The Heat of Dissociation of CO and the Electron Affinity of O

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An apparatus previously described has been employed in a study of the dissociation produced by primary electron impact in CO and O_2. The processes studied in O_2 are $O_2^- \rightarrow O^- + O$ at 2.9 v and $O_2^- \rightarrow O^- + O^*$ at 12.0 v with an estimated accuracy of ±0.2 v. These figures refer to the potential energy of the dissociation products, the normal molecule considered as zero. These results give two values of E_0, the electron affinity of the oxygen atom, both equal to 2.2±0.2 v. The processes studied in CO are $CO^- \rightarrow C + O^-$ at 9.5 v, $CO \rightarrow C^+ + O^-$ at 20.9 v, and $CO^+ \rightarrow C^+ + O$ at 22.8 v, with an estimated accuracy of ±0.1 v. It is concluded that $D(CO)$ may have one of two possible values, 9.6±0.1 or 11.6±0.1 v. These experiments are unable to decide between the two but most of the evidence from other sources points to the lower value. If $D(CO) = 9.6$ v we must admit the possibility of stable excited O^- ions. However, if $D(CO) = 11.6$ v, these experiments on CO give two values of E_0, 1.9 and 2.1 v. The processes involved in the formation of negative ions by electron impact are discussed.

INTRODUCTION

When an electron suffers an impact with a gas molecule the phenomena which may be exhibited are many and varied. Especially interesting are those phenomena in which the molecule after impact manifests ionization. This paper will deal with certain aspects of ionization in diatomic gases. Numerous mass-spectrograph studies[1] have shown that the most probable type of ionization by electron impact in diatomic gases is the removal of one electron from the molecule. Next in probability is the formation of atomic ions, positively charged. In recent years a distinctly different product of ionization has been observed—namely, the negative atomic ion.[2, 3, 4, 5, 6] This product is far less abundant than the products of simple ionization and dissociation with ionization.

Another new aspect of ionization phenomena is the observation of atomic ions with large kinetic energies (several volts). Such processes were studied by Bleakney[7] in H_2 and later by the author and others[4, 8, 9, 10] in H_2, N_2 and CO. They give important information on the molecular binding in different electronic states. A description of improved apparatus and revised results in H_2 and N_2 has recently been published.[10] This paper describes similar results in O_2 and CO.

The specific relation between the maximum kinetic energy of the ions formed and the electron energy may be repeated here for future reference.[4] If a molecule is put into an unstable state by the communication of potential energy V_i, and subsequently dissociates into two parts of masses m_1 and m_2, the kinetic energy of constituent 1 is given by

$$(\text{K.E.})_1 = [m_2/(m_1+m_2)][V_i - (U_2 - U_1)], \quad (1)$$

where U_1 is the potential energy of the molecule before impact and U_2 is the potential energy of the dissociated constituents of the molecule. This relation is a linear one with the slope determined by the ratio of the masses of the dissociating partners. The quantities measured experimentally are V_i (the appearance potential) and the kinetic energy of the ions; from these we calculate $U_2 - U_1$. Two procedures are available for this determination. One is to plot the kinetic energies of the ions against V_i and extrapolate the straight line to zero kinetic energy, at which point $V_i = U_2 - U_1$. The other is to substitute the experimental quantities into Eq. (1), by using the proper mass ratio, and solve for $U_2 - U_1$. Both procedures are used in the following report.

APPARATUS

Without repeating the description of the apparatus[10] we may recall that the ionization cur-

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* The experimental part of this work was done while the writer was a National Research Fellow.

[1] H. D. Smyth, Rev. Mod. Phys. **3**, 347 (1931).

[2] W. W. Lozier and Walker Bleakney, Phys. Rev. **36**, 1417L (1930).

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

[4] J. T. Tate and W. W. Lozier, Phys. Rev. **39**, 254 (1932).

[5] J. T. Tate and P. T. Smith, Phys. Rev. **39**, 270 (1932).

[6] H. D. Smyth and D. W. Mueller, Phys. Rev. **43**, 116 (1933).

[7] Walker Bleakney, Phys. Rev. **35**, 1180 (1930).

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

[9] W. W. Lozier, Phys. Rev. **43**, 776A (1933).

[10] W. W. Lozier, Phys. Rev. **44**, 575 (1933).

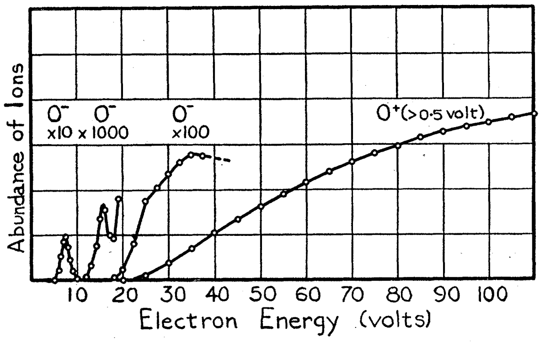

FIG. 1. Products of ionization of O_2, O_2^+ not included here.

rent reaching a collector is measured as a function of either the energy of the bombarding electrons or the potential retarding the ions. Letters used in the detailed description of procedure below refer to Fig. 1 of reference 10.

