specific activity (including the end products of tracer experiments), can be reconcentrated. A given sample of C^{14} (and C^{13}) may, therefore, be used repeatedly. When the use of C^{14} and C^{13} becomes widespread enough, it should be feasible for a commercial company to perform this task at a nominal cost.[33]

We cannot adequately express our gratitude to the members of the Chemistry and Physics Departments, as well as many others, for their help and encouragement. It is a pleasure to thank Professor E. O. Lawrence and the staff of the Radiation Laboratory for their assistance and cooperation. Financial assistance from the Research Corporation and the Rockefeller Foundation to the Radiation Laboratory is gratefully acknowledged.

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[33] The Eastman Corporation, at the suggestion, and with the cooperation, of Professor H. C. Urey, has begun the concentration of N^{15} on a small scale. It is reasonable to believe that the interest and demand for carbon tracers will far exceed the supply of the radioactive isotopes and, therefore, the large scale concentration of C^{13} is of considerable importance.

Note added in proof.—The estimate for the C^{14} half-life was made by three different methods (1) the yield of C^{14} coupled with an extrapolation of Amaldi's curve (cf. Bethe's review) for the $C^{12}(d,p)C^{13}$ reaction and Pollard's value for the yield ratio $C^{13}(d,p)C^{14}/C^{12}(d,p)C^{13}$, (2) the $C^{13}(d,p)C^{14}$ cross section was estimated by comparison with the $B^{10}(d,n)C^{11}$ yield at bombarding energies of 7–8 Mev, (3) the C^{14} yield from the slow neutron irradiation of NH_4NO_3. Method (1) gave $2 \cdot 10^4$ years while (2) yielded $2 \cdot 10^3$ years. Schultz and Watson, Phys. Rev. **58**, 1047 (1940), have found Pollard's $C^{13}(d,p)C^{14}/C^{12}(d-p)C^{13}$ yield ratio was high by a factor of 5–10. This seems to bring the first two C^{14} half-life estimates into agreement at 10^3 years. The $N^{14}(n,p)C^{14}$ experiments suggest a still longer half-life for C^{14}. Hence it seems reasonable to regard 10^3 years as a lower limit.

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Ionization and Dissociation of Diatomic Molecules by Electron Impact

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An extension of the mass spectrometric method of study of ionization and dissociation processes occurring in diatomic molecules under electron impact and the results of further investigation of the molecules H_2, CO, NO, N_2, and O_2 are discussed. The shapes of the peaks which appear in the graph of resolved ion current as a function of ion accelerating potential are analyzed and accounted for in terms of the wave-mechanical theory of the diatomic molecule and the characteristics of the mass spectrometer. It is indicated how the study of the peak shape coupled with appearance potential measurements has made possible conclusions concerning the nature of the dissociation process and the structure of the molecule. Differences between previous mass spectrometric data and those from other sources have been clarified either by obtaining better data with the mass spectrometer or by formulation of a satisfactory interpretation of the difference based on conclusions of an analysis of the ion peak shape. Values of dissociation energies, ionization potentials and interpretations of the processes that occur are given.

INTRODUCTION

COLLISIONS of electrons of low velocity with diatomic molecules may produce charged fragments of the molecule. The data on the minimum electron energy necessary to produce these fragments, the identification of them and of the processes involved may permit one to determine the heat of dissociation of the molecule. The relative abundance of the ion products and the probability of a process as a function of the electron energy are also of interest.

In the usual mass spectrometer the ions of a given m/e value are segregated and the dependence of the ion current on the energy of the bombarding electrons and on the gas pressure in the collision chamber is determined.[1–4] In the

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* Now at the Bell Telephone Laboratories, New York.

[1] For a review of all work previous to 1931 see H. D. Smyth, Rev. Mod. Phys. **3**, 347 (1931). Reviews have also been given by H. Kallmann and B. Rosen, Physik. Zeits. **32**, 521 (1931); W. de Groot and F. M. Penning, *Handbuch*

dissociation of diatomic molecules some fragments are given kinetic energy. This initial kinetic energy cannot be determined easily by the mass spectrometer. By means of a modified apparatus Lozier[5] studied the minimum electron energy at which an ion with a definite kinetic energy would appear. He was able to verify theoretical predictions on the dissociation of hydrogen. The retarding potential method of Lozier has been improved[6–10] and a number of diatomic molecules studied. The method is limited in that the m/e value of the ion cannot be determined.

It is the purpose of this paper to show how an analysis of the peaks in the curves of ion current observed with a mass spectrometer yields information on the ionization and dissociation of diatomic molecules which previously could be obtained in part from the retarding potential methods and in part from the mass spectrometer. Information on the potential energy curve involved in the dissociation process, a method of distinguishing between dissociation and ionization processes which yield ions with the same m/e values and new interpretations of measurements on the appearance potentials and relative abundance of ions have been obtained.

Data on H_2, O_2, CO, N_2, and NO are given. Earlier discrepancies are cleared up and some known dissociation processes are studied quantitatively for the first time.

Experimental Arrangement

The mass spectrometer is similar to that described by Tate, Smith and Vaughan[3] and by Nier.[11] The dimensions are shown in Fig. 1. The ions are formed in the electron beam of ribbon form and are accelerated to the slit S_1. Additional acceleration is given to them between the plates S_1 and S_2. The ion current passing through S_3 is plotted as a function of the accelerating field between the electron beam and S_2.

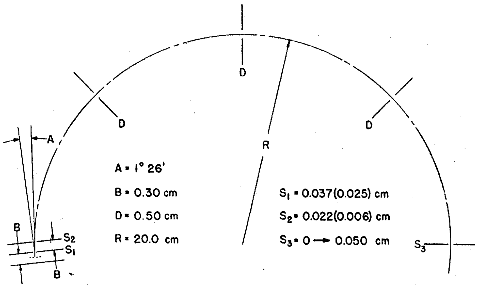

FIG. 1. Geometrical details of the mass spectrometer. Slits S_1 and S_2 were widened during the course of the work and both values of slit width are given. The width of slit S_3 is adjustable between the limits given but was usually kept about half open. The lengths of the slits are S_1 0.8 cm, S_2 0.8 cm, S_3 1.0 cm. A drawing-out field between the back plate and S_1 of about 30 volts per cm was used. The dimensions of the defining slit of the electron beam are 0.01×0.5 cm. The plane of the beam is half-way between the back plate and the first ion slit.

For a particular curve or peak it is essential that the field of the electromagnet be maintained constant and that there be no drift in the accelerating electric fields. The electromagnet is operated by storage batteries and the electric potentials are obtained from batteries or a 1000-volt stabilized rectifier.[12] No difficulty has been encountered in obtaining very steady operating conditions. The ion current is measured by a direct-current amplifier with a Western Electric electrometer tube D96475 in a modified Barth circuit described by Penick.[13]

A porcelain leak[14] admits gas to the system in which a pressure of 10^{-4} mm Hg is ordinarily maintained. A tungsten filament was used with H_2, N_2 and CO_2, and an oxide-coated filament with NO and O_2. Hydrogen, oxygen and nitrogen were obtained from commercial tanks and were admitted to the apparatus through a liquid-air trap. The carbon monoxide was prepared[15] by treating oxalic acid with concentrated sulphuric acid and washing of the resultant gases with concentrated potassium hydroxide and alkaline

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der Physik (J. Springer, Berlin, 1933), Vol. 23/1; H. Sponer, *Molekülspektren* (J. Springer, Berlin, 1936).

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

[3] J. T. Tate, P. T. Smith and A. L. Vaughan, Phys. Rev. **48**, 525 (1935).

[4] A. O. Nier and E. E. Hanson, Phys. Rev. **50**, 722 (1936).

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

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

[7] W. W. Lozier, Phys. Rev. **44**, 575 (1933); **45**, 840 (L) (1934).

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[11] A. O. Nier, Phys. Rev. **52**, 933 (1937).

[12] F. V. Hunt and R. W. Hickman, Rev. Sci. Inst. **10**, 6 (1939).

[13] D. B. Penick, Rev. Sci. Inst. **6**, 115 (1935).

[14] W. R. Smythe, Rev. Sci. Inst. **7**, 435 (1936).

[15] E. H. Archibald, *The Preparation of Pure Inorganic Substances* (Wiley and Sons, New York, 1932).

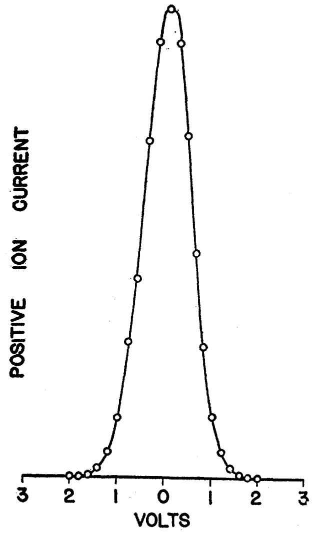

FIG. 2. Peak shape for an ion which is formed with no initial velocity. (type 0). This particular peak is for N_2^+ from N_2. The abscissas give ion accelerating potential measured from the center of the peak which corresponds to a total acceleration through approximately 500 volts.

pyrogallol solutions. The gas was dried by passing it through phosphorus pentoxide and a liquid-air trap. The NO was prepared[15] by the action of sulphuric acid on a solution of potassium nitrite and potassium iodide. The gases formed were passed through a dry-ice trap to remove water and the higher oxides of nitrogen and the NO collected in a liquid-air trap and fractionally distilled a number of times.

