been devised in this laboratory by Mr. T. J. Jones for an unpublished study of the thermal velocities of atomic mercury ions.

linear one, that the slope should be $m_2/(m_1+m_2)$ and that the intercept on the V_i axis is the value of U_2-U_1. The measurements of V_i and V_F may therefore be checked for linearity and for slope and the value of U_2-U_1 be determined by projecting the straight line to the V_i axis.

The quantity U_2-U_1 is of interest because it contains among other things the heat of dissociation of the normal molecule. If the values of the other things entering into U_2-U_1 are known the heat of dissociation may be calculated.

APPARATUS

Some initial studies were made on nitrogen with the apparatus described in the earlier work.[2] These were reported at the Chicago meeting of the American Physical Society.[4] Later the apparatus was extensively remodeled and nitrogen restudied. The results here given were obtained with the new form of apparatus.

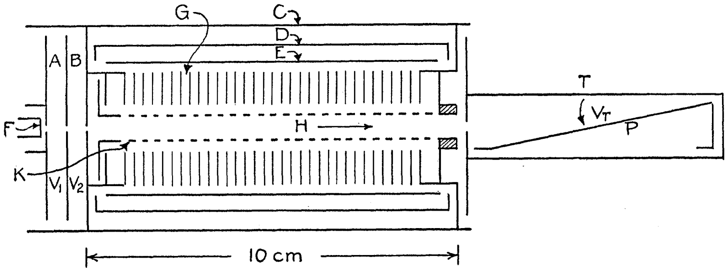

Fig. 1. Diagram of apparatus.

The new form of apparatus is shown in Fig. 1. The metal parts were of copper and were mainly cylindrical in form. The electrons from the filament F were accelerated through the first three holes, passed down the axis of the apparatus and finally entered the electron trap where they were directed by a potential V_T of 190 volts to the collecting plate P. A magnetic field H supplied by a solenoid external to the tube, constrained the electrons to move along the axis of the tube. Surrounding the electron beam was a cylindrical gauze K. Around this was the direction-defining system consisting of a number of thin, cylindrical disks G supported on three slotted bars (not shown). The electrometer collecting cylinder E of diameter 3.5 cm surrounded the disks, and around this were the electrometer guard cylinder D, from which E was supported, and finally the shield C.

The electrons, in traversing their path, ionize the gas and these ions pass through the gauze K. Of these a small portion—those having their direction of motion almost perpendicular to the electron beam—pass through the defining system G and travel toward the cylinder E. A radial electric field was applied between G and E for the purpose of measuring the kinetic energy of the ions. In the study of carbon monoxide, negative ions appeared in numbers great enough to interfere with the study of the energy of the positive ions.

[4] W. Wallace Lozier, Phys. Rev. **37**, 191 (1931) abstract.

Hence, the gauze K was added in order that an electric field might be applied (between G and K) to separate the negative from the positive ions.

The procedure for accelerating the electrons was that used by Smith[5] in a study of ultra-ionization potentials. The source of electrons was a strip of tungsten 1.5 cm long and 1 mm wide stretched across a hole a little less than 1 mm in diameter. In the region A a constant potential of 3.0 volts was applied to accelerate the electrons, while the variable accelerating potential was applied in the region B. With this arrangement the space charge around the filament and the magnitude of the electron current remain independent of the variable accelerating potential across B. The replacement of the slotted cylinder of the earlier apparatus[2] by the system of circular disks increased the intensities about five-fold without any loss in defining power. Finally, the new form of guard ring and the external shielding made the apparatus more free from external disturbances.

The nitrogen was generated by the action of bromine water on ammonia and the carbon monoxide by dropping formic acid into concentrated sulphuric acid. The respective gases were allowed to remain for several hours in contact with a liquid oxygen trap. The gas under study was admitted to the tube through a capillary leak, while the pumps ran continuously. The pressure in the experimental tube ranged from 10^{-5} to 10^{-4} mm Hg.

The ion currents were measured on a Compton electrometer of sensitivity 2300 mm per volt shunted by a high resistance and connected between D and E. Electron currents from 0.5 to 4.0 microamperes were used in the experiments. All the data on each figure have been reduced to the same pressure and electron current.

The initial-velocity correction for the electron current was determined in the studies of nitrogen by comparison with the first mercury ionization potential. In the study of carbon monoxide it was determined with respect to the ionization potential for the formation of CO^+ and hence depends on the correct value of this ionization potential. For reasons to be stated later this was taken to be 14.1 volts.

In the earlier paper[2] it was shown how the magnetic field caused the measured kinetic energy of the ions to be smaller than the true value. For ions as heavy as those of nitrogen and carbon monoxide, and with the smaller radius of the new apparatus, this effect is so small as to be comparable with the normal experimental uncertainties. For nitrogen the magnetic field used was 150 gauss, while that for carbon monoxide was 300 gauss.