The CO was generated by the action of formic acid on sulphuric acid and dried by liquid air. The O_2 was prepared electrolytically, and dried by P_2O_5. As before the rate of flow method was used for the admission of the gas into the tube. The gas pressure in the experimental chamber was maintained between 5×10^{-5} and 1×10^{-5} mm Hg.

RESULTS ON OXYGEN

Fig. 1 depicts, with the exception of O_2^+, the ionization products of electron bombardment of O_2 and gives a rough estimate of their relative numbers. The identification of the first and third groups (O^-) has been made by Bleakney.[11] The fourth group (O^+) has been observed in all mass-spectrograph investigations[1] of O_2. The second group of O^- ions at 15 v has not been identified or observed elsewhere but the data to be given almost certainly identify it as O^-. The first two groups of negative ions have been analyzed as regards their kinetic energy. The electron voltage scale was fixed by assuming the ionization potential[12] of O_2 as 12.5 v.

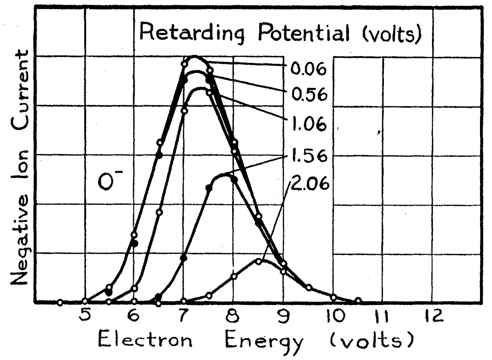

FIG. 2. O^- ionization curves in O_2 for different retarding potentials.

Let us consider first the group of O^- ions at 7.2 v. Fig. 2 illustrates the change with retarding potential of the O^- current *vs.* electron energy curves. These curves show no ions having energies below about one volt. Greater retarding potentials stop first the ions formed at low electron energies. The fact that the curves merge at high electron energies means that not only are high speed electrons necessary to form high speed ions but they form only high speed ions. Fig. 3 shows a plot of the kinetic energies of these ions against their appearance potentials. For kinetic energies greater than 1.3 v the curve obeys the requirements of Eq. (1), i.e., a linear relation with slope 0.5. A projection of this straight line to zero kinetic energy requires $U_2-U_1=2.9$ v.

In Fig. 4 are shown curves of the negative ions at 15 v electron energy. As mentioned above these ions have not been observed elsewhere and consequently have not been identified definitely as O^-. But the fact that they can possess kinetic energies

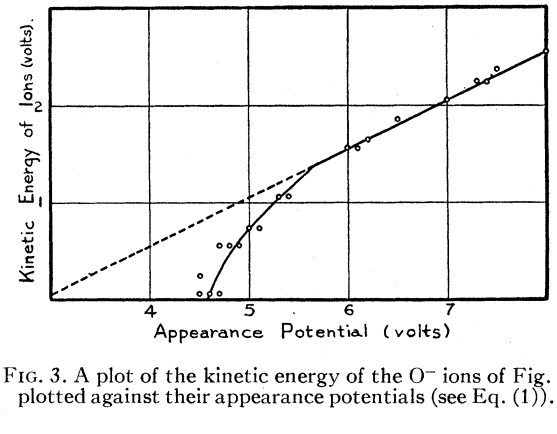

FIG. 3. A plot of the kinetic energy of the O^- ions of Fig. 2 plotted against their appearance potentials (see Eq. (1)).

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[11] Dr. Walker Bleakney very kindly analyzed a sample of the O_2 used.

[12] R. S. Mulliken and D. S. Stevens, Phys. Rev. **44**, 720 (1933) have calculated the I.P. of O_2 as 12.2 ± 0.2 v and cited reasons why the experimental values should be higher. Since our experimental conditions more nearly approximate those of reference 5, we use the older value and allow a greater probable error, ±0.2 v, to these measurements.

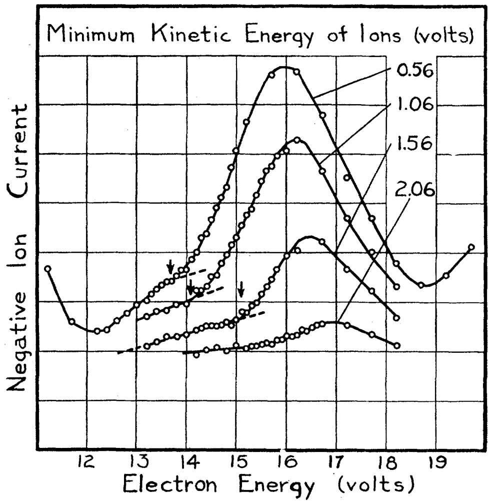

FIG. 4. O^- ionization curves in O_2 for different retarding potentials.

of as much as 2 v makes it almost necessary that the origin of this kinetic energy is a dissociation of the molecule into an atomic ion and a neutral atom. This ion being negatively charged must be O^- if it results from O_2. The possibility remains that it results from impurities. Our strongest evidence against this is that of all the other gases studied, none have negative ions at this electron energy. In lieu of any evidence to the contrary we shall designate this ion as O^- resulting from O_2.