For each gas a study was made of the abundances and appearance potentials of ions from impurities which have the same m/e as ions from the molecule under investigation. It was always possible to regulate the amounts of impurities present by baking out or further purification of the gas sample so that their effects were entirely negligible.

The minimum energy of the bombarding electron for the observation of an ion is called its appearance potential. In comparing appearance potentials, the amplifier is adjusted to give the same rate of increase of ion current above the break for each ion. The ionization potential of argon was used to obtain absolute values of electron energies. In studying the shape of ion peaks, the bombarding electrons were accelerated through a potential drop of 100 volts.

ANALYSIS OF PEAK SHAPES

Certain features of the shapes of the curves of ion current observed with a mass spectrometer have been noted by previous investigators.[3, 4] The peaks for certain ions "trail out" on the high mass side. This characteristic was attributed to ions which possess some initial kinetic energy. Hustrulid, Kusch and Tate[16] reported observation of a number of satellite peaks for ions from benzene vapor. The separate peaks were assumed to be formed by ions with relatively high kinetic energy in a narrow range.

The shape of an ion peak depends mainly upon two factors: (1) the characteristics of the instrument, (2) the distribution in initial kinetic energy of the ion. The ions with different initial velocities are not focused by our instrument at the same point. This characteristic permitted a study of these initial velocities from which some information on the structure of the diatomic molecule may be obtained.

Instrumental factors affecting the width of an ion peak are the finite width of slits and diaphragms, space charge effects, shape of electron beam and the fact that ions are formed at different points in the accelerating field below S_1 (Fig. 1). If the ion products have no initial energy other than that of thermal agitation and if ions with the small range of kinetic energy for this case are collected equally efficiently, the curve of ion current has the symmetrical form shown in Fig. 2. A curve of this form we shall designate as type 0. It is obtained when ions with essentially zero kinetic energy are formed as for example in a process involving only ionization.

An ion which is the result of dissociation may have initial energy of several electron volts. Since ions of the same m/e value must have the same velocity at the entrance slit to be focused on the exit slit, ions with different initial velocities will require different accelerating potentials to be brought to a focus. Thus a curve of ion current *vs.* accelerating potential will have a form different from that of Fig. 2 and will yield information on the initial velocities of the ions. From this information data on the structure of the molecule may be obtained.

The effect of the initial ionic velocity apart from instrumental factors on the collection of ions will now be considered. A complete solution which takes all factors into account becomes

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[16] A. Hustrulid, P. Kusch and J. T. Tate, Phys. Rev. **54**, 1037 (1938).

exceedingly involved. But one may rather easily carry through a simplified calculation to determine the percent of ions formed with different kinetic energies which pass through the *first slit* from a given point in the electron beam. The results are shown in Fig. 3. The method of obtaining the results is described in the figure caption. The final over-all curve showing the dependence of collection on the initial kinetic energy is curve 3 in Fig. 3. It is evident that ions of very low or zero kinetic energy are much more efficiently collected than those of higher energy.

Distribution in kinetic energy of ion products

Condon[17] has shown that the wave-mechanical formulation of the Franck-Condon principle predicts the dependence of the probability of transition between two molecular vibrational states in which a photon is emitted or absorbed upon the value of the so-called overlap integral:

$$[\int \psi_U \psi_L dr]^2. \tag{1}$$

In this expression ψ_U is the wave function of the upper state, ψ_L is the wave function of the lower state and r is the nuclear separation. The case of absorption for which ψ_U is the eigenfunction of a state above the asymptote in the continuum corresponds to a transition induced by electron impact resulting in dissociation of the molecule. The success of the application of the Franck-Condon principle to the prediction of possible electron impact processes in hydrogen[18–20] suggests the use of expression (1) in a more detailed discussion of electron impact processes in diatomic molecules.

The probability of transition produced by electron impact is a function of the energy of the transition (E_t), the energy of the bombarding electron (E_e) and of the overlap integral. For values of E_e well above that of E_t it appears that the probability depends mainly on the overlap integral. The value of E_e was 100 electron volts which is well above the usual value of 20 to 35 electron volts for E_t. The form of the function does not alter radically with E_t. This is evidenced by measuring as a function of E_e the efficiency of formation of ions collected at different points on an ion peak which involve different values of E_t.

The value of the probability of transition is found by methods suggested first by studies of the continuous absorption spectra.[21–23] The probability of finding the molecule with a given separation of the atoms is proportional to ψ_L^2. The probability of electronic transition with a given nuclear separation maintained is then taken as proportional to ψ_L^2 for that separation. If the upper potential energy curve representing the state to which the molecule is taken is known and the F-C principle is assumed to be valid, then the curve representing the distribution in

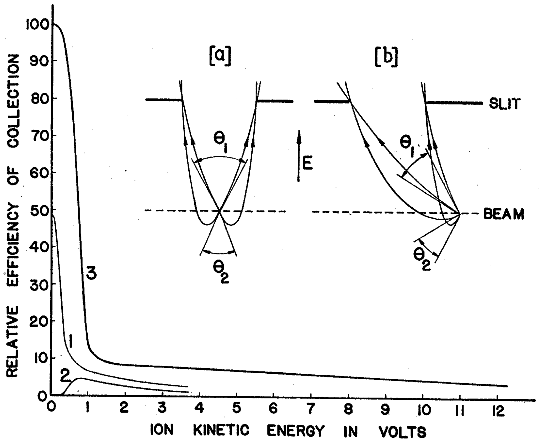

FIG. 3. Efficiency of collection of ions by the mass spectrometer as a function of initial kinetic energy. Investigation of the motion of ions in the collision chamber has been simplified by neglecting space charge and the magnetic field and by assuming that the ions are formed with velocity vectors pointing uniformly in all directions with zero components along the electron beam. (a) and (b) show the limiting paths of ions which pass through the first ion slit from two lines in the electron beam. Ions initially directed inside the angles θ_1 and θ_2 pass through the slit. Curve 1 gives qualitatively the relative efficiency for case (a), curve 2 for case (b). The second ion slit and analyzer diaphragms (see Fig. 1) perform a further selection by limiting the spread in angle at the first slit of the trajectories of ions which are collected. This discriminates against ions formed near the edges of the electron beam which, on the average, possess the greatest kinetic energy of the ions getting through the first slit. Curve 3 is the proposed "over-all" efficiency curve for the spectrometer used in the present work.

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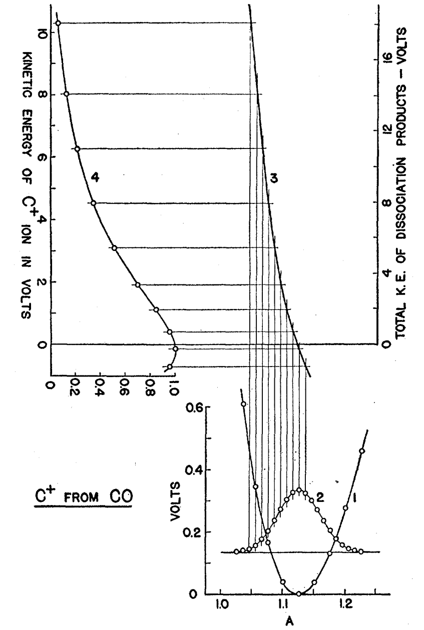

FIG. 4. Construction of the distribution in initial kinetic energy of C^+ ions from CO by the reflection method. Curve 1 is a part of the potential curve of the ground electronic state of the molecule; curve 2 is the square of the wave function of the lowest vibrational level (harmonic oscillator); curve 3 is a part of the upper potential curve to which transitions will yield curve 4, the distribution in kinetic energy. The ordinates of curves 2 and 4 are arbitrary. The position of curve 3 has been chosen so that a resultant ion peak of type I is obtained (see Fig. 5).

initial energy of the fragments of the molecule can be obtained.

The method is illustrated in Fig. 4. Curve 1 is the potential energy curve of the ground electronic state of the molecule, curve 2 is the square of the wave function (ψ_L^2), curve 3 is the upper potential energy curve. Curve 4 is then shown with ordinates representing the kinetic energy of an ion at dissociation. The ordinate of this scale will be proportional to that representing the total kinetic energy at dissociation of the molecule and will have its zero determined by the position of the asymptote (infinite nuclear separation) of the upper potential energy curve. The abscissas denote the probability of producing an ion with a given kinetic energy, and their values are taken as proportional to the value of ψ_L^2 for a particular value of r. Thus the probability is taken as proportional to the number of molecules having a nuclear separation such that when the electronic transition takes place and the molecule is raised to a new energy level, that is to a point on the upper curve, it will break up and yield an ion having a given kinetic energy. For example, in Fig. 4 the value of the probability that the C^+ ions have kinetic energy of 2 electron volts is proportional to the height of the ψ_L^2 curve at the nuclear separation value, which on curve 3 would yield an ion of that energy. In Fig. 4 the position of the upper potential energy curve is such that the most probable nuclear separation in the lower state (maximum ψ_L^2) results in zero kinetic energy of the dissociated parts. Curve 4 then has its maximum at zero kinetic energy. The values of negative kinetic energy indicated by the same construction for points of greater nuclear separation correspond to transitions in which excitation but no dissociation may take place.

