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A Study of Kinetic Energies of Atomic Ions Formed by Electron Impact in Nitric Oxide and Hydrogen Chloride

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A study was made of the kinetic energy of the atomic ions formed by electron impact in NO and HCl. Their energy distribution was measured as a function of the electron energies at impact, and their ionization potentials were determined. The most probable values of the heats of dissociation of the molecules and of the molecular ions were calculated. Negative ions possessing up to 2.5 volts kinetic energy were observed in NO, and the electron affinity of oxygen was calculated. Negative ions found in HCl had less than 0.5 volt energy. The following is a summary of the results and the probable processes:

PROBABLE PROCESS	KINETIC ENERGY OF IONS	HEAT OF DISSOCIATION
$NO^+ \rightarrow N^+ + O(^1D_2)$	0 to 6 VOLTS	
$NO^+ \rightarrow N + O^+$		9.3 ± 0.2 VOLTS
$NO \rightarrow N + O$		5.3 ± 0.2
$NO + e \rightarrow N + O^-$	1 to 2.5	ELECTRON AFFINITY OF $O = 2.1 \pm 0.5$
$HCl^+ \rightarrow H^+ + Cl(^2P)$	0 to 10	
$HCl^+(^2\Pi) \rightarrow H + Cl^+$		4.8 ± 0.2
$HCl^+ \rightarrow H^+ + Cl$	2 to 6	EXCITATION ENERGY OF $Cl \backsimeq 11.6$
$HCl \rightarrow H + Cl$		4.7 ± 0.2
$HCl \pm e \rightarrow H + Cl^-$	LESS THAN 0.5	ELECTRON AFFINITY OF $Cl \backsimeq 4.0$

INTRODUCTION

It was predicted by the quantum mechanics[1–4] that in hydrogen positive ions which would have kinetic energies much greater than the normal thermal energies could be formed by dissociation following electron impact. This was experimentally verified by Bleakney and Tate[5, 6] and later by Lozier,[7] who made a detailed study of the phenomenon.

Tate and Lozier,[8] and Lozier[9–11] have shown that such ions are also formed in all the molecular gases which they studied. Besides hydrogen the gases which have been studied are N_2, CO and O_2. Furthermore, it was shown that when negative ions are formed as dissociation products, they also might have several volts energy.

The formation of high energy ions is interpreted as arising from a transition to an unstable electronic state of the molecule. When this occurs, dissociation takes place, and the molecular components fly apart with velocities determined by: (1) the energy absorbed by the normal molecule, (2) the final states of the dissociation products and (3) the masses of the products. Thus in the process, $AB^+ \rightarrow A^+ + B$, the kinetic energy of the ion, A^+, is[8]

$$V_F = M_B/(M_A + M_B)[V_i - (U_2 - U_1)]. \quad (1)$$

M_A and M_B are the masses of the component atoms A and B, respectively, V_i is the energy absorbed by the normal molecule in its transition to the unstable state (i.e., the "ionization potential"), and $(U_2 - U_1)$ is the difference in potential energy between the final and the initial states of the molecule. Since the above formula was derived simply from considerations of the conservation of energy and of momentum it is, therefore, also applicable to the case of negative ions.

The heat of dissociation of the normal molecule and of the molecular ion may be calculated[8] if $(U_2 - U_1)$ is determined from measurements of V_F and V_i, and if the masses and the excitation energy of the products are known. The heat of dissociation of the normal molecule is given by

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[1] Heitler and London, Zeits. f. Physik **44**, 455 (1927).
[2] Burrau, Kgl. Dansk. Selsk. Math. Fys. **7**, 14 (1927).
[3] Morse and Stuekelberg, Phys. Rev. **33**, 932 (1929).
[4] Condon, Phys. Rev. **35**, 658 (1930).
[5] Bleakney and Tate, Phys. Rev. **35**, 658 (1930).
[6] Bleakney, Phys. Rev. **35**, 1180 (1930).
[7] Lozier, Phys. Rev. **36**, 1285 (1930).
[8] Tate and Lozier, Phys. Rev. **39**, 254 (1932).
[9] Lozier, Phys. Rev. **43**, 776 (1933).
[10] Lozier, Phys. Rev. **44**, 575 (1933).
[11] Lozier, Phys. Rev. **46**, 268 (1934).