PROCEDURE

In the case of each gas, measurements were directed toward the determination of the following: (1) The distribution of kinetic energy among the ions produced by electrons having a specified velocity; (2) The minimum electron energies necessary to produce an ion of specified energy; (3) The relative efficiencies of production of ions having a specified energy as a function of the velocity of the incident electrons.

---

[5] P. T. Smith, Phys. Rev. **37**, 808 (1931).

Energy distribution function of the ions

The energy distribution function of the ions was measured by the method described in the work on hydrogen.[2] For a given electron velocity various retarding potentials were applied between G and E. The change produced in the positive ion current reaching E by varying the retarding potential by a small amount ΔV, was taken to be proportional to the slope of the ion-current vs. retarding-potential curve, i.e., to the ordinate of the energy distribution curve. The minimum electron energies necessary to produce ions of specified energies were measured, as before, by applying a definite retarding potential between G and E and varying the accelerating potential of the electrons.

Efficiencies of production of ions having specified energies

An energy distribution function gives the relative probabilities of the production of ions of different energies for a fixed electron velocity. However, if one fixes his attention on one specified energy of the distribution and plots the corresponding energy distribution ordinate as a function of the electron velocity, there is obtained a curve which shows the manner in which the probability of production of an ion of a specified velocity varies with electron velocities larger than the necessary minimum. As seen from the above discussion this variation of probability could be obtained directly from the energy distribution data for the ions. However, it was determined directly from experiment by measuring the energy distribution ordinate for one specified energy as a function of the incident electron velocity. It is well to point out that all measurements concerning the energy distributions refer to the number of ions contained in a small differential range of energies in the neighborhood of the specified energy.

NITROGEN

Results

In Fig. 2 are shown experimental readings from which the minimum electron energies necessary to produce N^+ ions of specified energy were found. These ions result from dissociation of N_2^+ into $N^+ + N$; the ions were identified as N^+ ions by Vaughan[6] who used the mass spectrograph designed by Bleakney.[7] These readings were taken on the electrometer by the rate-of-charge method. The results are plotted, energies of ions against the minimum electron energies, in Fig. 3 along with another set of determinations taken by the steady deflection method for measuring the positive ion current. In this work the initial velocity correction was determined by using the known ionization potential of mercury. The intercept of Fig. 3 which equals $U_2 - U_1$ has a mean value of 22.9 ± 0.5 volts.

If the curves of Fig. 2 are carried to higher potentials, sharp upward changes of slope occur which are taken to indicate the setting in of new modes of

---

[6] A. L. Vaughan, Phys. Rev. **38**, 1687 (1931).

[7] W. Bleakney, Phys. Rev. **35**, 139 (1930).

dissociation. Fig. 4 shows the relation between the energies of the ions from these dissociation processes and the minimum electron energy necessary to produce them. The results are not very satisfactory, for it is difficult to locate accurately the position of the breaks on the electron velocity scale. Also the reproducibility of results was not very gratifying. But the fact that the points seem to group about two straight lines has an interesting interpretation, and furnishes corroboration for some independent work of Vaughan. The intercepts of these groups were taken as 33 ± 1 and 38 ± 2 volts.

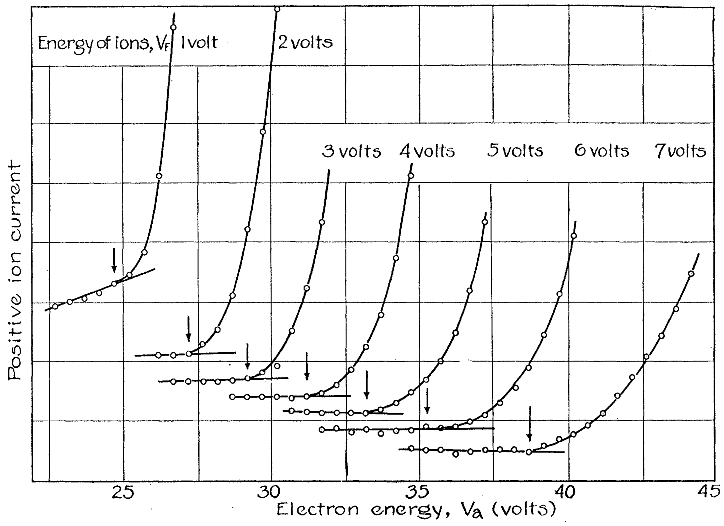

Fig. 2. Curves used to determine the minimum electron energies necessary to produce N^+ ions of different energies.