The position and shape of the upper potential curve are in general not known. The position of the curve is more or less arbitrary but there are, of course, general restrictions on its shape. It is so chosen that the resultant distribution obtained by the method just described is in accord with that which may be inferred from experimental measurement of the ion peak shape. This method of "working backwards" has also been used to obtain the course of the potential curve from the observed intensity distribution in continuous spectra.[24]

Construction and classification of ion peak shapes

Curve 4 of Fig. 4 indicates the distribution in energy of the ions at the moment of formation. Those having small velocities are collected at the first slit (S_1) the most efficiently (Fig. 3). The distribution in energy of the ion current passing through S_1 may be obtained by multiplying each point of curve 4 (Fig. 4) by the value of the corresponding efficiency (Fig. 3, curve 3). Curve 3 of Fig. 5 is the resultant curve. Because of finite widths of the collecting slits and of those in the diaphragm, and the slight differences in the acceleration of ions starting at different points in the electron beam, the actual observed ion peak is broader and has no discontinuity. It is shown in Fig. 5 (curve 4). The abscissas for

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[24] N. S. Bayliss, Proc. Roy. Soc. **158**, 551 (1937).

this curve are determined by changes in the values of the electric field between S_1 and S_2 (of the order of 1000 volts/cm) which, with a given magnetic field, sweeps the ion beam over the collecting slit S_3. In curve 4 of Fig. 5 the zero has been placed at the maximum and it is assumed that then the abscissas as shown measure the initial kinetic energy of the ions.

Ion current peaks of the form of curve 4 (Fig. 5) are called type I. They result when the ions formed with zero or very near zero kinetic energy are most probable. Examples are H^+ ions from H_2, N^+ ions from N_2 and N^+ ions from NO.

Figures 6 and 7 show the construction of a peak for ions which result from transition to a potential curve lying at larger nuclear separation than that of Fig. 4. The resultant peak shape possesses two maxima, one due to the maximum in the "original" distribution corresponding to the maximum transition probability, the other to the rise in the efficiency of collection by the spectrometer near zero kinetic energy. Such a peak shape, to be designated as type II, has been observed for O^+ ions from NO and is to be expected whenever ions of kinetic energy *near* zero are present but with reduced abundance when comparison is made with type I.

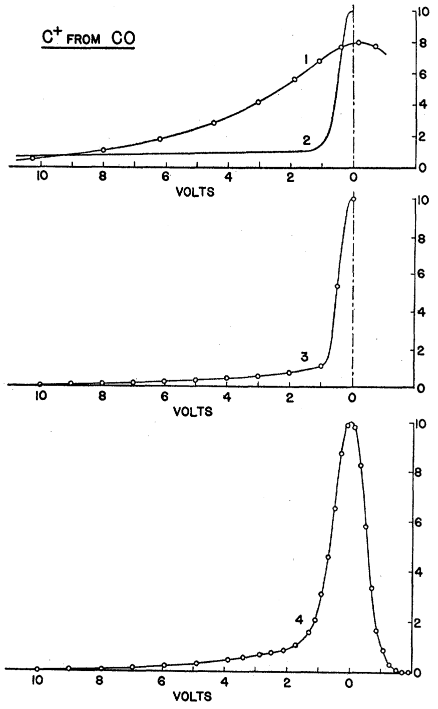

FIG. 5. Construction of the peak shape from the distribution in initial kinetic energy of C^+ from CO. Curve 1 is the distribution from Fig. 4 (curve 4); curve 2 is the instrumental efficiency curve; curve 3 is the predicted peak shape obtained by multiplying curves 1 and 2. Curve 4 is the observed peak shape. The abscissas of curve 4 are determined as they were in Fig. 2.

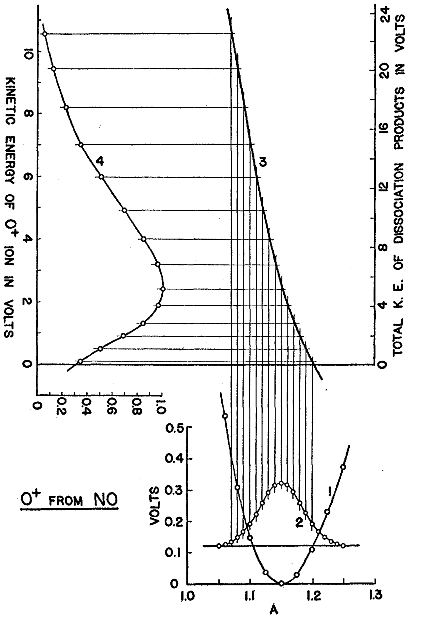

FIG. 6. Construction of the distribution in initial kinetic energy of O^+ ions from NO by the reflection method. See caption of Fig. 4 for the designation of the curves. The position of curve 3 has been chosen so that a peak of type II is obtained (see Fig. 7).

If the upper potential curve lies at still larger values of r the probability of formation of ions of very low or zero initial kinetic energy may be zero. The distribution in kinetic energy possesses a minimum kinetic energy greater than zero because the upper potential curve crosses its asymptote outside the Franck-Condon region. By virtue of the shape of the function $\psi_L^2=0$ for the ground state (curve 2 of Fig. 4) the probability of formation of ions possessing kinetic energies near the minimum is relatively low. The instrumental efficiency is relatively constant over the range of values of initial kinetic energy possessed by the ions; hence the shape of the peak, designated as type III, approximates that of the distribution at formation and the maximum appears at about the kinetic energy corresponding to the maximum transition probability. The O^+ ions which result from the dis-

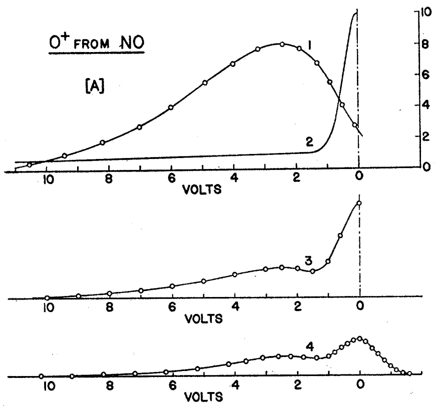

FIG. 7. Construction of the peak shape from the distribution in initial kinetic energy of O^+ from NO by method *A*. See caption of Fig. 5 for the designation of the curves.

sociation of CO exhibit a peak shape of this type (Fig. 8). This type occurs when ions of kinetic energy less than one volt (approximately) are absent.

A distribution may possess a minimum kinetic energy greater than zero for a second reason. If the potential curve to which transition takes place has a maximum at a value of r greater than that existing at transition, the total kinetic energy of the products must not be less than the height of this maximum above the asymptote. In this case there need be no restriction on the probability of formation of ions possessing kinetic energies near the minimum. If the point on the curve, transition to which results in the products of minimum energy, lies near the center of the Franck-Condon region the probability of transition to points near it is relatively large. The distribution in kinetic energy of the products then cuts off abruptly at the minimum energy.

A situation in which there is a maximum in the potential energy curve but in which the minimum kinetic energy is only a few tenths of an electron volt may appear as type I or II because of the rise of the instrumental efficiency *near* zero energies.

Variation of peak height with drawing-out field

If the ions have very little initial kinetic energy, the ion current collected will saturate at a small drawing-out field. If, however, the ions initially have velocities in random directions, more and more ions will be directed to the slit and the current will continue to increase with increasing field. Also, a small retarding field will reduce the current to zero if the initial kinetic energy is zero but ions with initial kinetic energy can be collected against a retarding field. Thus curves of ion current against the drawing-out field will yield some information of the process of formation of ions. The height of peaks of types O, I and II should not vary with the field. The height of peak type III should increase with increasing field. Figure 9 shows experimental results.