It is difficult to obtain a test of Eq. (1) from the curves of Fig. 4. The upper curve shows traces of an unresolved peak on the low electron energy side of the main group, making impossible a precise determination of the appearance potential. The next two curves have determinable appearance potentials separated by 1 v which satisfies the condition that the linear relation of Eq. (1) must have a slope of 0.5. The smallness of the ion current in the lower curve prevents the determination of the appearance potential. On inserting the two observable appearance potentials in Eq. (1) there results $U_2-U_1=12.0$ v.

No data are presented on the other groups of ions shown in Fig. 1. For above 20 v electron energy it was impossible to obtain a condition of zero current to the collecting electrode in spite of a field arrangement suitable for keeping away all ions formed at the electron beam. This effect is probably associated with the photoelectric effect of excited gas molecules on the electrodes and is certainly due to the O_2 because of its nonexistence in the other gases studied.

DISCUSSION OF RESULTS ON OXYGEN

We have observed two groups of O^- ions whose kinetic energies satisfy the requirements of Eq. (1) and therefore result from dissociation of O_2^- into O^- and O. U_2-U_1 for these two groups are, respectively, 2.9 and 12.0 v. In neither of these cases do we know the state of excitation of the dissociation products. We know that U_2-U_1 for dissociation into normal atoms, i.e., $O(^3P)+O(^3P)$ is 5.1 v. Thus from the first group of negative ions E_0, the electron affinity of the oxygen atom, is equal to $(5.1-2.9)$ v plus the excitation energy of the O and O^-.

Thus E_0 is ≥ 2.2 v. The neutral atom is probably unexcited for if it were in even the first excited state (^1D), E_0 would be ≥ 4.2 v. A plot of the square root of the ionization potential *vs.* atomic number curve for the proper series (FI, Ne II) gives E_0 as 3 to 4 volts and these curves, in all cases where the electron affinity is known, give too large a value. The O^- is very probably in a normal state for general considerations make it improbable that a negative ion will have many stable excited states. If such states exist they probably lie very near the ionization limit and this coupled with the 2.2 v binding energy mentioned above would call for a very large electron affinity, $E_0 \gg 2.2$ v.

Very little is known of the energy states of negative ions. However, the following examples support our contentions that stable excited states are scarce. The empirical data on the energy of the $1s2p\,^1P^0$ state of two electron systems can be fitted to a power series in Z, the atomic number $aZ^2+bZ+\cdots$. On extrapolating to $Z=1$, we find this state is unstable for H^- (by about 0.3 v).

Likewise, Fermi[13] has made a rough calculation of the electron affinity of the iodine atom using the Fermi-Thomas atomic field. He finds a stable normal state but only unstable excited states of I^-.

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[13] E. Fermi, Leipziger Vorträge, 109 (1928).

This scarcity of stable states of negative ions is undoubtedly due to the extremely rapid decrease of the atomic field outside the extranuclear electron cloud where the nuclear charge is very completely shielded. The above discussion[14] is no assurance of the non-existence of stable excited states; but it is probable that such states will lie near the continuum, i.e., they will not be very stable.

Proceeding to a discussion of the second group of O^- ions with $U_2 - U_1 = 12.0$ v, we point out that the lower portion of the energy level system of OI is well separated[15] with ^3P at 0.0 v, ^1D at 1.96 v, ^1S at 4.17 v, $^5S^0$ at 9.10 v and $^3S^0$ at 9.47 v. The identification of the neutral atom as any of the first three excited states is improbable because it would require the O^- ion to possess more potential energy than normal O. The next possibility is that the neutral atom is in the $^5S^0$ state which would make $E_0 = 2.2$ v plus any excitation energy of the O^- ion. For the same reasons as given above we assume the O^- is unexcited. This is exactly the same value for E_0 as we obtained before. Having made the identification of the neutral partner as $O(^5S^0)$ we can say the dissociation products $O(^1D$ and $^1S)$ would be concealed by the 7.2 v peak.

Results on Carbon Monoxide

A general idea of the types of ions and their relative abundance is shown in Fig. 5 as a function of the incident electron energy. The CO^+ curve was not determined in this work but was taken from that of Vaughan.[3] In the following discussion we shall consider in detail the different ions shown here. The absence of O^+ ions is confirmed by the work of Vaughan.