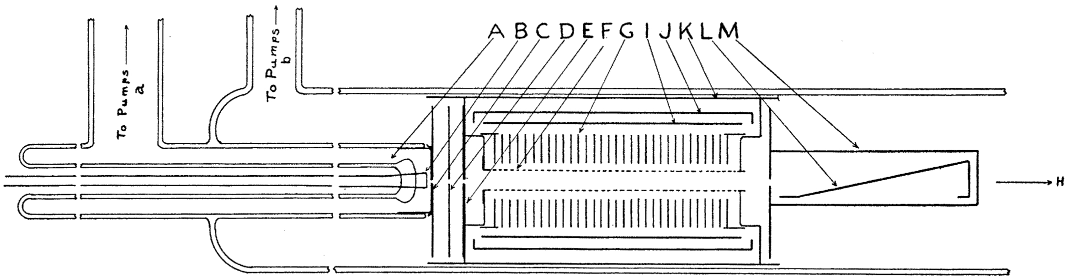

FIG. 1. The experimental tube. The filament chamber *A* is formed by closing the Pyrex tube with a snugly fitting spun copper cup. A 0.5 mm diameter hole in the center of this cup allows electrons to pass and be accelerated to the desired energy by controlled potentials placed between the disks *C*, *D* and *E*. After passing down the axis of the tube (in the direction of a collimating magnetic field *H*) these electrons are collected in the trap *LM*. The cylindrical wire gauze *F* is connected to *E* to give a field free region of ionization. The disks *G* allow only those ions to pass whose velocity is 98 percent perpendicular to the electron beam. The ions which qualify in direction of travel and which have sufficient energy to penetrate the differences of potential which may be placed between the elements *F*, *G* and *I* are collected on the cylinder *I*. *J* is a guard ring, while *K* is an electrical shield.

the formula,

$$D(AB) = (U_2 - U_1) - I_A - E,$$

where I_A is the ionization potential of atom A (assuming that A comes off charged) and E is the total excitation energy of the products. The heat of dissociation of the normal molecular ion, AB^+, is given by

$$D(AB^+) = (U_2 - U_1) - I_m - E, \tag{2}$$

where I_m is the ionization potential of the molecular ion. Similarly, if negative ions having large kinetic energies are formed in the gas, the electron affinity of the atom may be calculated. Thus, if B^- ions having kinetic energy are formed, the electron affinity of B is

$$E(B) = D(AB) - (U_2 - U_1) - E. \tag{3}$$

Thus, aside from showing the presence of unstable electronic levels in the ionized molecule, a study of the formation of high velocity ions by electron impact is valuable in that it gives values for heats of dissociation and electron affinities.

APPARATUS

The experimental tube, a modification of Tate and Lozier's apparatus,[8] was built entirely from copper, tungsten and Pyrex. Because NO and HCl are easily dissociated by a hot tungsten filament, it was necessary to employ differential pumping to maintain as low a pressure as possible around the filament while the pressure in the remainder of the tube was high enough to allow accurate measurements to be made. The leads *a* and *b* (Fig. 1) go to the same set of pumps; a difference in the rates of effusion through the two leads is effected by the difference in their diameters. A mercury cut-off in series with *b* can be used to lower its effusion rate still more.

In all cases the apparatus was baked out first in a quartz furnace at 800°C under a vacuum, and later in the Pyrex tube for thirty hours at 360°C.

The flow method was used to admit the gas to the apparatus, the pumps being run continuously while the gas leaked in through a capillary tube. The pressure behind the capillary was adjusted to give a working pressure in the experimental tube of about 5×10^{-5} mm of Hg.

The nitric oxide was prepared by the action of nitric acid on electrolytic copper and purified by being passed through water and over potassium hydroxide and by being fractionally distilled. A mass-spectrograph analysis by Dr. A. L. Vaughan showed the only measurable impurity was N_2O in concentration less than one percent.

The sample of hydrogen chloride was prepared by the action of H_2SO_4 on NaCl. It was dried over P_2O_5, and fractionally distilled in the usual manner. A mass-spectrograph analysis run in collaboration with Mr. A. O. Nier showed no measurable impurities.

A vacuum tube electrometer[12] was used to measure the ion currents. When used with an input resistor of 2.3×10^{10} ohms, the maximum

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[12] Distad and Williams, Rev. Sci. Inst. **5**, 289 (1934).

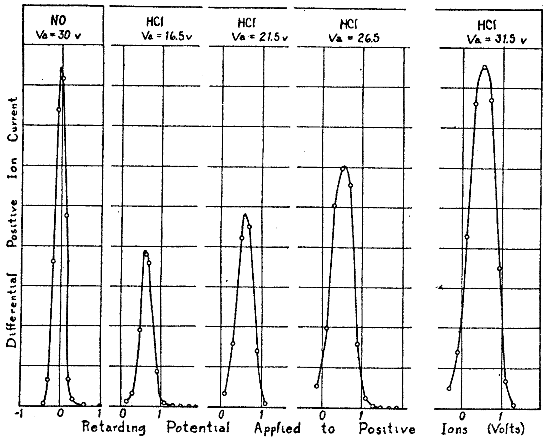

FIG. 2. Distribution in kinetic energy of molecular ions.

current sensitivity available was 3.3×10^{-16} amp./mm with random fluctuations of less than 2 mm.

METHOD

Two types of data were obtained: (1) the minimum electron energy V_i necessary to form an ion having a kinetic energy V_F, and (2) the kinetic energy distribution of ions for various electron energies.