Appearance potentials and relative probability of dissociation processes

From the construction of curves for types I and II, it is evident that the peaks are formed by ions which have the least kinetic energy of those formed in the dissociation process, even though such ions are not the most abundant of those formed in the electron beam. If the upper potential energy curve is of the usual type without a maximum, the appearance potential of those ions which appear at the peak of the experimental curve locates a dissociation limit of the molecule since the initial kinetic energy of the ions is zero. Dissociation energies obtained from the appearance potentials of H^+ from H_2, N^+ from N_2, N^+

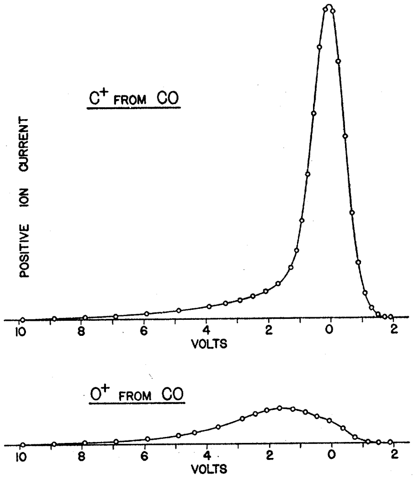

FIG. 8. Peak shapes for the C^+ and O^+ ions from carbon monoxide at 100 volts electron energy. The abscissas give ion kinetic energy in volts. Ion accelerating potential increases to the right, the maximum of the C^+ peak corresponding to about 300 volts. It is explained in the text how the scale of ion kinetic energy for each peak was calibrated.

from NO agree with those obtained from retarding potential methods and from spectroscopic data.

If comparison with other data indicates the appearance potential is higher than a dissociation limit, it must be concluded that ions of zero kinetic energy were not formed. Since peaks of type I or II are considered, the probability of formation of ions near the minimum energy must be fairly large. This situation may be explained by assuming a potential energy curve with a maximum between the F-C region and the dissociation region. Then it is possible to have a large number of ions formed with the minimum energy which may be some tenths of an electron volt above zero. Comparison of data obtained in our experiments with those from retarding potential methods and spectroscopy aids in determining the position of the zero on the abscissa scale in experimental curves (curves 4, Figs. 5, 7, 8). The location of the zero of these curves is sometimes a difficult matter but a very important one in the interpretation of the results.

The conclusion that the maximum of a peak of type I corresponds to ions of zero initial kinetic energy if such ions are formed in the process has been confirmed in another manner. A test was made to see if the maximum of the ion peak of N^+ from N_2 appears at the "position" on the scale of accelerating potential for ions of zero initial velocity and $m/e=14$. In order to avoid complications due to contact potentials and uncertainties of calibration of the voltage divider which applies the ion accelerating potential to the slit system of the spectrometer the following procedure was adopted. Argon and nitrogen were admitted into the spectrometer at the same time. The voltage interval (about 350 volts) between the maxima of the N^+ and the N_2^+ ion peaks was measured. The magnetic field was then adjusted so that the A^+ peak appeared at the position on the voltage scale previously occupied by N_2^+ and the interval between A^+ and A^{++} determined. As the ratios of the m/e values of A^+ and A^{++} and of N_2^+ and N^+ are equal these intervals should be equal if the maximum of the N^+ peak corresponds to the ion of zero initial velocity. It was found that the two voltage intervals agreed within 0.2 volt which is within the estimated experimental error.

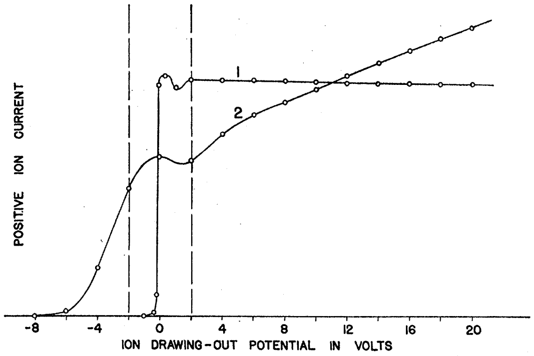

FIG. 9. Variation of peak height with the drawing-out field in the collision chamber of the mass spectrometer. The abscissas give the potential applied across the collision chamber between the back plate and the first ion slit (0.3 cm apart). Curve 1 is for CO^+ from CO (type 0) and curve 2 for O^+ from CO (type III). The curve for a peak of type I or II would approximate curve 2 for negative fields and curve 1 for positive fields. When the drawing-out field is small, stray fields apparently "reach into" the collision chamber causing peculiar focusing effects. For this reason, the shapes of the curves for potentials near zero (between the vertical dashed lines) have no significance in the present discussion.

Ions of initial velocity near zero are not formed in a process which gives rise to an ion peak shape of type III. Since ions of appreciable initial kinetic energy focus at the maximum of such a peak the appearance potential measured at the maximum may be considered only as an upper limit for the energy level of the asymptote of the potential curve. A more accurate determination of the position of the dissociation limit can be made if it is possible to determine the kinetic energy corresponding to some point on the distribution. How this was accomplished for the single process of this type observed in this work is discussed in the section of the paper which deals with CO (Process F).

The study of the shapes of ion peaks indicates that neither the height of the peak nor the area under the curve is a direct measure of the abundance of an ion. Instrumental and other factors determine the height and area. A peak of type I may be ten times as high as one of type III even though the total number of ions formed is the same in each case. Nevertheless it is possible to estimate the relative abundance of the ions formed.

EXPERIMENTAL RESULTS

In the presentation of the experimental results the following symbols will be used: $I(X)$—ioniza-

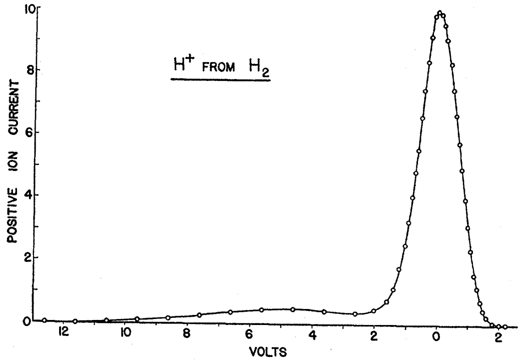

FIG. 10. H^+ ion peak from H_2 for electrons of 100 volts energy. The abscissas give the kinetic energy of the ions in electron volts (accelerating potential in volts) measured from the position of the maximum. Total accelerating potential increases to the right, that corresponding to the maximum of the peak being about 300 volts. The peak is a superposition of two peaks of types I and III.

tion potential of X which may be an ion, an atom or a molecule. $A(X^+)$—appearance potential of X^+. This is understood to refer to the product of zero initial kinetic energy unless otherwise specified. $D(X)$—heat of dissociation of X. $EA(X)$—electron affinity of X. $E(X)$—excitation energy of X.

Hydrogen

The restudy of the hydrogen molecule was undertaken primarily as a check on the operation of the mass spectrometer and the analysis of peak shapes. Bleakney[20] has demonstrated experimentally that two modes of formation of H^+ as a primary ion product from H_2 under electron impact can be distinguished. These entail transition to the $^2\Sigma_g{}^+$ and $^2\Sigma_u{}^+$ states of the molecule ion. By retarding the ions in the collision chamber of the spectrometer Bleakney showed that they possess initial kinetic energies in the ranges predicted by theory. This work was corroborated by Lozier[5] who used the retarding potential method.

From the course of the potential curves one should expect H^+ peaks of types I and III for the ions resulting from transitions to the $^2\Sigma_g{}^+$ and $^2\Sigma_u{}^+$ states of $H_2{}^+$, respectively. The resultant peak observed with the mass spectrometer (Fig. 10) is a superposition of two such peaks. It is to be distinguished from a peak of type II which may also possess a double maximum although only a single potential curve is involved.

An attempt has been made to construct from the theoretical potential curves the H^+ peak by the method described. Qualitatively the constructed and observed peak shapes agree very well. It is impossible to predict the relative heights of the two maxima of the peak, however, as the relative probability of transition to the two states at the same nuclear separation is not known. Considering this limitation, it is believed that the results of this study indicate that the essential features of the peak shape have been accounted for.

Appearance potential measurements at the maxima of the $H_2{}^+$ and H^+ peaks yielded the data:

$$A(H_2{}^+) = 15.4 \pm 0.1 \text{ volts},$$
$$A(H^+) = 18.0 \pm 0.2 \text{ volts}.$$

These data and the values of $D(H_2)$ and $D(H_2{}^+)$ predicted by them agree within experimental error with the results of previous electron impact work,[7, 20] band spectroscopic[25] and thermochemical[26] investigations and wave-mechanical calculation.[25] It is believed that data for other molecules taken in the same manner are of comparable accuracy when interpreted correctly even though knowledge of the structure of the molecule does not permit so rigorous a check as in the case of hydrogen.

Carbon monoxide[27]

A summary of data on CO is given in Table I. A number of processes in which the ions may be

TABLE I. *Summary of electron impact data for* CO. *Appearance potential in volts.*

	$A(CO^+)$	$A(CO^{++})$	$A(C^+)$	$A(O^+)$	$A(O^-)$
Hogness, Harkness* (mass spectrometer)	13.9		22.8	24	
Vaughan[2] (mass spectrometer)	13.9 ±0.2	43.0 ±1.0	22.5 ±0.2		9.5 ±1.0
Tate, Smith, Vaughan[3] (mass spectrometer)				27 ±1	
Tate, Smith[28] (total ion current)	14.1 ±0.1				
Lozier[8] (retarding potential)			20.9 ±0.1 22.8 ±0.1		9.5 ±0.1 20.9 ±0.1
Present work (mass spectrometer)	14.1 ±0.1	42.0 ±0.5	20.9 ±0.2 22.8 ±0.2	23.1 → 23.5	9.5 ±0.2 20.9 ±0.2

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

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[25] See H. Beutler and H. O. Jünger, Zeits. f. Physik **100**, 80 (1935) for a summary of values obtained for the dissociation and ionization energies of H_2 from spectroscopic observations and theoretical calculation.