Let us consider first the group of O^- ions having their efficiency maximum at an electron energy of about 10 v. The identification of the ions was made by Vaughan[3] and they have been observed by others.[4, 5, 9] Fig. 6 shows this same current as a function of electron energy for different retarding potentials on the ions. The electron voltage scale was corrected by the observation of CO^+ ionization, which is known to appear at 14.1 v.[1, 5] Fig. 7 shows the complete curves for which Fig. 6 gives the initial portions.

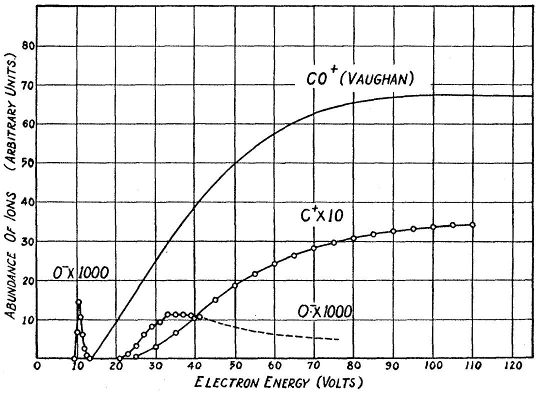

FIG. 5. Products of ionization of CO, with their relative numbers, as a function of electron energy.

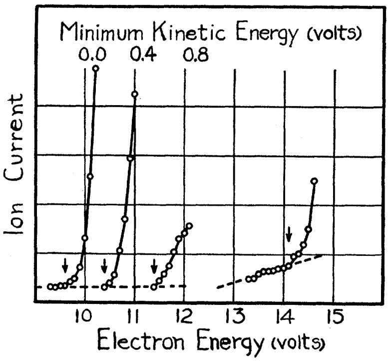

FIG. 6. Curves showing onset of O^- ionization in CO for different retarding potentials.

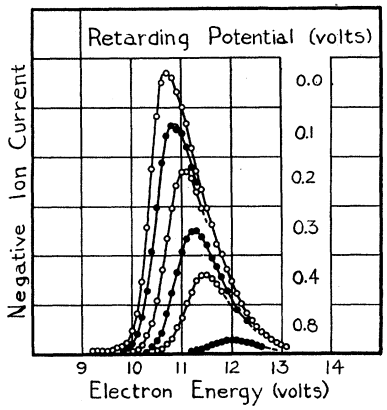

FIG. 7. Curves showing O^- ionization in CO for different retarding potentials.

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[14] O. Oldenberg, Phys. Rev. **43**, 534 (1933). See especially footnote 9 there.

[15] All atomic energy values are from Bacher and Goudsmit, *Atomic Energy States*, McGraw-Hill (1932).

These curves bear some similarity to those of Fig. 2—namely, they merge at higher electron energies. However in CO, the O^- ions have kinetic energies lying between zero and one volt; while in O_2 no O^- ions have less than $\sim$1.3 volts energy.

Using Eq. (1) and the data of Fig. 6 we find for U_2-U_1 the values 9.6, 9.5 and 9.5 volts. The constancy of these figures shows that the data satisfy the linear requirements of Eq. (1). Thus 9.5 v represents the potential energy of the dissociated system $C+O^-$ measured from normal CO.

We shall next consider in detail the C^+ and O^- ionization shown in Fig. 5 occurring at about 20 v electron energy. In the earlier work it was suspected that this O^- ionization resulted from dissociation of CO into C^+ and O^-. The obvious test of this hypothesis is that the C^+ and O^- should appear at the same electron energy and occur in equal numbers. The results of this test are shown in Figs. 8 and 9.

To obtain the data shown in Fig. 8 the C^+ and O^- ions were separated by the following procedure. To observe the C^+ ionization a potential of 10 v retarding O^- ions was applied to the interval $L-M$ (see reference 10, Fig. 1) and a potential of 10.57 v retarding C^+ ions was placed on the interval $O-L$, the net effect being the collection of C^+ ions having energies greater than 0.57 v. To record the O^- current the potentials were reversed and the net potential retarding O^- ions was made 0.43 v. These energies 0.57 (C^+) and 0.43 (O^-) are in the ratio 4 to 3, the inverse ratio of the masses; so that, in accordance with the law of conservation of momentum, when all C^+ ions having energies >0.57 v are collected, all their dissociation partners (O^-) will be able to traverse a retarding potential of 0.43 v. The total minimum kinetic energy associated with the two ions is 1.0 v. Fig. 8 illustrates the behavior of C^+ and O^- current subject to the conditions described above, the lower curve shows the difference C^+-O^-. From an electron energy of 22.0 to 23.8 v the C^+ and O^- occur in equal numbers indicating that the O^- results from a splitting of the CO molecule in C^+ and O^-. At 23.8 v a new process contributes to the formation of positive ions. This process has a much greater probability than the splitting process. Fig. 9 shows the difference current C^+-O^- for higher retarding potentials subject to the same conditions as in Fig. 8. As in Fig. 8 the curves are characterized by the equality of C^+ and O^- ionization up to the indicated potentials, where the excess positive ionization occurs. The appearance potential of this ionization shifts by 1 v in successive curves. This likewise is the increment of ion kinetic energy between successive curves assuming the positive ionization is due to C^+. The equality of these increments verifies the identification of this positive ionization as C^+. Use of Eq. (1) yields U_2-U_1 as 20.9 v for the equal C^+ and O^- ionization and U_2-U_1 as 22.8 v for the excess positive ionization.