The velocity distribution of the ions was found by the retarding potential method. The ions, in traversing the region from gauze to defining disks to collector, lost or gained an energy equal to the algebraic sum of the voltages applied between these elements. It was customary in the work on positive ions to apply a drawing out potential of 3 volts in the gauze-grid region, while this potential plus the retarding potential was applied in the opposite direction in the grid-collector region. With the electron energy fixed at some value V_a, the retarding potential V_R was changed in steps of ΔV_R and the corresponding change in positive ion current ΔI^+ was measured. ΔI^+ was, then, proportional to the number of ions having energies between $V_R - \Delta V_R/2$ and $V_R + \Delta V_R/2$. A plot of ΔI^+ *vs.* V_R gives the kinetic energy distribution of the ions. In practice ΔV_R was 0.4 volt for NO and 0.2 volt for HCl. To make it possible to utilize a high sensitivity in the amplifier, the potential drop across the input resistor was balanced by a potentiometer between the input grid and the positive end of the resistor. The sensitivity utilized in the amplifier was then 10^{-14} amp./mm.

When a retarding potential V_R will just prevent an ion from reaching the collector, the ion must have started from the electron beam with a kinetic energy equal to V_R unless there were other fields present or if there were a magnetic field present to curve the path of the ions. Since a magnetic field of 158 oersteds parallel to the tube axis was used, the ions must have started with an energy $(300b^2eH^2)/(8mC^2)$ volts[7] greater than the retarding potential. To measure the contact potentials and the space charge that might exist in the tube, use was made of the fact that the most abundant ions, the molecular ions, have only thermal velocities of a few hundredths of a volt. Velocity distribution curves of these ions are given in Fig. 2. Their maxima should within experimental error appear at $V_R = 0$ volts; their measured position gives the value of the inherent potentials in the tube and therefore the

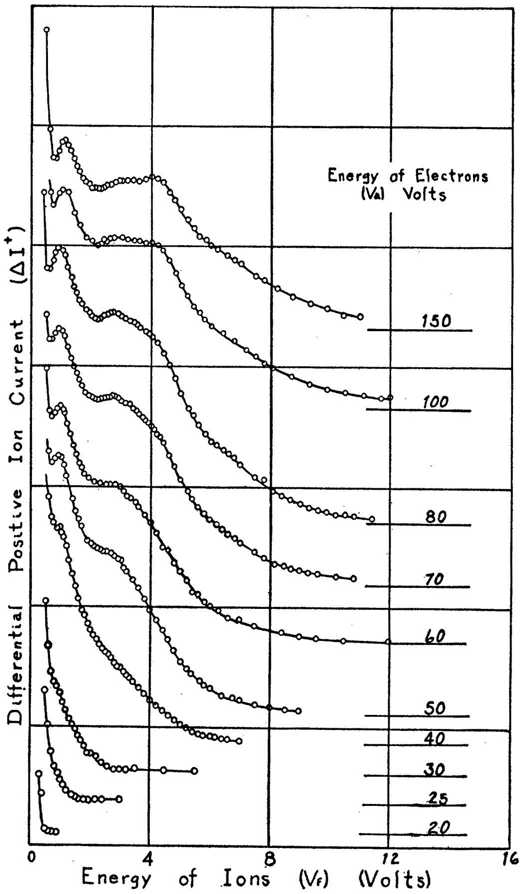

FIG. 3. Distribution in kinetic energy of positive ions formed in NO at various electron energies.

corrections to be applied to V_R. Space charge in the tube appeared to be negligible since the position of the maxima in Fig. 2 did not vary with pressure or electron current.

To measure the minimum electron energies V_i necessary to produce ions having kinetic energies V_F the following method was used: With the retarding potential set to give the desired V_F, the energy V_a of the electrons was varied and the ion currents were recorded. An upward break in the curve thus obtained gave the onset potential of the ion having the kinetic energy V_F. The voltage scale for the electrons was calibrated from the observed onset potential of the molecular ion and from the known ionization potential of the molecule. (Drawing-out potentials in the gauze-grid-collector regions served to sweep the molecular ions into the collector.) For the work on NO, Tate and Smith's value[13] of 9.5 volts was used for the ionization potential; for the work on HCl the ionization potential used was 12.9 volts from the work of A. O. Nier and the author.[14]

Negative ions were studied in much the same way as the positive ions. In addition the relative efficiency of formation of the total number of negative ions was measured as a function of the electron energy.

RESULTS AND CONCLUSIONS

Nitric oxide

The distribution in kinetic energy of the positive ions is given in Fig. 3. The increments in ion current have been reduced to the same pressure and electron current. As one might expect, the ions of higher velocity become relatively more abundant as the incident electron energy is increased. We note that the curves have two maxima, a broad maximum at about 3 volts kinetic energy, and a very sharp peak at about 1 volt. The sharp peak, which is present in all the curves above 30 volts electron energy, is probably due to ions formed by the dissociation of NO^+ (excited) from a flat repulsive potential energy curve. The ions in the broad peak must be due to a dissociation of NO^+ from a rather steep potential energy curve, there being a rise of about 10 volts in the Frank-Condon region.