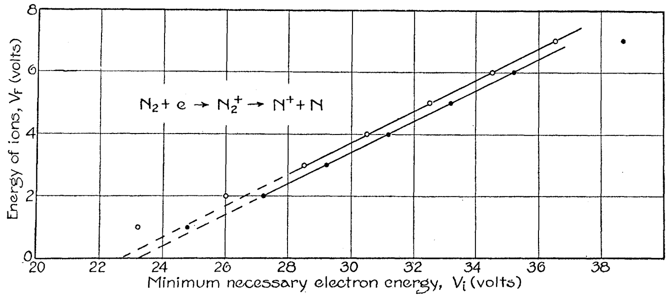

Fig. 3. Results of Fig. 2 (and another determination) plotted to show the energy of N^+ ions V_F as a function of the minimum electron energies V_i necessary to produce them; the slope of the lines has the theoretical value 1/2.

The energy distribution of the ions for various electron energies is shown in the curves of Fig. 5. The common distinctive characteristics of the curves taken at 75 and 85 volts are real and appeared on all curves taken at these potentials. Below 1 volt the N_2^+ ions having the low velocities of temperature agitation begin to mask the curves for the N^+ ions.

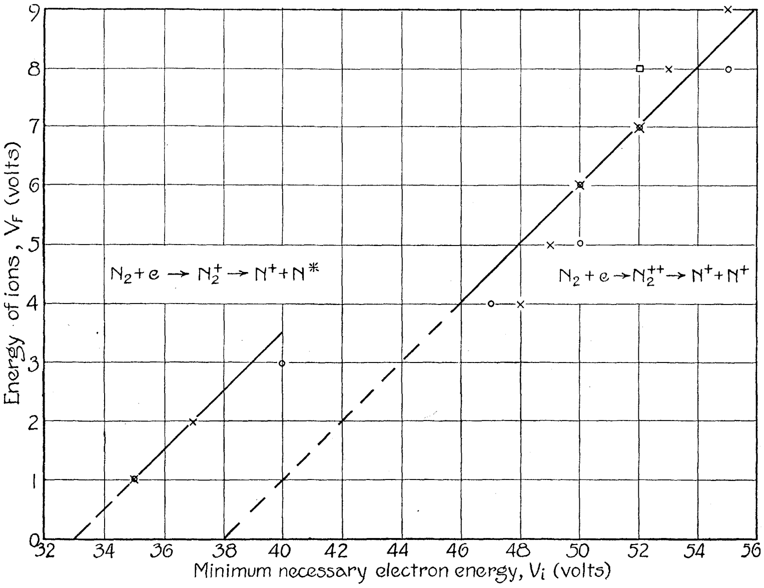

Fig. 4. Energies of N^+ ions plotted against some higher ionization potentials; the slopes are drawn with the theoretical value 1/2.

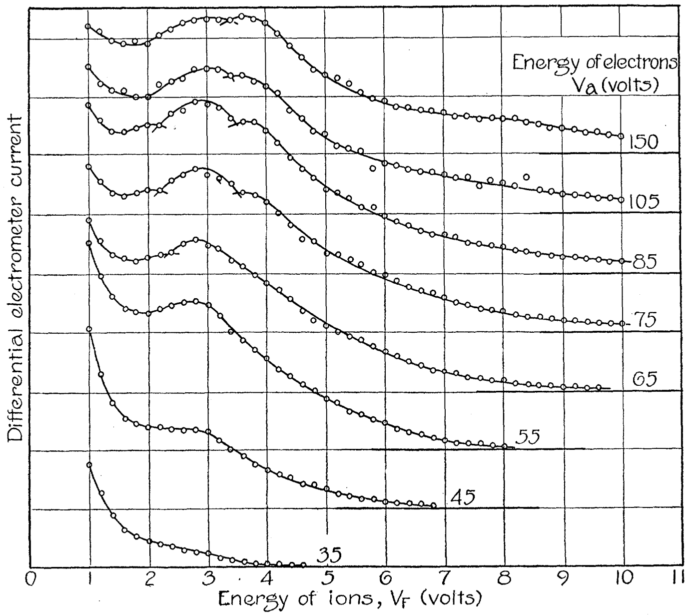

Fig. 5. Energy distribution curves of N^+ ions for various electron energies V_a. The differentiating potential was 0.24 volt.

In Fig. 6 are shown the efficiency curves for the production of ions of various specified energies. An ordinate on one of these curves is proportional to the number of ions lying in a small energy interval (0.24 volt) at the energy given for the curve and shows how this varies with electron voltage.

Some negative ions were present but they were so few in number that it was uncertain whether they were due to nitrogen or to impurities (such as H_2O).