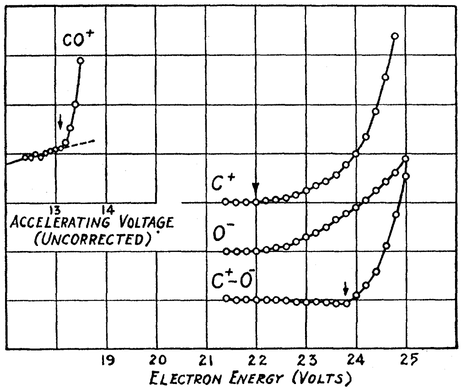

FIG. 8. Curves showing the equality of the initial portions of the C^+ and O^- ionization curves, suggesting splitting of CO into C^+ and O^-.

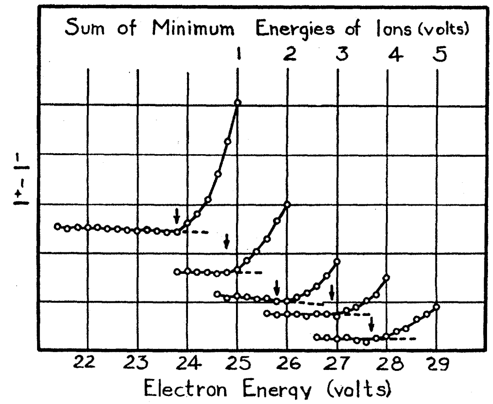

FIG. 9. Curves of difference between C^+ and O^- ionization for retarding potentials higher than in Fig. 8. The numbers at the top refer to the curves which terminate immediately below.

Independent evidence for the correctness of our identification of these latter ions comes from the work of Vaughan.[3] His mass-spectrograph studies of CO showed the appearance of the main part of the C^+ ionization at 22.5±0.1 v. However, his C^+ curves[16] show current, which he attributed to imperfect resolution of H_2O^+ and C^+, persisting down to about 20.5 v electron energy. We believe this current is due to the C^+ ions associated with the O^- ions occurring at 20.9 v. The failure of Vaughan[3] to observe O^+ ionization agrees with our identification of the ionization beginning at 22.8 v as due to the dissociation of CO^+ into $C^+ + O$.

Discussion of Results on CO

To summarize our findings we may say that the potential energies of the dissociation products are as follows: $C+O^-$ at 9.5 v, $C^+ + O^-$ at 20.9 v, and $C^+ + O$ at 22.8 v. These values are believed accurate to ±0.1 v. Since our experiments can tell us nothing concerning the state of excitation of these dissociation products, we must have recourse to independent information. If we can make the proper identification we can calculate $D(\mathrm{CO})$ and obtain information concerning E_0, the electron affinity of the oxygen atom.

In the following it will be shown that there are two interpretations between which we cannot discriminate with certainty. The first of these is based on the assumption of normal dissociation products for the system $C^+ + O$ at 22.8 v. This requires $D(\mathrm{CO})$ to be 11.6 v. We note that the products $C^+ + O^-$ lie below $C^+ + O$ by 1.9 v while $C+O^-$ lie below $C+O$ by 2.1 v. These figures 1.9 and 2.1 v would then be interpreted as the affinity of O for an electron. These values are in agreement with the value 2.2±0.2 v obtained from the results on O_2.

The other interpretation is based on the assumption that the dissociation products $C^+ + O$ at 22.8 v are excited. Possible identifications and the consequent values of $D(\mathrm{CO})$ are given below.

C^+	O	$D(\mathrm{CO})$
^2P	^1D	9.6 v
^2P	^1S	7.4
^4P	^3P	6.4

Of these, the last two are unreasonably low. The first is in good agreement with the hitherto accepted value of $D(\mathrm{CO})$. This value, 9.8 v, is obtained from the following equations:

$$\begin{array}{rl} O \rightarrow \tfrac{1}{2}O_2 & -2.55\ \mathrm{v}^{17} \\ C\underset{\mathrm{gas}}{\rightarrow}C_{\mathrm{solid}} & -6.1^{18} \\ C_{\mathrm{solid}} + \tfrac{1}{2}O_2 \rightarrow CO & -1.14^{19} \\ \hline C_{\mathrm{gas}} + O \rightarrow CO & -9.8\ \mathrm{v}.^{20} \end{array}$$

The 0.2 v difference could be ascribed to errors in the thermochemical data, especially the heat of sublimation of carbon.