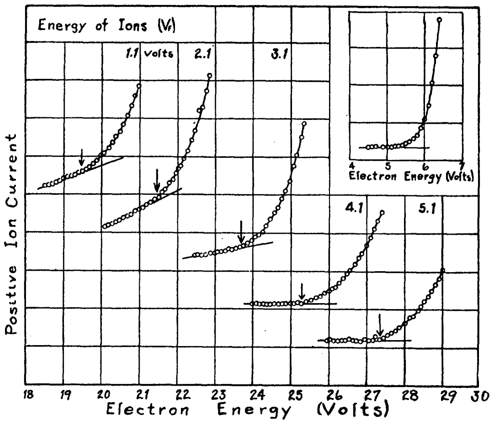

FIG. 4. Ionization potentials of positive ions having kinetic energy in NO.

In Fig. 4 we have a sample of the curves used to determine the onset potentials, V_i, of ions having kinetic energies, V_F. The curve in the inset is for the onset of NO^+, and it is used to calibrate the electron voltage scale. The mass-spectrograph studies of Hogness and Lunn,[15] and of Tate, Smith and Vaughan[16] have shown that both N^+ and O^+ are formed in NO. Vaughan[17] has also shown that the amount of O^+ formed was less than 5 percent of the N^+ formed. The upward breaks in the above curves were therefore assumed to be due to the onset of N^+ ions. This assumption gives good agreement with the experimental value of the slope of the V_i *vs.* V_F curve given in Fig. 5. From Eq. (1) we note that V_F is a linear function of V_i. The experimental values of these quantities are plotted in Fig. 5 and a straight line of the theoretical slope 16/30 is drawn through the points. The closed circles are from data taken earlier on another sample of gas. The intercept gives $(U_2 - U_1) = 21.7$ volts as the weighted mean. It is to be noted that Hogness and Lunn[15] and also Tate, Smith and Vaughan[16] give 22.0 volts for the ionization potential of N^+. One would expect the mass-spectrograph value to be higher inasmuch as the kinetic energy carried by the ions is not corrected for. To calculate the probable observational error, $(U_2 - U_1)$ was calculated for each of the 21 observations and the probable error obtained from the method of least squares. The value so

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[13] Tate and Smith, Phys. Rev. **39**, 270 (1932).

[14] Nier and Hanson, Phys. Rev. **48**, 477 (1935).

[15] Hogness and Lunn, Phys. Rev. **30**, 26 (1927).

[16] Tate, Smith and Vaughan, Phys. Rev. **48**, 525 (1935).

[17] Vaughan, Thesis, Univ. of Minn. (1934).

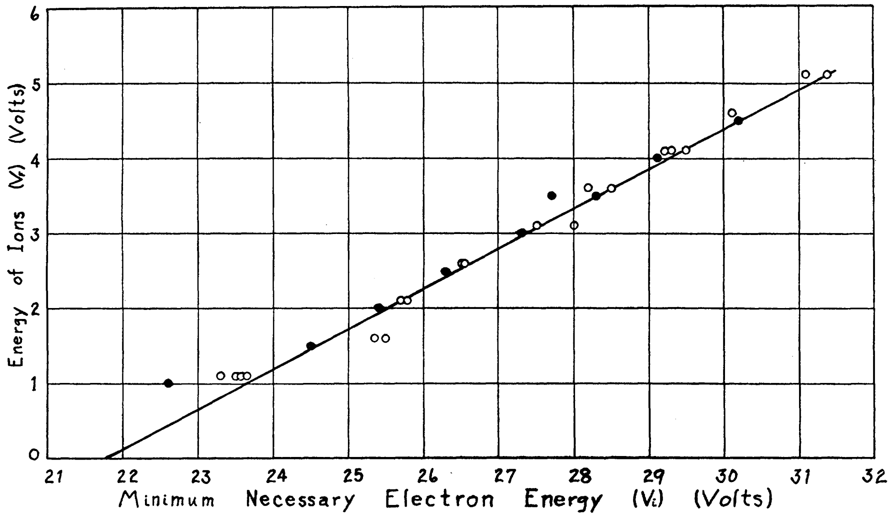

FIG. 5. Kinetic energies *vs.* ionization potentials of positive ions in NO.

obtained was ±0.03 volt; however, it was felt that a safer estimate for the probable systematic error would be ±0.2 volt.

If one assumes the process for forming these kinetic energy ions in NO to be $NO^+ \rightarrow N^+ + O$, the heat of dissociation of NO would be $D(NO) = 21.7 - 14.48 = 7.22$ volts, where 14.48 volts is the spectroscopic value for the ionization potential of atomic nitrogen. Kaplan,[18] however, has shown from band spectra that $D(NO) \leqq 6.1$ volts. We must therefore assume that one of the products is in an excited state. In Table I are given the possible states of excitation[19] of N^+ and O with the corresponding values of $D(NO)$. The only reasonable values for $D(NO)$ are those obtained from the combinations $N^+(^1D_2) + O(^3P_0)$ and $N^+(^3P_0) + O(^1D_2)$. From Lozier's work[10, 11] it appears that it is more probable for the uncharged dissociation product to be excited. Also if N^+ were excited, it would involve a double electron jump, which is perhaps unlikely.[20] The difference between the two possible values of $D(NO)$ is only 0.06 volt, which is well within our probable error.