[26] R. F. Bichowsky and L. C. Copeland, J. Am. Chem. Soc. **50**, 1315 (1928).

[27] A part of this work on CO was presented at the Washington Meeting of the American Physical Society, April 29, 1939. H. D. Hagstrum and J. T. Tate, Phys. Rev. **55**, 1136A (1939).

formed have been identified. These will be considered now.

Process A: $CO+e \rightarrow CO^{+}+2e$.—$CO^{+}$ ions were found to appear first at 14.1±0.1 volts. This datum agrees very well with the results of previous work (see Table I). Further consideration of Vaughan's data by Tate and Smith[28] gave 14.0 instead of 13.9 volts.

Process B: $CO+e \rightarrow CO^{++}+3e$.—A value of $A(CO^{++})=42.0\pm0.5$ volts has been obtained. It is in substantial agreement with Vaughan's value of 43.0±1.0 volts.

Process C: $CO+e \rightarrow C+O^{-}$.—The onset potential of the resonance process yielding O^{-} ions was found to be 9.5±0.2 volts (Fig. 11), in good agreement with the results of previous investigations. The fact that this potential measured with the ion accelerating potential of the mass spectrometer adjusted to the maximum of the peak agrees with the extrapolated value of Lozier for ions of zero initial kinetic energy indicates that such ions are produced in the process in appreciable abundance. This result confirms Lozier's observation that O^{-} ions of kinetic energy from zero to approximately one volt are formed. The potential curve to which transition takes place must lie very near the asymptote in the Franck-Condon region and perhaps crosses it there. This would indicate that the curve possesses a minimum and Lozier suggests that a careful search with a mass spectrometer might reveal CO^{-} ions. A search was made for such ions but none could be detected. If they are formed their abundance cannot be greater than 0.01 percent of the CO^{+} ion. Massey[29] suggests that in low pressure experiments of this type it will not be possible to observe the formation of negative molecular ions because they will dissociate by the reverse process before making sufficient collisions to get rid of their excess vibrational energy.

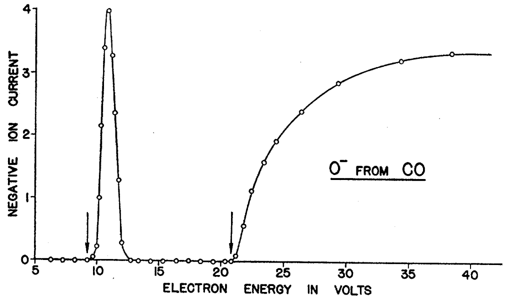

FIG. 11. Efficiency of formation of O^{-} ions from carbon monoxide as a function of the energy of the impacting electrons. The ion accelerating potential was adjusted to the maximum of the peak.

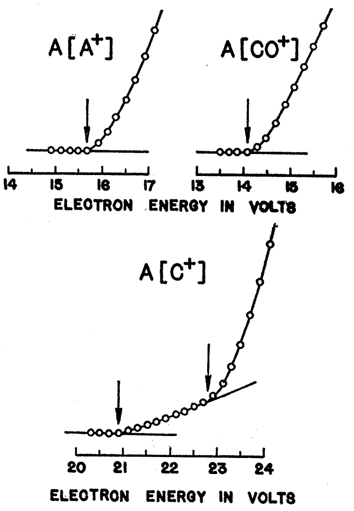

FIG. 12. Typical appearance potential curves for ions from carbon monoxide. The C^{+} curve was obtained with the ion accelerating potential held constant at the value corresponding to the maximum of the peak for higher electron energies.

Process D: $CO+e \rightarrow C^{+}+O^{-}+e$.—The first appearance potential of C^{+} ions at 20.9 volts (Fig. 12) coincides within experimental error with the second appearance potential of O^{-} ions. (Fig. 11). This potential agrees very well with Lozier's value.

Lozier demonstrated quite conclusively that the numbers of positive and negative ions formed for electron energies between 20.9 and 22.8 volts electron energy are equal. This has been verified within experimental error in the present work for the C^{+} and O^{-} ions. Any doubt as to the identification of the ions involved has thus been removed.

Process E: $CO+e \rightarrow C^{+}+O+2e$.—That this process is much more probable than process *D* is seen from the rates at which the C^{+} ion current rises with electron energy below and above 22.8 volts. Thus the C^{+} peak observed at 100 volts electron energy is made up in the main of ions from this process. The shape of the peak is shown in Fig. 8. It is seen to be of type I. The good agreement of the position of the second break at 22.8 volts in the curve for C^{+} against electron

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

[29] H. S. W. Massey, *Negative Ions* (Cambridge, 1938), p. 42.

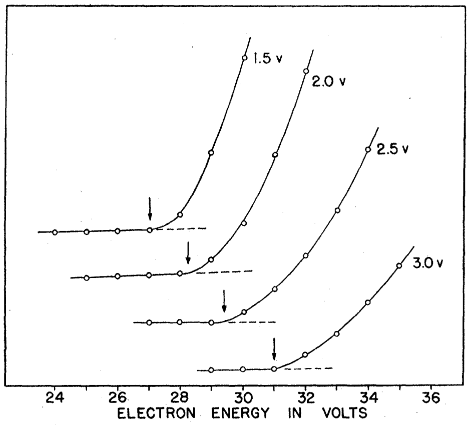

FIG. 13. One set of appearance potential curves for O^+ ions of 1.5, 2.0, 2.5 and 3.0 volts initial kinetic energy. It was found that no better data could be obtained by attempting to take readings at smaller voltage intervals because of the extremely low ion current and the fact that the position on the peak could be checked only before and after the data for each curve were obtained.

energy with Lozier's extrapolated value indicates that ions of zero initial velocity are formed in the process and that for this reason the potential curve involved cannot possess a maximum. Vaughan's conclusion that the C^+ ions possess kinetic energy is untenable if it is to be interpreted as meaning that ions of zero initial kinetic energy are not formed.

Process F: $CO+e\rightarrow C+O^++2e$.—O^+ ions from CO have been observed by previous investigators but have not been studied in any detail. The only quantitative data on them were given by Tate, Smith and Vaughan[3] who report the peak to be 10 percent as high as that of C^+ at 100 volts electron energy and the appearance potential as 27±1 volts. It thus appears to be of interest and importance to ascertain the reason for the low peak height and to attempt to fit energy determinations into the interpretation of other processes.

The dissociation process from which the O^+ ions result could be either $CO+e\rightarrow C^-+O^++e$ or $CO+e\rightarrow C+O^++2e$. Failure to detect C^- ions eliminates the first of these possibilities.

The O^+ peak is plotted below that of C^+ from CO to the observed relative abundance in Fig. 8. The shapes of the two peaks are entirely different, that of O^+ being of type III. It is evident that the low peak height for O^+ ions in comparison with that for C^+ ions is due to the nature of the distribution in kinetic energy of the products rather than to any significant difference in the probability of occurrence of the processes from which they result. The parts of the peaks corresponding to initial kinetic energies of more than 2 volts are about equally high. Thus the assumption that the O^+ ion is not present in any appreciable abundance because the total peak height is small is erroneous.

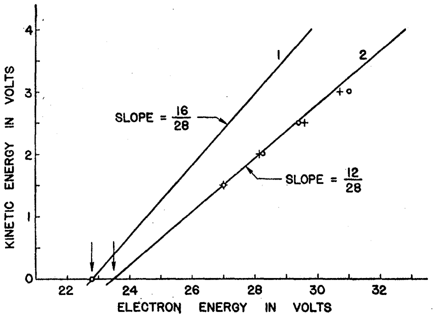

FIG. 14. Relation of the appearance potential and kinetic energy of ions from the dissociation of CO. Curve 1 is for C^+ and curve 2 for O^+. The lines are drawn with the values of slope predicted by the laws of conservation of energy and momentum applied to the dissociation process (see reference cited in footnote 7). Two sets of data are plotted for O^+. In placing curve 2 the data for lower kinetic energies were favored since they were obtained at the higher intensity portions of the peak (see Fig. 8).

The location of the dissociation limit for this process requires a different technique from that used for process E since ions which focus at the maximum of the peak possess an unknown amount of initial kinetic energy. The scale of kinetic energy was calibrated by using as the zero point the position of the maximum of the small O^+ "impurity peak" which remained when the electron energy was reduced to a value below the appearance potential of any ions from CO. The shape of this peak and the fact that the ions result in the main from the dissociation of water vapor impurity are taken as good evidence that the peak is composed of ions possessing almost no initial velocity. The appearance potentials (Fig. 13) of O^+ ions of 1.5, 2.0, 2.5 and 3.0 volts initial kinetic energy were measured by adjusting the ion accelerating potential to the proper positions on the peak of Fig. 8.