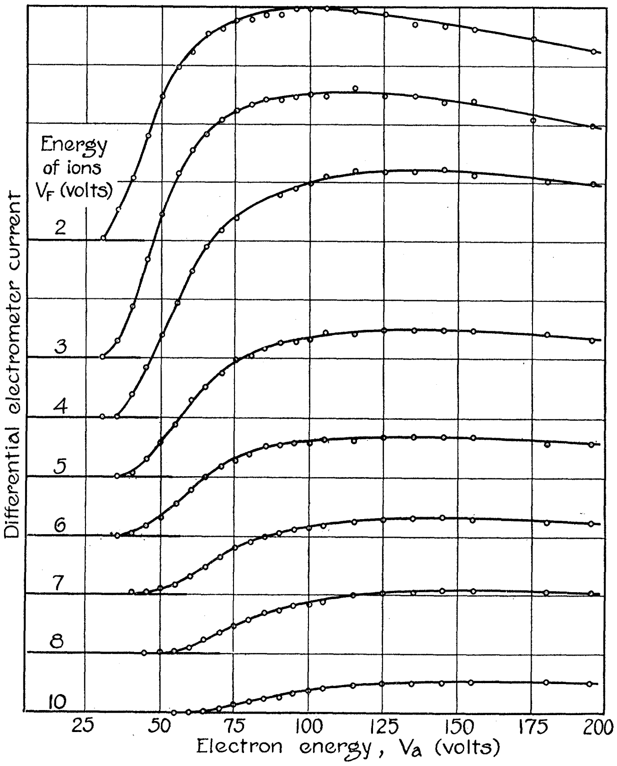

Fig. 6. Curves showing the variation with electron energy V_a of the probability of production of an N^+ ion of specified energy.

In the results reported at the Chicago meeting, the statement was made that above 60 volts electron velocity the N^+ ions exceeded in numbers the N_2^+ ions.[8] This statement has been found to be untrue. The magnetic field is theoretically capable of preventing the collection of ions of nitrogen possessing thermal velocities. But when the pressure was greater than 10^{-4} mm Hg it was found that N_2^+ ions were able to reach the collector even though the magnetic field was 300 gauss. However, with pressures below 10^{-5} mm Hg, the N_2^+ ions were not collected. It is not possible to measure

---

[8] Unfortunately this statement has been quoted by Kallman and Rosen, Phys. Zeits. **32**, 534 (1931).

relative numbers of the molecular and atomic ions with this apparatus. This has been done by Vaughan.[6]

Discussion of results

In Fig. 3 the two sets of data give an intercept differing by only 0.7 volts. The mean, 22.9 volts, has been given an experimental uncertainty of 0.5 volt. This, as has been pointed out, equals U_2-U_1, the increase in potential energy of the molecule, measured before impact and after dissociation. This process undoubtedly represents the dissociation of N_2^+ into $N^+ + N$. Hence U_2-U_1 can be evaluated in two ways. It equals, on the one hand, the heat of dissociation D_m of normal N_2 plus the ionization potential I_A of the nitrogen atom. On the other hand it is not greater than and probably is nearly equal to the sum of the ionization potential I_m for the formation of stable N_2^+ and the heat of dissociation D_I of N_2^+ into $N^+ + N$.

Thus $U_2-U_1=22.9\pm0.5$ volts $=D_m+I_A\leqq I_m+D_I$. From spectroscopy[9] I_A is known to be 14.5 volts; thus $D_m=8.4\pm0.5$ volts. Earlier values obtained from vibrational level extrapolations were as much as 3 volts higher, but these have been revised downward. The latest value given by Birge[10] is 9.1 volts.

Turner and Samson[11] have combined measurements on the excitation potential of the negative bands of N_2^+ with spectroscopic data to obtain a value for I_m+D_I of 22.9 volts, with which our value is in agreement. The analysis made by them is probably correct giving $I_m=15.8$ volts and $D_I=7.1$ volts.[12] Recent work of Vaughan[6] supports this value of 15.8 for I_m.

The range of energies in Fig. 3 for which the observations fall on a straight line appears to extend from about 2 to 7 volts. This probably is related to the shape of the potential energy curve in the Franck-Condon region—the region defined by the range of nuclear separations associated with the normal molecule in its lowest vibration state. This range for the nitrogen molecule covers about 0.1A, which is approximately one-fifth the extent of that for H_2. Invoking the Franck-Condon principle we would expect the potential energy curve to cross the boundaries of the Franck-Condon region approximately 16 and 4 volts above the asymptotic value of 22.9.[13] Considering the narrowness of the region and the range of energies, 16 to 4 volts, traversed by the curve therein, this probably implies, as pointed out by Smyth,[14] that the curve does not have a negative slope at all points; but rather, it may have a minimum at a nuclear separation much greater than that for the normal molecule. In Fig. 4 are observed two groups of ion-energies and

---

[9] H. N. Russell, Astrophys. J. **70,** 16 (1929).

[10] R. T. Birge, Faraday Society, Molecular Spectra and Molecular Structure, p. 713 (1929).

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

[12] Later Birge mentioned some objections to the values of Turner and Samson. R. T. Birge, Phys. Rev. **34,** 1062 (1929).

[13] Vaughan (reference 6) finds that N^+ ions appear at 24.5 ± 9.1 volts. We were not able to determine accurately the potential at which N^+ ions first appeared.