Using our value of 5.27 volts for $D(NO)$, and the known value for $D(O_2)$ in the thermochemical equation,

$$(1/2)D(N_2) + (1/2)D(O_2) - 0.94 = D(NO),^{21}$$

we obtain for $D(N_2)$ the value 7.32 volts. The latest value given by Kaplan[22, 23] from the band spectra is 7.4 volts, with which our value is in very good agreement.

A limit may be sent on $D(NO^+)$. The mass-spectrographic work mentioned above[15, 16] showed that O^+ was formed about one volt lower than N^+. For the process, $NO^+ \rightarrow N + O^+$, $(U_2 - U_1)$ should be less than the corresponding value for the process $NO^+ \rightarrow N^+ + O$ by the difference in the ionization potentials of N and O, i.e., by $14.48 - 13.55 = 0.93$ volt. Therefore, $(U_2 - U_1)$ for the first process above is $21.7 - 1.95 - 0.93 = 18.82$ volts, and $D(NO^+) = 18.82 - 9.5 = 9.3$ volts, where 9.5 is the ionization potential of NO.

TABLE I. *Possible states of excitation of N^+ and O and the corresponding heats of dissociation.*

	N^+		O	
State	Term Value (electron volts)	State	Term Value (electron volts)	$D(NO)$ (electron volts)
$^3P_0$	0	$^3P_0$	0	7.22
$^3P_0$	0	$^1D_2$	1.95	5.27
$^3P_0$	0	$^1S_0$	5.27	3.05
$^1D_2$	1.89	$^3P_0$	0	5.33
$^1D_2$	1.89	$^1D_2$	1.95	3.48
$^1S_0$	4.03	$^3P_0$	0	3.19

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[18] Kaplan, Phys. Rev. **37**, 1410 (1931).

[19] Bacher and Goudsmit, *Atomic Energy States* (McGraw-Hill Book Company, 1932).

[20] Mulliken, Phys. Rev. **46**, 144 (1934).

[21] Landolt Bornstein **2**, 1495 (1923).

[22] Kaplan, Phys. Rev. **45**, 898 (1934).

[23] Lozier, Phys. Rev. **46**, 268 (1934).

This value is independent of the ionization potential of NO since it was also used to calibrate the electron voltage scale. We can only set a limit on $D(NO^+)$ since r_e, the internuclear equilibrium distance, is not known.

Negative ions in NO

In Fig. 6 is given the relative efficiency of production of negative ions in NO. The shape of the curve and the position of the maxima agree in general with the curve given by Tate and Smith.[13] These ions, which have been identified as O^-,[16] have an appreciable amount of kinetic energy. The ionization potentials of the kinetic energy ions are given in Fig. 7. The currents that were measured were very small, which accounts for the points not falling very well on a smooth curve. In Fig. 8 is given the straight line of the theoretical slope 14/30 obtained by plotting V_1 *vs.* V_F. For values of V_F lower than 1.1 and greater than 2.1 volts, the points deviate consistently from a straight line. The intercept of the line gives $U_2-U_1=3.2$ volts, with a systematic error estimated to be less than ±0.5 volt. If the process is $NO+e\rightarrow N+O^-$, the electron affinity of oxygen is $E(O)=D(NO)-3.2=2.1 \pm 0.5$ volt. This is in good agreement with Lozier's value[11] of 2.2 volts. It is not likely that the nitrogen atom comes off excited in the process since this would make the value of $E(O)$ greater than 4.4 volts. This would mean that in Lozier's experiment O^- would have to possess at least 2.2 volts excitation energy. The little that is known about excited states in negative ions seems to indicate that they are for the most part unstable.[11]

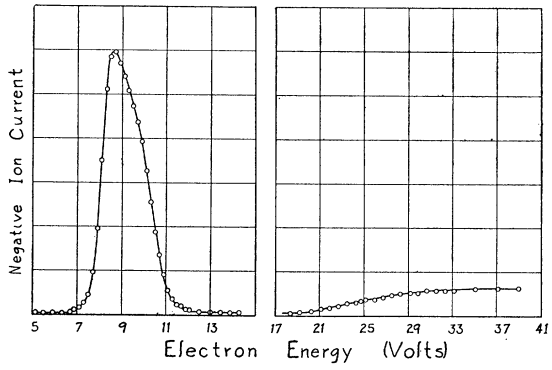

FIG. 6. Relative efficiency of formation of negative ions in NO.

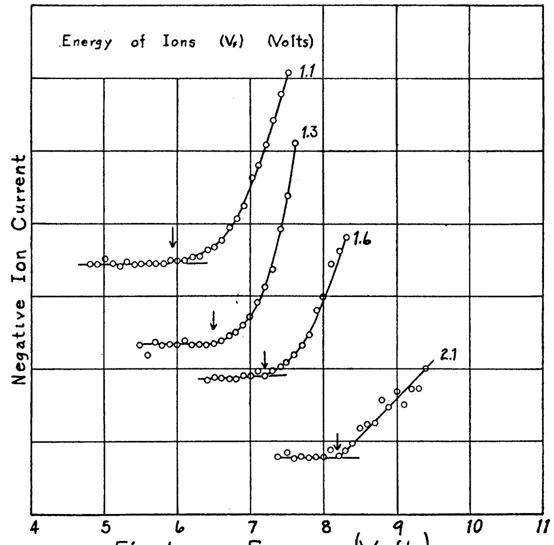

FIG. 7. Ionization potentials of negative ions having kinetic energy in NO.