The interpretation of other results of this paper are more involved for $D(\mathrm{CO}) = 9.6$ v than for 11.6 v. We have observed the products $C+O^-$ at 9.5 v and $C^+ + O^-$ at 20.9 v. Using $D(\mathrm{CO}) = 9.6$ v we calculate $C^+ + O$ (both normal) to be at 20.8 v. We observe that the systems $C+O^-$ and $C^+ + O^-$ occur experimentally at just the energy we calculate for the corresponding products with uncharged O. This points to two possibilities; either the electron affinity is very small ($\backsimeq 0.1$ v) or the products $C+O^-$ and $C^+ + O^-$ observed in our experiments are in each case excited, furthermore the excitation energy $\backsimeq$ the electron affinity. The results on O_2, giving $E_0 = 2.2 \pm 0.2$ v, exclude the first of these alternatives. Following out the interpretation demanded by the second alternative we immediately find it impossible to assume that the C^+ or C possess this 2.2 v excitation energy. C^+ has no appropriate excited states, the lowest being at 5.2 v. C has ^1D at 1.25 v and ^1S at 2.67 v.[21] The $C+O^-$ data could be interpreted as $C(^1D)+O^-$ (~1 v excited) or as $C(^3P)+O^-$ (~2 v excited). But the $C^+ + O^-$ products necessitate $C^+(^2P)+O^-$ (~2 v excited). We may summarize the consequences of the interpretation on the basis of $D(\mathrm{CO}) = 9.6$ v by saying that they require the existence of the stable excited negative ion (O^-).

The results of the above discussion can be put briefly as follows. $D(\mathrm{CO})$ may have one of two possible values 11.6 or 9.6 v. The first value

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[16] See Fig. 5 in reference 3.

[17] W. Jevons, *Report on Band Spectra of Diatomic Molecules*, Cambridge Press (1932).

[18] H, Kohn and M. Guckel, Zeits. f. Physik **27**, 305 (1924).

[19] Int. Crit. Tab. **5**, 181.

[20] H. Sponer, *Landolt-Börnstein*, 2nd Ergänzungsband, 2nd part, pp. 1611–20.

[21] The unknown $^5S°$ term of CI need not be considered here for Backer and Goudsmit, using a new method, have calculated its energy as 4.1 v, Phys. Rev. **45**, 559A (1934).

(11.6) would yield $E_0=1.9$ and 2.1 v for our results on O^-; while the second (9.6) would require the O^- ion to have about 2 v excitation energy. If the latter value (9.6) is correct, the observation of a discrete negative ion spectrum should be possible. These experiments in themselves are unable to discriminate between $D(CO)=11.6$ and 9.6 v; however, the numerical values of the possibilities are correct and if subsequent experimental data should ever fix upper or lower limits which fall in this range we can immediately state the proper value.

There is one bit of evidence which supports the numerical correctness of our two possibilities for $D(CO)$. CO possesses an electronic level, designated the F level, discovered by Birge and Hopfield.[22] This state is characterized[17] by $\omega_e=2112$ cm^{-1} and by extremely large $\omega_e x$ (198 cm^{-1}). A linear extrapolation yields a vibration level convergence between levels 4 and 5 and a heat of dissociation of 0.57 v. Since levels are known to v=4, 0.57 volt should be an accurate estimate of D(F).[23] Using $\nu_0=12.30$ v, the total energy of the dissociation products of the F level is 12.87 v. Possible identifications of the dissociation products and the consequent values of $D(CO)$ follow.

C	O	$D(CO)$
^1D	^3P	11.62 v
^3P	^1D	10.91
^1S	^3P	10.20
^1D	^1D	9.66

We find that both our values 9.6 and 11.6 v are possible. This merely supports the numerical correctness of our results without deciding between them. An identification of the multiplicity of the F level would help to decide this question.[24] A singlet state would require $D(CO)=9.6$ v while a triplet state would allow the other three possibilities.

We can present now the evidence which discriminates between the two possibilities for $D(CO)$. First, let us present the data for $D(CO)=9.6$ v. Coster and Brons[25] have recently observed a predissociation at 11.07 v in the upper state of the Angstrom bands of CO. This requires $D(CO)\leq 11.07$ v. However, they have further interpreted the observation as a predissociation into $C(^1D)+O(^3P)$ giving $D(CO)\leq 9.82$ v.

Secondly, Kaplan[26] has interpreted the nonappearance of more than one vibrational level for the b state of CO as a predissociation. This occurs at an energy of 10.34 v, requiring $D(CO)\leq 10.34$ v. Both of these results give upper limits for $D(CO)$ which lie below our higher possibility; then according to our work $D(CO)=9.6\pm 0.1$ v.

Probably the most important consequence of a knowledge of the correct value of $D(CO)$ is the calculation of λ_c, the heat of sublimation of carbon to atoms. This quantity has been the subject of a number of researches and discussions[27] during the past fifteen years. The vapor pressure data of Kohn and Guckel[18] have until recently been considered reliable and interpreted as giving $\lambda_c=140$ Cal. (6.1 v). Using the cycle already mentioned we calculate λ_c using the two possibilities of $D(CO)$.