[14] H. D. Smyth, Rev. Mod. Phys. **3,** 372 (1931).

minimum necessary electron energies. The lower group with an intercept value of $U_2-U_1=33\pm1$ volts probably represents dissociation of N_2^+ into N^++N^*, where the energy of excitation of the N atom is 10 ± 1 volts. According to Compton and Boyce[15] there are two groups of metastable levels for the nitrogen atom at 2.37 and 3.56 volts. These lie so close to the energy of normal N that we would not be able to distinguish dissociation to these levels from that to N^++N (22.9 volts). However at 10.3[15] volts a group of quartet P levels appears. This excitation energy agrees very closely with the postulated excitation energy of the process given above. The range of energies of the ions formed is very narrow 1 to 2 volts which would indicate that to bring the normal atom and the 10 volt excited atom to within about 1.0A of each other does not require an energy expenditure of more than about 4 volts. This would indicate that the potential energy curve is quite flat.

When the energy of the impacting electron is great enough to remove an electron from each nitrogen atom any dissociation into N^++N^+ should be detected because of the registration of both products of dissociation on the electrical apparatus. This is in all probability the process represented by the higher velocity group of Fig. 4. The value of U_2-U_1 for this process should be $22.9+14.5=37.14$ volts which agrees with the experimental value of the intercept, 38 ± 2 volts. The range of energies of the ions extends from about 4 to 8 volts. As a first approximation the potential energy curve might be represented by the Coulomb repulsion curve e^2/r. If one draws this curve, he finds it crosses the Franck-Condon region 12 volts above the asymptotic energy. This would yield N^+ ions of 6 volts energy. It is interesting to note that this is approximately the center of the observed range.

Finally, Vaughan,[6] in his study of nitrogen, found two upward breaks in the efficiency curve for N^+ ions. These occurred at 40 ± 1 and 47 ± 1 volts electron energy. From our discussion above we would suspect the two potential energy curves last discussed to cross the Franck-Condon region 35 to 37 volts and 46 to 54 volts above the normal molecular state. The figures given by Vaughan are close to these two regions.

The energy distributions in Fig. 5 present nothing essentially new except the peculiar structure of the curves for electron velocities of 65 and 85 volts. Three distinct groups of ions appear to be present which probably result from the three processes of dissociation discussed above. The lower energy group at about 2 volts would be correlated with the dissociation products N^++N^*, the next group at 3 volts with N^++N, and the last at 4 volts with N^++N^+. The trailing out of the curves of Fig. 5 to higher energies is probably to be correlated with the multitude of dissociation products possible at higher electron velocities.

The efficiency curves of Fig. 6 bear a general resemblance to those for the probability of ionization of various atomic gases by electron impact, although our curves do not decrease so rapidly at higher voltages. As yet no satisfactory theoretical interpretation has been given to these curves.

---

[15] K. T. Compton and J. C. Boyce, Phys. Rev. **33**, 145 (1929).

Carbon Monoxide

Both positive and negative ions are formed by electron impact in carbon monoxide. In order to be able to study satisfactorily the processes of their formation the gauze *K*, Fig. 1, was introduced. By applying to *K* a suitable potential the passage of either positive or negative ions through the slit system could be prevented.

Positive ions of carbon monoxide. Results

In Fig. 7 are plotted experimental curves from which the minimum electron energies necessary to produce positive ions of specified energy were determined. These ions were identified by Vaughan[6] as C^+ and most likely result from dissociation of CO^+ into $C^+ + O$. In the inset are shown the readings used in determining the electron voltage correction where the ionization current is due to CO^+.

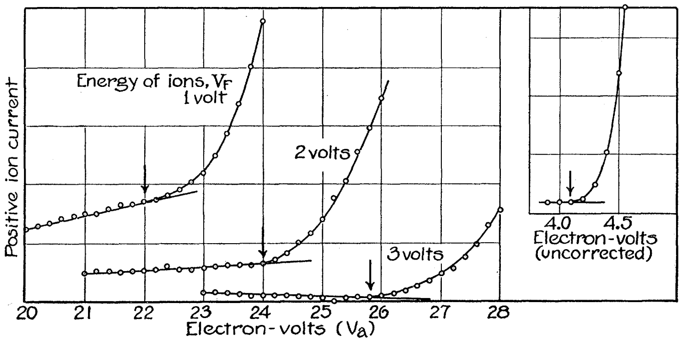

Fig. 7. Curves used to determine the minimum electron energies necessary to produce C^+ ions of different energies.

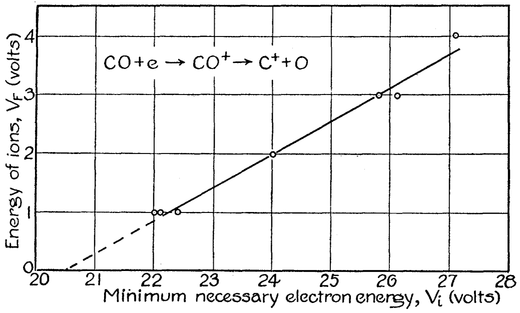

Fig. 8. Energies of C^+ ions plotted against the minimum electron energies necessary to produce them; the slope is drawn with the theoretical value 4/7.