By an empirical method of extrapolation, Glockler[24] has estimated the value of $E(O)$ to be 3.8 volts. To reconcile our value to this would require O^- to have 1.7 volts excitation energy, a value that seems high from the standpoint of stability. Since Glockler's extrapolation was rather long, the discrepancy is not as serious as it might appear.

HYDROGEN CHLORIDE

In Fig. 9 are given the kinetic energy distribution curves for positive ions in HCl. It is obvious that these ions are H^+ ions since from momentum and energy considerations neither HCl^+ nor Cl^+ could possess such velocities. That these ions were H^+ was confirmed by Nier and the author[14] by using a mass spectrograph. The most prominent features of the curves in Fig. 8 are the three sharp maxima that become evident above 40 volts electron energy. The sharpness of these peaks indicates that the repulsive potential energy curves which describe the dissociation process must be rather flat in the Franck-Condon region. The most likely process for the formation of the ions of the peaks is $HCl^{++}\rightarrow H^+ + Cl^+(^3P)$. To form an H^+ ion having 6 volts kinetic energy by this process would require 37 volts electron

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[24] Glockler, Phys. Rev. **46**, 268 (1934).

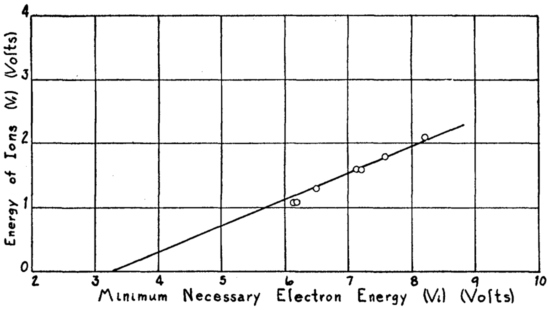

FIG. 8. Kinetic energy *vs.* ionization potentials of negative ions in NO.

energy, while if the Cl^+ were excited to the next energy level it would require 48.5 volts energy to form such an ion. To explain the triplet structure of the peaks we might assume that there exists for each J value of $Cl^+(^3P)$ an unstable potential energy curve. Since the separation in energy of the three peaks is much greater than the corresponding differences in the triplet levels of $Cl^+(^3P)$, the highest potential energy curve must be the steepest and the highest energy peak should be the broadest. It is of interest that this is true. Mulliken[25] has tentatively constructed such triplet repulsive potential energy curves for the process $HCl^+ \rightarrow H + Cl^+(^3P)$. The above data are evidence in favor of the existence of such states for the doubly charged molecular ion.

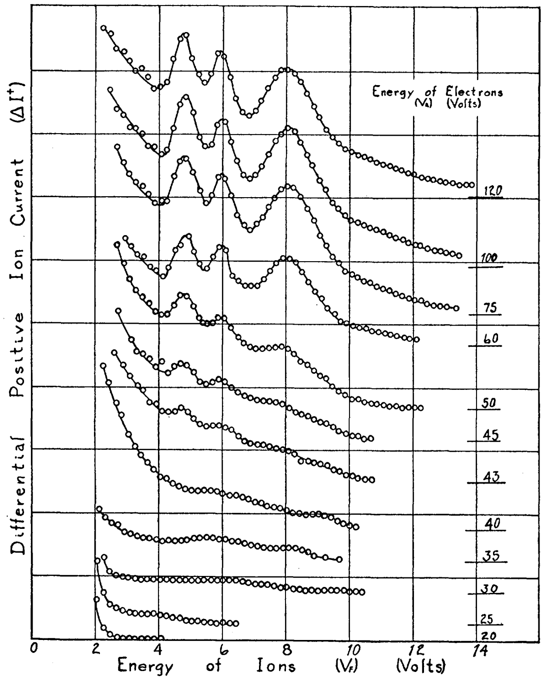

FIG. 9. Distribution in kinetic energy of positive ions formed in HCl.

In Fig. 10 are given samples of the ionization potential curves for kinetic energy ions. In the inset is given the corresponding curve for the onset of HCl^+; it is used as a calibration curve for the electron voltage scale. The readings for these curves were staggered, the open circles being for one sequence of readings, while the closed circles are for another sequence. The negative slope of the base lines of these curves was probably due to negative ions from a small amount of NO which existed as an impurity in the tube. These small negative currents did not interfere with the measurement of the positions of the breaks in the ionization curves.