$D(CO)$	λ_c
11.6 v	7.9 v (182 Cal.)
9.6 v	5.9 v (136 Cal.)

Vaughan and Kistiakowsky[28] have recently shown that the interpretation (and possibly the data) of Kohn and Guckel is inconsistent with statistical calculations and come to the conclusion that λ_c is somewhat higher than 140 Cal. In a later paper Kistiakowsky and Gershinowitz[29] showed by a number of thermochemical cycles that λ_c can scarcely be less than 150 Cal. If these considerations are reliable we can say from the above discussion that the only possible value of λ_c is 182 Cal. and therefore $D(CO)=11.6\pm 0.1$ v is the correct value. As a matter of fact Marshall and Norton[30] have recently obtained $\lambda_c=177$ Cal. in good agreement with our value 182 Cal.

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[22] J. J. Hopfield and R. T. Birge, Phys. Rev. **29**, 922A (1927).

[23] I am indebted to Professor R. T. Birge for sending me the detailed information concerning this electronic state.

[24] See reference 17, p. 109.

[25] D. Coster and F. Brons, Nature **133**, 140 (1934); Physica **1**, 155 (1934); see also D. N. Read, Washington Meeting, Am. Phys. Soc., Phys. Rev. **45**, 752A (1934).

[26] J. Kaplan, Phys. Rev. **37**, 1406 (1931).

[27] For a discussion see article by A. L. Marshall in Treatise on Phys. Chem. Vol. I, p. 326, D. Van Nostrand (1931).

[28] W. E. Vaughan and G. B. Kistiakowsky, Phys. Rev. **40**, 457 (1932).

[29] G. B. Kistiakowsky and H. Gershinowitz, J. Chem. Phys. **1**, 432 (1933).

[30] A. L. Marshall and F. J. Norton, J. Am. Chem. Soc. **55**, 431 (1933).

Concerning this quantity it is pertinent to mention the observations of Smyth and Blewett.[31] In the primary ionization of CS_2 by electron impact they have observed the occurrence of C^+ ions at an electron energy of 21.5 ± 1.0 v. The interpretation advanced is that this corresponds to the formation of C^++S+S giving the products $C+S+S$ at 10.3 ± 1.0 v. Thermochemistry plus band spectrum[32] data tell us $CS_2+4.5\text{ v}\rightarrow C_{\text{solid}}+S+S$. The combination of these results gives 5.8 ± 1.0 v for λ_c. When we consider that the measurements of Smyth and Blewett can give only an upper limit for the potential energy of C^++S+S; we see that in spite of the large probable error this presents good evidence for $\lambda_c=5.9$ v and $D(\text{CO})=9.6$ v.

In spite of the simplicity of the interpretation of our results on the basis of $D(\text{CO})=11.6$ v we believe the weight of evidence favors $D(\text{CO})=9.6$ v as the proper interpretation of our data. In this connection we would emphasize that this requires that the negative ions in CO possess excitation energy. In spite of previous failures with other atoms, it may be possible to observe a portion of the negative ion spectrum of the oxygen atom.

At this point something can be said of the process of formation of the O^- ions represented by Figs. 2 and 7. Smyth and Mueller[6] have discussed in detail the similar H^- formation in H_2O. Though the case of H_2O is complicated by its being triatomic, they reached the conclusion that the negative ions were formed as a result of primary impact. We have determined that the O^- current of Fig. 7 is linear with electron current and pressure; these are facts which, coupled with the absence of positive ions at these electron energies, require a primary impact resulting in the attachment of the incident electron and spontaneous dissociation.

As we have already mentioned, Figs. 2 and 7 tell us that the range of electron energies over which we can obtain an O^- ion with a specified kinetic energy is very small—in fact, our data are not inconsistent with this range being just the energy distribution of electrons in the incident beam. This would mean that an electron of a given energy can produce a negative ion having only a precise kinetic energy and not a range of kinetic energies.

Consider the potential energy curve of the interaction of the dissociation products—a neutral atom and a negative atomic ion. If the potential energy of this curve, for nuclear separations of the order of those present in the normal molecule vibration, is above the potential energy of infinite separation, the distinctive features of Figs. 2 and 7 can be explained. The first step in the negative ion formation would be the excitation of the normal molecule to this unstable state of the negative molecular ion. The capture of the incident electron requires a very close equality between the kinetic energy of the incident electron and the potential energy of the unstable state; the conversion of a given electron energy means excitation to one definite point on the potential energy curve; and this gives rise to a definite ion energy.

There is this difference in the results on the negative ions in the two gases. The process in CO giving $C+O^-$ at 9.5 v produces O^- ions with kinetic energies 0 to ~1 volt. This means that the potential energy curve involved is probably not strictly repulsive but possibly has a minimum; and a careful search with a mass-spectrograph might reveal CO^- ions at about 9.5 v. In O_2, however, the process giving $O+O^-$ at 2.9 v produces no O^- ions with energies lower than ~1.3 v. This points to a repulsive potential curve and the non-existence of O_2^-.