Extrapolation of the relation of appearance potential and kinetic energy to zero kinetic energy (Fig. 14) yields 23.5 volts for the level of the dissociation limit above the ground state of the molecule. An interesting comparison may be made here with the datum of Tate, Smith and Vaughan. Their appearance potential, presumably measured on the maximum of the peak, would, according to the lower curve of Fig. 8, be that of ions of approximately 1.5 volts initial kinetic energy. From Fig. 13 it is seen that this ion should be formed first at about 27 volts which is just the value given by Tate, Smith and Vaughan.

The low intensity of the O^+ ion current and the limitations of the method of calibration of the scale of kinetic energy make it necessary to consider the value of 23.5 volts as an upper limit. Any possible correction can be no more than a few tenths of a volt, however, and it is estimated that the true dissociation limit lies no lower than 0.4 volt below 23.5 volts.

Heat of Dissociation of CO · (D(CO))

The energy relations set up for the processes in which O^+, O^- and C^+ are formed limit the values which can be assigned to $D(CO)$. The largest value of $D(CO)$ compatible with the dissociation limit of process F lies in the range 9.5 to 9.6 electron volts. Interpretation[8] of various processes which led to $D(CO)=11.6$ electron volts seems untenable. The value 9.6 volts remains as the only value of $D(CO)$ which yields a consistent interpretation of all the electron impact processes observed in CO.

We have, for example, in process D

$$A(C^+)=D(CO)+I(C)+E(C^+)+EA(O^-)+E(O^-),$$
$$20.9=9.6+11.3+0-2.2+2.2.$$

TABLE II. *Summary of electron impact data for* NO. *Appearance potential in volts.*

	$A(NO^+)$	$A(NO^{++})$	$A(N^+)$	$A(O^+)$	$A(O^-)$
Hogness, Lunn* (mass spectrometer)	9		22	21	
Tate, Smith[28] (total ion current)	9.5 ±0.1				
Tate, Smith, Vaughan[3] (mass spectrometer)	9.5 ±0.1	41 ±1	22±0.5	21	
Hanson[9] (retarding potential)			21.7±0.2		3.2×0.5
Present work (mass spectrometer)	9.5 ±0.1	41.3 ±0.3	19.9±0.2 21.8±0.2	20.5 ±0.2	7.0±0.3 20.0±0.3

* T. R. Hogness and E. H. Lunn, Phys. Rev. **30**, 26 (1927).

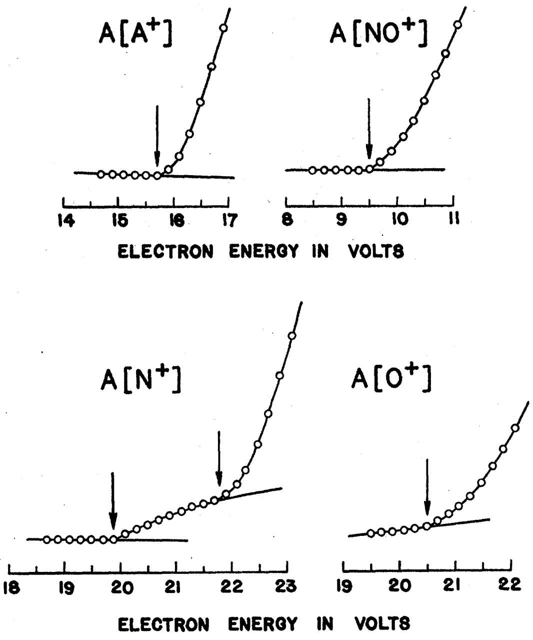

FIG. 15. Typical appearance potential curves for ions from nitric oxide. The slight slope of the O^+ curve below the break is due to amplifier drift and a small amount of ion current from dissociation of water vapor impurity.

For process E we have

$$A(C^+)=D(CO)+I(C)+E(C^+)+E(O),$$
$$22.8=9.6+11.3+0+1.96,$$

For process C we have

$$A(O^-)=D(CO)+E(C)-EA(O^-)+E(O^-),$$
$$9.5=9.6+0-2.2+2.2.$$

In process F the relations are

$$A(O^+)=D(CO)+I(O)+E(C)+E(O^+),$$
$$23.1=9.6+13.5+0+0.$$

The assignments of $E(C)=E(C^+)=0$ and $EA(O^-)=E(O^-)=2.2\pm0.2$ seem reasonable from spectroscopic data and earlier data on impact phenomena. It should be noted that the value $D(CO)=9.6$ volts depends on the appearance potentials in processes C, D and E which are not subject to the same error involved in $A(O^+)$. They were determined from peaks of a different type.

The value $D(CO)=9.6$ volts is not in agreement with either of two values proposed by band spectroscopists, however. Schmid and Gerö[30] interpret the three predissociation limits at 9.61,

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[30] R. Schmid and L. Gerö, Zeits. f. Physik **99**, 281 (1936).

11.11 and 11.60 volts as corresponding to three dissociation limits of the molecule leading directly to $D(\mathrm{CO}) = 6.921$ volts.[31] Schmid[32] has attempted to reconcile the electron impact data of Lozier with this value of $D(\mathrm{CO})$ by assuming tetravalent carbon products. He calculates the level of $\mathrm{C}^+({}^4P) + \mathrm{O}({}^3P)$ as 23.5 volts above the ground state. This is outside the experimental error for $A(\mathrm{C}^+)$ at 22.8 volts. Furthermore if $A(\mathrm{C}^+)$ is in error it would in all probability be *higher* than the actual dissociation limit.

Herzberg,[33] on the other hand, considers only the predissication at 11.11 volts as corresponding to a dissociation limit of the molecule. The predissociation at 11.60 volts is considered to be only an upper limit for the level of some asymptote and that at 9.61 volts as accidental predissociation. Herzberg's final conclusion is that $D(\mathrm{CO})$ is most probably 9.144 volts[31] with the limit at 11.11 volts corresponding to $\mathrm{C}({}^3P) + \mathrm{O}({}^1D)$. It is possible to interpret only process *C* of the dissociation processes observed in CO under electron impact on this basis, however. This can be done by assuming unexcited O^- and C in the ${}^1S$ state. If $D(\mathrm{CO}) = 9.144$ volts it is necessary to assume an experimental error in the appearance potentials for processes *D* and *E* of about 0.5 volt. This conclusion seems a little severe on the basis of the agreement of independent electron impact experiments in H_2, N_2 and NO by different methods with each other and with band spectroscopic data which is much more conclusive than that for CO.

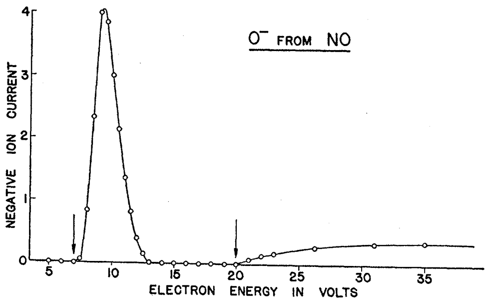

FIG. 16. Efficiency of formation of O^- ions from nitric oxide as a function of the energy of the impacting electrons. The ion accelerating potential was adjusted to the maximum of the ion peak at each reading.

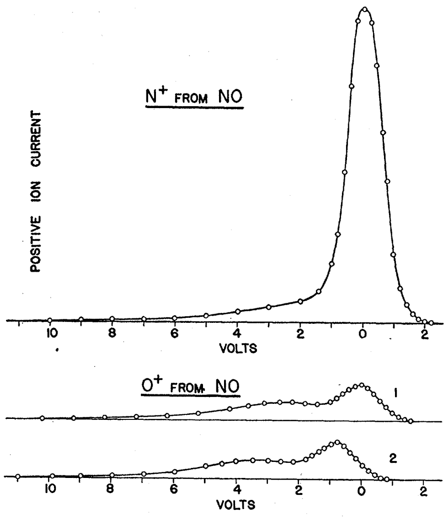

FIG. 17. Peak shapes for N^+ and O^+ ions from nitric oxide. Position 1 of the O^+ peak relative to the scale of kinetic energy corresponds to the construction of the peak by method *A*, position 2 to method *B* (see text and Fig. 7). The maximum of the N^+ peak corresponds to an accelerating potential of about 300 volts.

All thermochemical data on the heat of sublimation of carbon, $L(\mathrm{C})$, published prior to Jan. 1, 1934 have been reviewed by Bichowsky and Rossini[34] who conclude that the value most probably lies in the range 110 to 170 kcal. $D(\mathrm{CO}) = 9.6$ volts (221.3 kcal.) yields $L(\mathrm{C}) = 5.9$ volts (136.3 kcal.).