For the V_F *vs.* V_i graph of Fig. 11 the mean straight line was drawn with the theoretical slope 35/36. The intercept gives for $U_2 - U_1$ the value 18.35 volts. The appearance potential of H^+ ions in the mass-spectrograph[14] study was 18.6±0.3 volts; this is higher as one would expect if all the H^+ ions carried some kinetic energy. From a calculation on the deviation of $U_2 - U_1$ from its mean for each individual observation on the basis of least squares the probable observational error is 0.002 volt; we feel

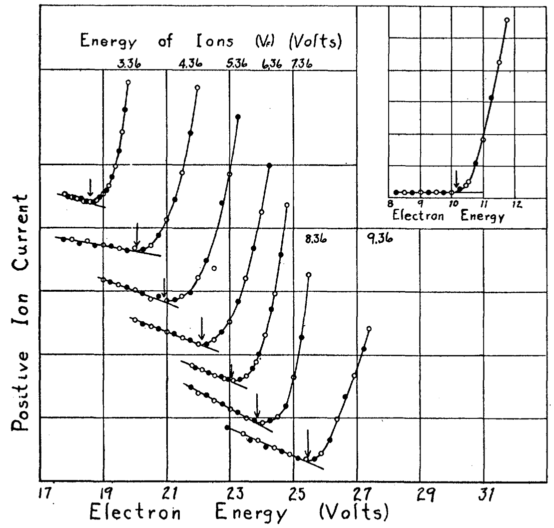

FIG. 10. Ionization potentials of positive ions having kinetic energy in HCl.

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[25] Mulliken, Rev. Mod. Phys. 4, 6 (1932).

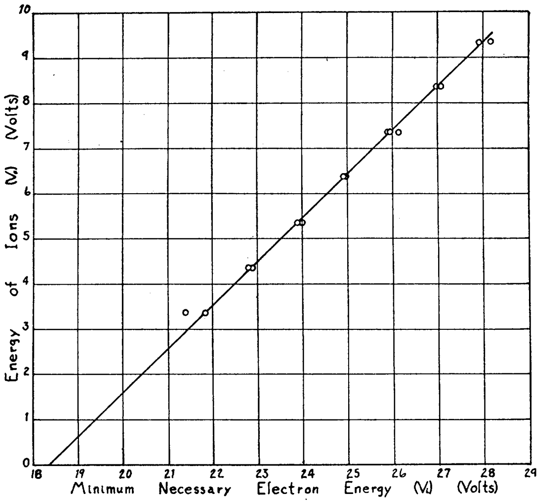

FIG. 11. Kinetic energies *vs.* ionization potentials of positive ions in HCl.

certain that the systematic error must be less than 0.2 volt.

Assuming that the process for the formation of these ions is $HCl^+ \rightarrow H^+ + Cl(^2P^0_{3/2})$, we get for $D(HCl)$ the value $18.35 - 13.54 = 4.8 \pm 0.2$ volts, which is 0.4 volt higher than the rather reliable chemical value.[26] The only other possible process would be $HCl^+ \rightarrow H^+ + Cl(^2P^0_{1/2})$; if we assume this process, $D(HCl) = 4.7 \pm 0.2$ volts, which still does not agree within the probable error with the chemical value of 4.42 volts. The explanation for this may be that the ionization potential of HCl, upon which our value for $U_2 - U_1$ depends, is actually lower than the value used. It should be pointed out that the values for the ionization potential of HCl given previous[27, 28] to the work of Nier and Hanson[14] would give for $D(HCl)$ a value 0.9 volt still higher.

The heat of dissociation of HCl^+ may be calculated. Two stable states for HCl^+ have been observed from band spectra,[29, 30] a $^2\Pi$ and a $^2\Sigma^+$ state. The $^2\Sigma^+$ state when dissociated gives $H^+ + Cl$; the $^2\Pi$ state is made up of $H + Cl^+$. Therefore, the horizontal asymptote of the $^2\Pi$ potential energy curve must lie below the

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[26] Landolt Bornstein **2**, 1489 (1923); Frank, Trans. Faraday Soc. **21**, 536 (1926).

[27] Knipping, Zeits. f. Physik **7**, 328 (1921).

[28] McKaye, Phys. Rev. **24**, 319 (1925).

[29] Brice and Jenkins, Nature **123**, 944 (1929).

[30] Kulp, Zeits. f. Physik **67**, 7 (1931).