CONCLUSIONS

From the O_2 data two types of dissociation have been considered and interpreted as follows

$$O_2^-\rightarrow O(^3P)+O^-\text{ (normal) at }2.9\pm0.2\text{ v.}$$
$$O_2^-\rightarrow O(^5S^\circ)+O^-\text{ (normal) at }12.0\pm0.2\text{ v.}$$

These data have permitted a determination of E_0, the electron affinity of the oxygen atom, as 2.2 ± 0.2 v.

From the CO data three types of dissociation processes have been discussed.

$$CO^-\rightarrow C+O^-\text{ at }9.5\pm0.1.$$
$$CO\rightarrow C^++O^-\text{ at }20.9\pm0.1\text{ v.}$$
$$CO^+\rightarrow C^++O\text{ at }22.8\pm0.1\text{ v.}$$

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[31] H. D. Smyth and J. P. Blewett, Washington Meeting, Am. Phys. Soc., Phys. Rev. **45**, 752A (1934).

[32] *Landolt-Börnstein*, Vol. 2, p. 1490; 1st Ergänzungsband, p. 809; and 2nd Ergänzungsband, p. 1498. Also A. Christy and S. M. Naudé, Phys. Rev. **37**, 903 (1931).

From these data we have determined that $D(\mathrm{CO})$ may have one of two possible values, 9.6 or 11.6 v. The assumption of the first requires the O^- ion in both cases to have excitation energy; while the assumption of the value 11.6 v allows the calculation of E_0 as 1.9 and 2.1 v. Evidence is given which points to the lower value as the correct one.

The processes involved in the formation of the negative ions have been discussed.

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Ionization of Carbon Disulphide by Electron Impact

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The ionization of $\mathrm{CS_2}$ by electron impact has been studied. It has been found that the $\mathrm{CS_2^+}$, $\mathrm{CS^+}$, $\mathrm{S^+}$ and $\mathrm{C^+}$ ions are produced at 10.4±0.2, 14.7±0.5, 14.0±0.5 and 21.5±1.0 volts, respectively. The absence of $\mathrm{S_2^+}$ ions and the high appearance potential for $\mathrm{C^+}$ indicate a linear molecule. By raising the filament temperature free CS and $\mathrm{S_2}$ are produced and their I.P.'s determined as 10.6±0.3 and 10.7±0.3 volts. Heats of dissociation for various processes are deduced from the experimental data.

IN several previous papers[1, 2] results have been reported on the ionization of common triatomic molecules by electron impact. Here we wish to record similar data on the ionization of carbon disulphide.

It may be well to recall briefly the method used. It is to determine by a mass-spectrograph the nature of the ions produced in the gas by electrons of known energy. The numbers of different types of ions are then studied as functions of electron energy.

The particular apparatus used on carbon disulphide was that used previously by Smyth and Stueckelberg[1] and Smyth and Mueller.[2] Considerable difficulty was experienced in investigating $\mathrm{CS_2}$ on account of dissociation by the heat of the filament. This dissociation occurred in spite of the gas flow method employed to prevent it and could be overcome only by using an oxide-coated filament operated at the lowest possible temperature and removed two millimeters further from the ionization space than it had been in previous work.

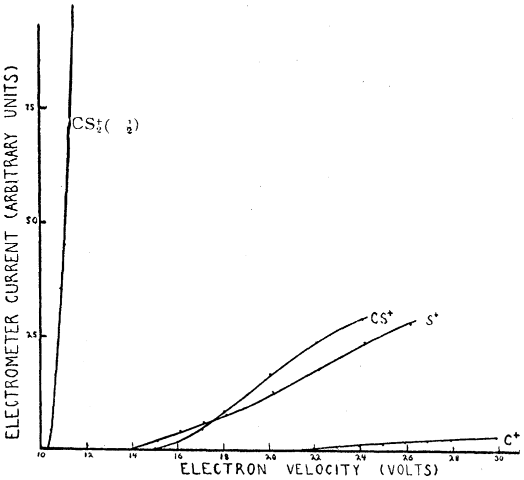

FIG. 1. Current *versus* voltage curves for various ions formed by electron impact in $\mathrm{CS_2}$.

Under these conditions with $\mathrm{CS_2}$ that had been redistilled in vacuum, ions were observed at masses 76, 44, 32 and 12. No ion was detected at mass 64. Current *vs.* voltage curves for these ions are shown in Fig. 1. No negative ions were observed. The voltage scale was calibrated by the ionization of mercury vapor. Runs taken in mixtures of mercury and $\mathrm{CS_2}$ and in the pure gases agreed in showing the ionization potential for the production of $\mathrm{CS_2^+}$ the same

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[1] Smyth and Stueckelberg, Phys. Rev. **36**, 472 & 478 (1930).

[2] Smyth and Mueller, Phys. Rev. **43**, 116 & 121 (1933).