Fig. 8 is a plot of the relation between the energy of the C^+ ions and the minimum energy of the electrons necessary to produce them. The solid line is drawn with the slope 4/7 which is the value appropriate to the C^+ ions from CO. The intercept on the axis of abscissas is taken as 20.5 ± 0.5 volts.

In Fig. 9 are shown the energy distribution curves for the positive ions. The differentiating potential is 0.30 volts. The curves showing the efficiencies of formation of ions of various specified energies as a function of electron velocities are shown in Fig. 10.

Discussion of results

As already noted the value of $U_2 - U_1$ taken from Fig. 8 is 20.5 volts. This value rests upon the assumption that the ionization potential of CO^+ is 14.1 volts. This is usually taken to be 14.2 volts but recent work of Vaughan[6] indicates that it should be lower than this, probably 13.9 ± 0.2 volts. The mean of these, 14.1 volts, certainly is not far wrong. Regardless, however, of the correct value for I_m (the ionization potential of the CO molecule) it is clear that in Fig. 8 we have measured correctly the difference between $U_2 - U_1$ and I_m and found it to be 6.4 volts. From the relation $U_2 - U_1 \leqq I_m + D_I$ it follows that the heat of dissociation of the CO^+ ion is not less than 6.4 volts. The value given by Birge and Sponer[9] is 9.8 volts which they obtained by a rather uncertain extrapolation of vibration levels. If we assume that $U_2 - U_1$ is 20.5 volts and that the ionization potential of the carbon atom is 11.2 volts we obtain from the relation $U_2 - U_1 = I_A + D_m$ a value of 9.3 ± 0.5 volts for the heat of dissociation of the CO molecule. This is again much

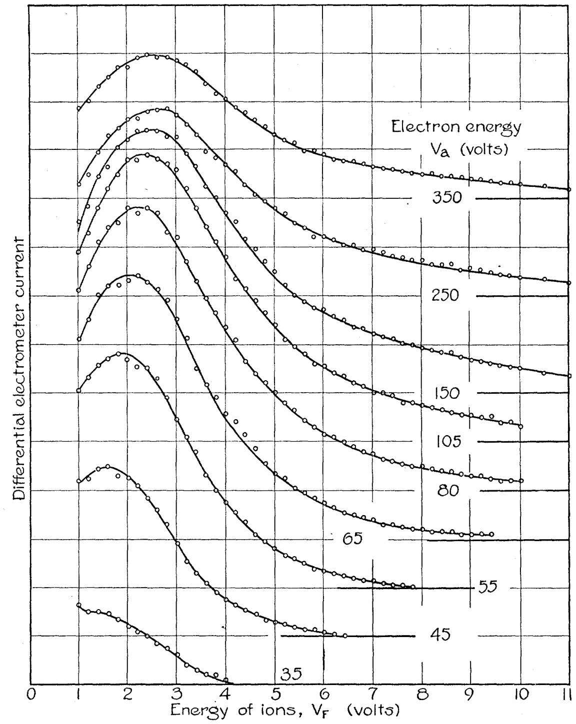

Fig. 9. Energy distribution curves of C^+ ions for various electron energies V_a; the differentiating potential was 0.30 volt.

lower than the value 10.3 volts given by Birge.[16] If his calculation is revised by introducing a more recent value of the heat of dissociation of O_2, the heat of dissociation of CO comes out to be 8.9 volts, a value which is in fair agreement with our own.

The energy distribution curves of Fig. 9 are without any peculiar structure in agreement with the observation that no higher ionization potentials (as in Fig. 4 for N_2) were observed. The narrowness of the distribution is in agreement with the narrow range of the straight line of Fig. 8, namely energies from 1 to 4 volts. This probably can be correlated with the narrow Franck-Condon region (less than 0.1A). Here again it is impossible to state whether the slope of the potential energy curve is everywhere negative or whether the curve has a minimum to the right of the Franck-Condon region. The efficiency curves of Fig. 10 are very similar to those of Fig. 6.