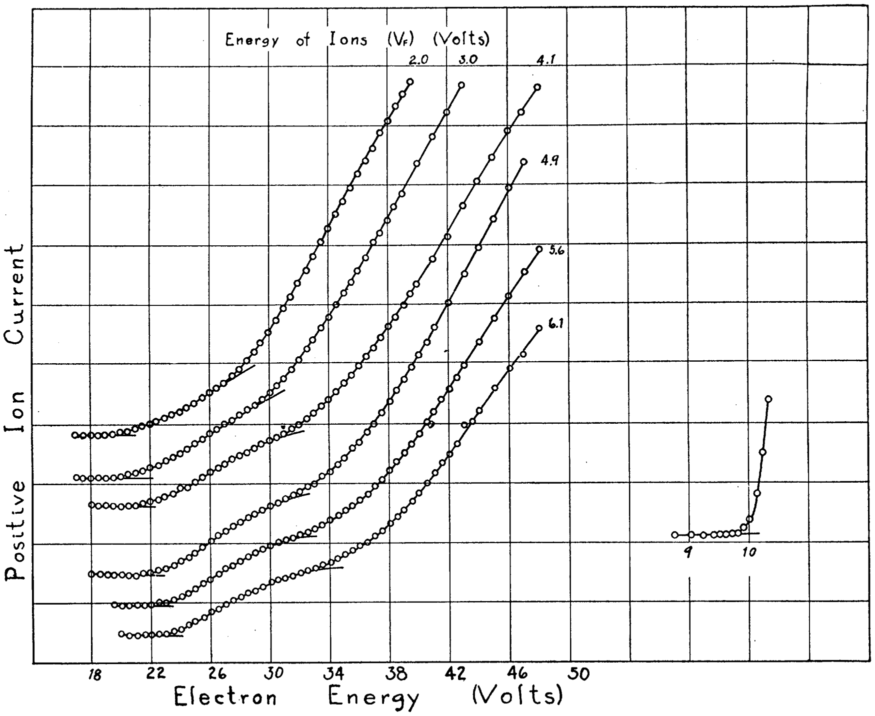

FIG. 12. The first and second ionization potentials of kinetic energy ions in HCl.

asymptote of the ${}^2\Sigma^+$ curve by the difference in the ionization potentials of atomic hydrogen and atomic chlorine, i.e., by 0.58 volt. Subtracting the ionization potential of HCl from $U_2-U_1-0.58$ we get $D(\mathrm{HCl}^+\,{}^2\Pi)=4.76$ volts. This value is independent of the ionization potential of HCl since that quantity is contained in U_2-U_1 as an additive constant. Since r_e is nearly the same for $\mathrm{HCl}^+({}^2\Pi)$ as it is for HCl,[30] we can do more than set a limit on $D(\mathrm{HCl}^+\,{}^2\Pi)$.

When the curves for the determination of the ionization potentials of high velocity H^+ ions were continued to higher electron energies, a second break was found in the curves. In Fig. 12 are given a few such curves. In Table II is given a summary of the results and the calculated values of U_2-U_1 for the process. Within experimental error U_2-U_1 is constant and equal to 29.5 volts in the region $V_F=3.0$ to 6.1 volts. This indicates that the process is $\mathrm{HCl}^+\rightarrow \mathrm{H}^+ + \mathrm{Cl}$ (excited), where the excitation energy of Cl is 11.6 volts. We note that there are several energy levels in Cl near this value, notably the so called 4° level at 11.6 volts.[19] The excitation energy is too low to give the process $\mathrm{HCl}^{++}\rightarrow \mathrm{H}^+ + \mathrm{Cl}^+$.

Negative ions in HCl

Negative ions, which have been identified as Cl^-,[14, 31] were observed. The kinetic energy of these ions was definitely less than 0.5 volt.

TABLE II. *The second ionization potentials of positive ions with kinetic energy in HCl.*

V_F	V_i(corrected)	$U_2-U_1=V_i-36/35V_F$
2.0 volts	30.3 volts	28.2 volts
3.0	32.5	29.4
4.1	33.6	29.4
4.9	34.5	29.45
5.6	35.4	29.6
6.1	35.9	29.6
7.1	38.1	30.8
8.2	38.8	30.3
9.5	40.8	31.3

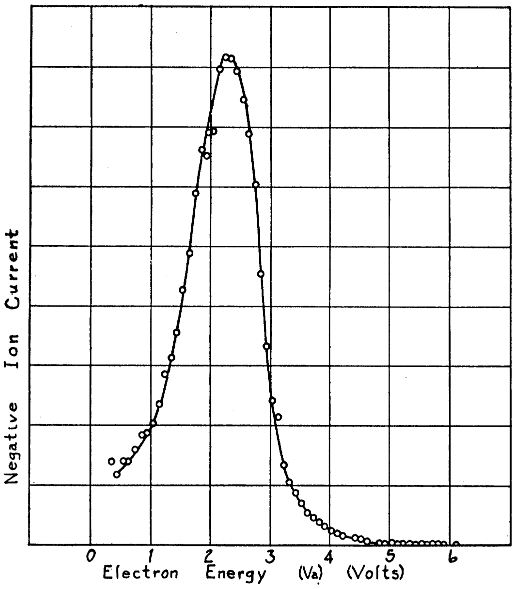

FIG. 13. Total negative ion current per unit electron current in HCl.

In Fig. 13 is given the relative efficiency of production of these ions. The curve exhibits the characteristic sharp peak usually observed for negative ions. Because the electron and the ion currents became very small in the region near an electron energy of zero, it was not possible to determine whether the relative efficiency became zero for $V_a>0$. When we extrapolate the symmetrical portion of the curve to zero efficiency, we get 0.4 volt for the onset potential. This makes the electron affinity of Cl equal to or greater than $D(\mathrm{HCl})-0.4=4.0$ volts. In view of our long extrapolation, the agreement with the value 3.7 volts cited by Glockler[24] is good.

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[31] Aston, *Isotopes* (Longmans Green & Co., 1924), p. 65.