Goldfinger and Jeunehomme[35] have calculated vapor pressure curves for C from three values for $L(\mathrm{C})$ (170.2, 124.8 and 108.3 kcal.)[31] which are in agreement with the predissociation limit in CO at 11.11 volts. It was found that the direct measurements of the vapor pressure of C described in the literature lie mostly between the curves calculated for $L(\mathrm{C}) = 170.2$ kcal. and 124.8 kcal. Although $L(\mathrm{C}) = 170.2$ kcal. gives the better agreement, it was eliminated for spectroscopic reasons and $L(\mathrm{C}) = 124.8$ kcal. corresponding to $D(\mathrm{CO}) = 9.144$ volts taken as the most probable value. It should be pointed out that the value

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[31] The new conversion factor of 8066.0 cm^{-1} per electron volt has been used in this paper. For this reason a number of the values cited differ slightly from those given in the original papers. See Table 2 in G. Herzberg, *Molecular Spectra and Molecular Structure, I. Diatomic Molecules* (Prentice-Hall, New York, 1939).

[32] R. Schmid, Zeits. f. Physik **99**, 274 (1936).

[33] G. Herzberg, Chem. Rev. **20**, 145 (1937).

[34] R. F. Bichowsky and F. D. Rossini, *The Thermochemistry of Chemical Substances* (Reinhold, New York, 1936).

[35] P. Goldfinger and W. Jeunehomme, Trans. Faraday Soc. **32**, 1591 (1936).

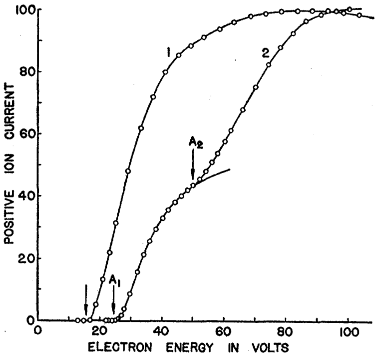

FIG. 18. Efficiency of formation of ions from N_2. Curve 1 is for N_2^+ ions and curve 2 for ions of $m/e=14$. A_1 indicates the onset potential of process C and A_2 that of process B. The ordinates of each curve have been arbitrarily chosen and have no relative significance.

$L(C)=136.3$ kcal. based on $D(CO)=9.6$ volts is perhaps in better agreement with vapor pressure measurements as it is somewhat higher than the "spectroscopic" value chosen by Goldfinger and Jeunehomme.

Nitric oxide[36]

Of particular interest in studying NO is the process $NO \rightarrow N^+ + O^-$ and the dissociation process in which O^+ is formed. The results of this paper and of earlier work are given in Table II. A number of processes have been identified.

Process A: $NO+e \rightarrow NO^+ + 2e$.—The value $I(NO)$ (Fig. 15) agrees very well with previous measurements.

Process B: $NO+e \rightarrow NO^{++} + 3e$.—$A(NO^{++})$ was found to be 41.3 ± 0.3 volts.

Process C: $NO+e \rightarrow N+O^-$.—The efficiency of formation of O^- ions as a function of electron energy is shown in Fig. 16. The onset potential of the resonance process measured at the maximum of the ion peak is 7.0 ± 0.3 volts. The fact that this potential is higher than that obtained by extrapolation by Hanson[9] indicates that ions of zero initial kinetic energy are *not* formed in the process.

Process D: $NO+e \rightarrow N^+ + O^- + e$.—This process has been identified for the first time in this work. The value of $A(N^+)$ is found at 19.9 ± 0.2 volts (Fig. 15). 20.0 ± 0.3 volts was obtained for $A(O^-)$. The appearance potential $A(N^+)$ was measured with the same ion accelerating field as was used to obtain the N^+ peak in process E and it is believed that the ions (N^+) had zero kinetic energy here as they did in process E.

The onset potential of this process is very nearly equal to the electron energy calculated from $D(NO)$[37] and $I(N)$ at which the unexcited products N^+ and O should appear. (19.84 volts).[38, 31] If Lozier's value (2.2 volts) is assumed for $EA(O)$[8] it is necessary that $E(N^+)+E(O^-)$ equal approximately 2.2 volts. The nearest state in N^+ is the ^1D at 1.90 volts. Identification of this value with the 2.2-volt excitation is a possibility but better numerical agreement is obtained if the analogy with the process $CO+e \rightarrow C^+ + O^- + e$ is carried out and the excitation assigned to the O^- ion. This excited state of O^-, lying very near the positive energy continuum, is the only one which the theory of the negative ion renders at all probable.[39]

Process E: $NO+e \rightarrow N^+ + O + 2e$.—The N^+ peak shown in Fig. 17 is to be attributed mainly to ions from this process. The shape of the peak is of type I. The appearance potential of 21.8 ± 0.2 volts (second break in the C^+ curve of Fig. 15) measured at the maximum of the peak is in better agreement with Hanson's extrapolated

TABLE III. *Summary of electron impact data for* N_2. *Appearance potential in volts.*

	$A(N_2^+)$	$A(N^+)$	$A(N_2^{++})$	$A(N^{++})$
Vaughan[2] (mass spectrometer)	15.8 ± 0.1	24.5 ± 0.1	40 ± 1(?) 47 ± 1	
Tate, Smith[28] (total ion current)	15.7			
Lozier[7] (retarding potential)		24.27 ± 0.1		
Tate, Smith, Vaughan[3] (mass spectrometer)	15.65 ± 0.1			
Present work (mass spectrometer)	15.7 ± 0.1	24.3 ± 0.2	49.5 ± 0.5	64 ± 2

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[36] A part of this work on NO was presented at the New York Meeting of the American Physical Society February 24, 1940. H. D. Hagstrum and J. T. Tate, Phys. Rev. **57**, 561A (1940).

[37] $D(NO)=5.29$ volts calculated from $D(N_2)=7.384$ volts, $D(O_2)=5.082$ volts and the heat of formation of NO from thermochemistry. See G. Herzberg, *Molecular Spectra*, etc., Table 36 and R. F. Bichowsky and F. D. Rossini, reference 34.

[38] Atomic excitation and ionization energies have been taken from R. F. Bacher and S. Goudsmit, *Atomic Energy States* (McGraw-Hill, New York, 1932).

[39] For a discussion of the possibility of excited states in negative ions see O. Oldenberg, Phys. Rev. **43**, 534 (1933) (especially footnote 9 in this reference); W. W. Lozier, Phys. Rev. **46**, 268 (1934) and H. S. W. Massey, reference 29, p. 19.

value of 21.7±0.2 volts than previous mass spectrometric data. This agreement between the data of the two electron impact methods is again taken as evidence that ions of zero initial velocity are formed in the process. The N^+ product is unexcited whereas the O atomic product is in its ^1D state. The energy difference between the two breaks in the N^+ curve of Fig. 15 (1.9 volts) is thus to be interpreted as the excitation of the ^1D state rather than the electron affinity of the oxygen atom.

Process F: $NO+e\rightarrow N+O^+ +2e$.—The O^+ peak is shown in Fig. 17 drawn to the same scale used in the curve for N^+. The peak is assumed to be of type II. In curve 1 the ions which focus at the maximum are assumed to have no kinetic energy. But the appearance potential of 20.5±0.2 volts (Fig. 15) is not compatible with the known value of $D(NO)$ and excitation energies. One must assume then that the dissociation products are unexcited but have kinetic energy. The total kinetic energy turns out to be $20.5-18.9$ or 1.6 electron volts of which the O^+ ion possesses 0.75 electron volt. The correct position of the O^+ peak is then that shown in curve 2 in which the maximum is at 0.75 volt.

The experimental curve 2 can be most satisfactorily constructed from the curve showing the distribution in kinetic energy of the ions at the instant of formation by assuming that the upper potential energy curve has a maximum of 1.6 volts.

Herzberg and Mundie[40] have assumed a potential maximum of 1.3 volts to explain a predissociation limit. It appears that the possible existence of potential curves with maxima as high as is necessary to postulate here is not in doubt.

TABLE IV. *Summary of electron impact data for* O_2. *Appearance potential in volts.*

	$A(O_2^+)$	$A(O_2^{++})$	$A(O^+)$	$A(O^-)$
Hogness, Lunn* (mass spectrometer)	13		20	
Kallmann, Rosen** (mass spectrometer)	13		19.5	
Tate, Smith[28] (total ion current)	12.5			6
Lozier[8] (retarding potential)				2.9±0.2 12.0±0.2
Present work (mass spectrometer)	12.3±0.1	50.0±0.5	19.2±0.2	3.0±0.4 18.9±0.4

* T. R. Hogness and E. G. Lunn, Phys. Rev. **27**, 732 (1926).
** H. Kallmann and B. Rosen, Zeits. f. Physik **61**, 61 (1930).