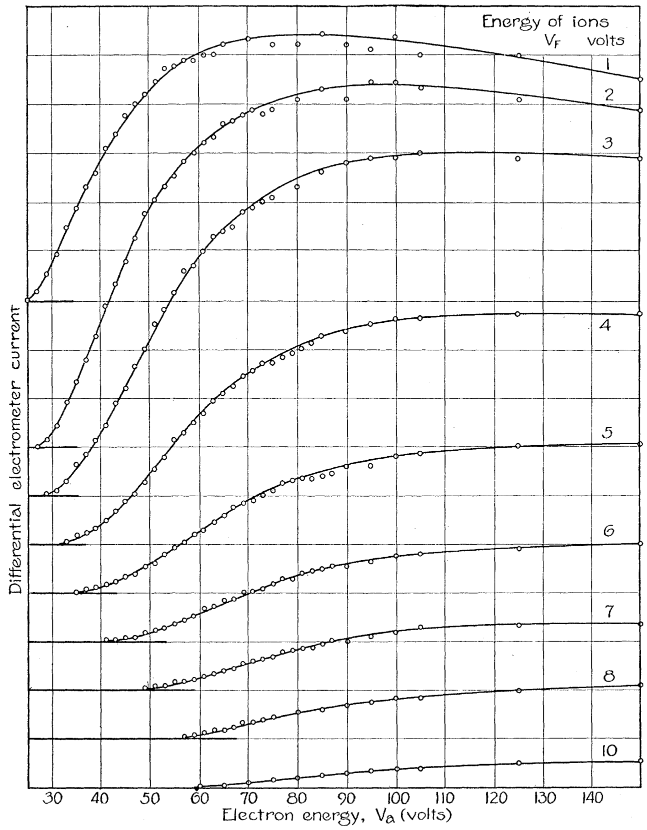

Fig. 10. Curves showing the variation with electron energy V_a, of the probability of production of a C^+ ion of a specified energy.

Negative ions in carbon monoxide. Results

When an electric field was placed between *K* and *G* (Fig. 1), sufficient to keep positive ions from being collected, a negative current was registered on

---

[16] R. T. Birge, Phys. Rev. **28**, 277 (1926).

the electrometer. This negative current as a function of the electron energy is shown in Fig. 11. The trailing off on the low velocity side is probably due to negative ions from water vapor.[17] An attempt was made to measure the kinetic energies of the two groups of ions. The electron velocity of maximum

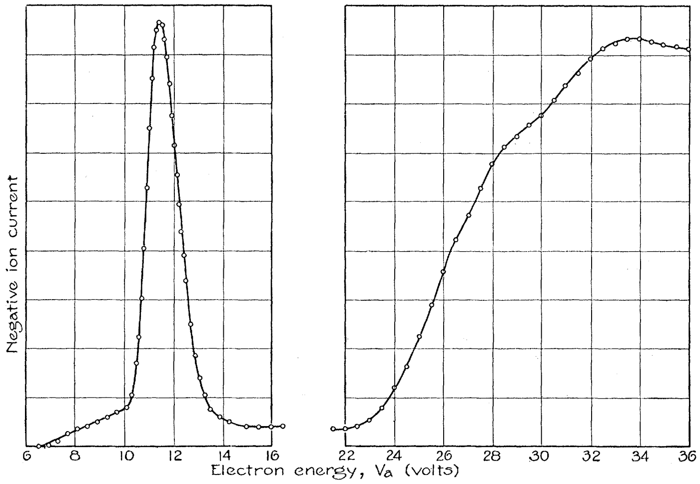

Fig. 11. Curves showing observed O^- current as a function of electron energy V_a.

efficiency in producing the low velocity group was 11.4 ± 0.3 volts. At this velocity the most probable energy possessed by the ions was about 0.4 volt and the maximum energy they had was about 0.9 volt. The negative ions of

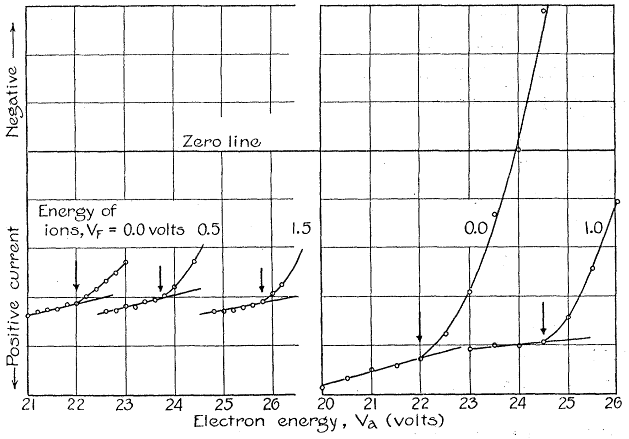

Fig. 12. Curves used in determining the minimum electron energies necessary to produce O^- ions of various energies. The current below the line is positive and is discussed in the text.

the second group, appearing at 22 volts electron energy were found to possess kinetic energy and we succeeded in getting values for the minimum electron velocities necessary to produce negative ions of specified energies. These readings are shown in Fig. 12. The currents were small and were measured by the rate-of-deflection method. There is a background to the current which is due partly to the leak of the electrometer system and partly to another cause, mentioned later. The results of Fig. 12 are shown plotted in Fig. 13. The straight line has an intercept of 22.2 ± 0.5 volts.

Discussion of results

These negative ions were also observed by Vaughan[6] and definitely identified as O^-. The narrow group of Fig. 11 can very likely be considered as similar to those H^- ions found by one of us in some earlier work[17] and later observed by Smyth and Mueller.[18] The process of formation is probably represented by $CO+e \rightarrow CO^- \rightarrow C+O^-$. If this be correct, at the voltage of maximum efficiency (11.4 ± 0.3) the O^- ion has a maximum energy of 0.9 volt and thus the C atom and the O^- ion would possess a total kinetic enrgy of $7/3 \times 0.9 = 2.1$ volts. This would mean that the energy of the dissociated system $C+O^-$ lies 9.3 ± 0.3 volts above normal CO and 0.5 volt below $C+O$ (9.8 volts). This allows only 0.5 volt for the electron affinity of O if the C atom and the O^- ion are unexcited. Trustworthy values are not known for the affinity of O for an electron. Senftleben[19] gives a value of 8.9 volts and Grimm[20] gives 6 volts. When one considers the processes involved in getting these values, their reliability becomes very questionable. If one takes the iso-electronic sequence of F I and Ne II and plots the square root of the ionization potential against the atomic numbr and extrapolates this to atomic number 8, he obtains an oxygen electron affinity of 3.2 volts. The reliability of this, too, is questionable.[21] It is entirely possible, of course, that one or both of the products of dissociation are excited. In that case the electron affinity would be 0.5 volt plus whatever the excitation energy turned out to be. The C atom has a ^1D level 1.3 volts above the ground state and another, the ^1S, lying 2.7 volts above normal C.[22]

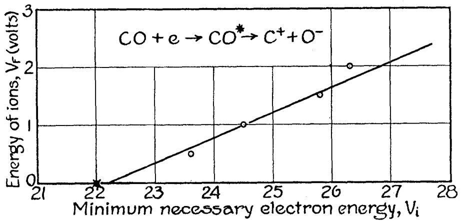

Fig. 13. Energies of O^- ions plotted against the minimum electron energy necessary to produce them; the slope has been given the theoretical value 3/7.

---

[17] W. Wallace Lozier, Phys. Rev. **36,** 1417 (1930).

[18] D. W. Mueller and H. D. Smyth, Paper 11, Program of Schenectady Meeting of American Physical Society, September 11, 1931.

[19] H. G. Grimm, Zeits. f. Elektrochem. **31,** 474 (1925).

[20] H. Senftleben, Zeits. f. Physik **37,** 539 (1926).

[21] This method gives chlorine an electron affinity of 5.4 volts to compare with 5.0 and 4.8 volts quoted by Foote and Mohler, Origin of Spectra, p. 179.,

[22] Paschen u. Krueger, Ann. d. Physik **7,** 1 (1930).

The narrow range of electron velocities involved in this group certainly leads one to suspect a capture of an electron by the neutral molecule. For if the impacting electron strikes the molecule, and loses all its energy, it is at rest with respect to the molecule and conditions are favorable for the capture of the impacting electron. Another fact which points to the correctness of this explanation is the observation that no positive ions were formed below 14.0 volts. Therefore, the charge on the O^- ions necessarily comes from some source external to the original molecule.

The O^- ions appearing at 22 volts possess considerably more kinetic energy than the group just discussed. The dissociation products are probably C^+ and O^-. The peculiar shape of the efficiency curve in the neighborhood of 30 volts is real—this has been checked by Vaughan and probably is indicative of another process, perhaps dissociation products of different degrees of excitation. The straight line in Fig. 13 has been drawn with the proper slope for O^- ions (3/7) and fits the experimental points fairly well. If the dissociation products are unexcited C^+ and O^-, we would expect a value of U_2-U_1 less than that for C^++O by the electron affinity of oxygen. It comes out 1.7 volts higher, a fact which indicates that the products of the dissociation must be excited. If we take the value of 3.2 volts for the electron affinity of O we would have excitation energy of amount 4.8 volts. The ground state of C^+ consists of a close doublet. The next known level of C^+ according to Grotrian[23] lies 9.2 volts above this. Thus, we have no knowledge of how to account for the energy of excitation of the products.

It is well to point out, that all current below the zero line in Fig. 12 is a positive current. One can see from the arrangement of the electric fields that these positive ions must have been formed in the region exterior to the defining system *G*. This effect has earlier been observed by Liska at the University of Minnesota and is under investigation now.

In conclusion we acknowledge our gratitude to Professor R. S. Mulliken, Professor A. G. Shenstone, Dr. P. T. Smith and Dr. J. E. Boyce for their helpful discussions and kindness in locating for us spectroscopic data. Also we are indebted to the Graduate School of the University of Minnesota for financial assistance during a part of this work.

---

[23] W. Grotrian, Handbuch d. Astrophysik, Band III, Zweite halfte, p. 574.