Nitrogen

Data from previous electron impact studies in N_2 are given in Table III. Restudy of this molecule with a mass spectrometer was undertaken to extend the experimental study of peak shapes and to obtain, if possible, a definite interpretation of the increases in the efficiency of production of ions of $m/e=14$ observed by Vaughan.[2]

Process A: $N_2+e\rightarrow N_2^+ +2e$.—The value of 15.7±0.1 volts obtained for $I(N_2)$ is in agreement with previous electron impact data listed in Table III and with the value of 15.581 volts determined from the limit of a Rydberg series of bands in the molecular spectrum.[41, 31]

Process B: $N_2+e\rightarrow N_2^{++}+3e$.—The efficiency of formation of ions of $m/e=14$ as a function of electron energy is shown in Fig. 18. The second break at 49.5±0.5 volts does not agree very well with the position of either break reported by Vaughan[2] but is undoubtedly to be identified with the more pronounced break in his curve at 47 volts. It is believed that the first break in Vaughan's curve at 40 volts may be the onset of the formation of CO^{++} ions. CO was an acknowledged impurity in the apparatus. Furthermore the energy difference between the breaks (7 volts) is just the difference found in this work between $A(CO^{++})$ and the second break in curve 2 of Fig. 18. No definite identification of the ionization or dissociation process responsible for this increase in the ion current has as yet been made. It will be indicated in the discussion of process *C* that the break of 49.5 volts may now be ascribed to the onset of double ionization of the molecule. Such a process is to be expected from the results for other molecules.

Process C: $N_2+e\rightarrow N^+ +N+2e$.—The peak at $m/e=14$ for 100-volt electrons is of type I and is very similar in appearance to the peaks for C^+ from CO and N^+ from NO. (see Figs. 8 and 17). The appearance potential measured at the maximum of the peak is 24.3±0.2 volts. Agreement with Lozier's extrapolated value of 24.27 volts[7]

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[40] G. Herzberg and L. Mundie, J. Chem. Phys. **8**, 263 (1940).

[41] R. S. Mulliken, Phys. Rev. **46**, 144 (1934); A. van der Ziel, Physica **4**, 373 (1937); R. E. Worley and F. A. Jenkins, Phys. Rev. **54**, 305 (1938).

indicates that ions of zero initial velocity are formed.

The ion peak at 100 volts electron energy is also made up of ions from the process which begins at 49.5 volts. These ions may be either N_2^{++} or N^+ from a second mode of dissociation of the molecule. The efficiency of formation of ions of 2 volts initial kinetic energy as a function of electron energy was determined by setting the ion accelerating potential at a value 2 volts less than that corresponding to the maximum of the peak. The curve shows no second break at any point and resembles curve 1 of Fig. 18. This result indicates that the process starting at 49.5 volts is double ionization of the molecule. If the ions were N^{++} a second break should have been observed at about 53.5 volts electron energy in the efficiency curve for 2 volt ions.

Process D: $N_2+e\rightarrow N^{++}+N+3e$.—An extremely small ion peak was observed at the ion accelerating potential corresponding to $m/e=7$. The abundance of the ion relative to N_2^+ is only 0.006 percent. These ions could either be N^{++} resulting from dissociation of the molecule or N_2^{++++}. Since no N_2^{+++} ions were found at the $m/e=9.35$ position it is likely that the ions of $m/e=7$ are N^{++}. Furthermore the shape of the ion peak appears to be of type III indicating that the ions possess considerable initial kinetic energy. This could be possible only if the ions are products of dissociation rather than multiple ionization. The appearance potential of the ions at the maximum of the distribution was found to be 64±2 volts. Lack of knowledge of the kinetic energy of the ions precludes any further interpretation of the process.

Oxygen[42]

The work on oxygen revealed the formation of O_2^{++} and O^{++} and gave additional information on processes in which other ions were formed. The results of this and other recent experiments are shown in Table IV.

Process A: $O_2+e\rightarrow O_2^++2e$.—A value of 12.3±0.1 volts was obtained for $I(O_2)$. This is lower than the value of 12.5 volts obtained by Tate and Smith[28] but is in better agreement with the value of 12.2 volts obtained by means of the cycle $I(O_2)=D(O_2)+I(O)-D(O_2^+)$ and spectroscopic determinations of $D(O_2)$, $I(O)$ and $D(O_2^+)$.[43]

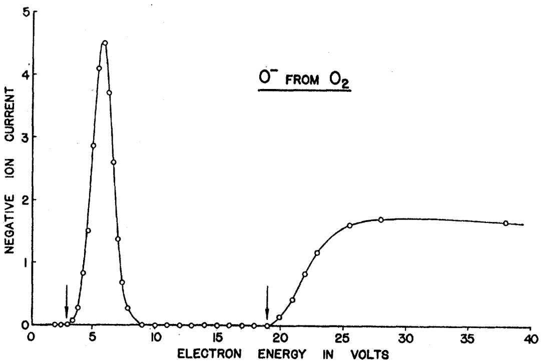

FIG. 19. Efficiency of formation of O^- ions from oxygen. The spectrometer was adjusted to collect ions of zero initial kinetic energy.

Process B: $O_2+e\rightarrow O_2^{++}+3e$.—The relative efficiency of formation of ions of $m/e=16$ from O_2 by electrons of energies up to 100 electron volts has been measured. The curve is similar to that for ions of $m/e=14$ from N_2 shown in Fig. 18 (curve 2). In this case, however, the second break occurs at 50.0±0.5 volts. It has been demonstrated by the method used for process *B* in N_2 that this break indicates the onset of the production of O_2^{++}.

Process C: $O_2+e\rightarrow O+O^-$.—The efficiency of formation of O^- ions as a function of electron energy is shown in Fig. 19. The first appearance potential at 3.0±0.4 volts is undoubtedly to be identified with the value of 2.9 volts obtained by extrapolation by Lozier[8] for ions of zero initial kinetic energy. At first sight this result appears to contradict Lozier's observation that ions of kinetic energy less than 1.3 volts are not formed. It is possible, however, that the ions observed in this work and those observed by Lozier result from transitions to different potential curves having the same asymptote. Massey[44] has interpreted the resonance process observed by Lozier as transition to the unstable Σ_u state of O_2^-. It is suggested that the process observed in

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[42] A part of this work on O_2 was presented at the Washington Meeting of the American Physical Society, April 26, 1940. J. T. Tate and H. D. Hagstrum, Phys. Rev. **57**, 1071A (1940).

[43] R. S. Mulliken and D. S. Stevens, Phys. Rev. **44**, 720 (1933).

[44] H. S. W. Massey, reference 29, pp. 28 and 52.

this work with a mass spectrometer involves transition to the Π_u state. If the potential curve for this state has the position proposed by Massey ions of zero initial kinetic energy could be formed. Furthermore if the ions from this process possess initial kinetic energies no greater than a fraction of a volt they would not be observed by the retarding potential method.

Process D: $O_2+e\rightarrow O^++O+2e$.—The shape of the O^+ ion peak at 100 volts electron energy is of type I. Ions of kinetic energy *near* zero are relatively numerous. The appearance potential measured at the maximum of the peak (19.2±0.2 volts), however, is 0.5 volt greater than the potential at which ions of zero initial velocity should appear. $[D(O_2)+I(O)=5.08+13.62=18.7$ volts]. On the basis of the accuracy of similar measurements in other molecules this difference is considered to be well outside the experimental error. It cannot be attributed to excitation of the products, as neither O nor O^+ possesses an appropriate state. The appearance potential must then correspond to ions of 0.25 volt initial kinetic energy. The peak shape analysis is compatible with a potential curve which has a maximum 0.5 volt above the asymptote (see the discussion of process *F* in NO).

Process E: $O_2+e\rightarrow O^++O^-+e$.—The second appearance potential of O^- ions from O_2 is 18.9±0.4 volts. (Fig. 19). This value is 0.2 volt higher than the potential energy of the products O^++O above the ground state of O_2. There can, however, be little doubt that two values should be identified. The accuracy of the datum for this process is not to be compared with that for process *D* which is about 20 times as probable.

Since it is not possible to identify the appearance potential with any other dissociation limit of the molecule, the products O^++O^- are excited by very nearly the amount $EA(O)=2.2$ volts. Since the lowest state of O^+ is the $^2D^0$ at 3.3 volts the O^- ion must assume all of this energy. This is an additional example of the formation of the O^- ion in the "loosely bound" state.[39]

The curve of O^+ ion current as a function of electron energy exhibits only the single break at 19.2 volts which has been identified with process *D*. Since O^- ions from process *E* are observed at 18.9 volts one questions why O^+ ions which are formed in equal numbers in the process are not observed at the same potential. This is to be explained as follows. The measurement of $A(O^+)$ was made at the maximum of the O^+ peak which has been shown to correspond to ions of 0.25 volt kinetic energy. When the electron energy was varied the ion accelerating potential was not changed so that ions of 0.25 volt kinetic energy were being collected when the onset potential of process *E* was measured. Since the dissociation limits for $O^+(^4S^0)+O(^3P)$ and $O^+(^4S^0)+O^-$ (excited by 2.2 volts) almost coincide, only one appearance potential should be observed for O^+ ions of any initial velocity.

Process F: $O_2+e\rightarrow O^{++}+O+3e$.—An extremely small ion peak was observed at the $m/e=8$ position. Its abundance was of the order of 0.01 percent of O_2^+. Failure to find any ions at the position corresponding to O_2^{+++} indicates that the ions of $m/e=8$ are more likely O^{++} than O_2^{++++}. No appearance potential or peak shape measurements were attempted. Because of the effect of O_2 on the filament of the spectrometer the gas pressure and the electron beam intensity could not be run high enough to make such measurements possible.

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