TABLE I. *Deviation of position of maximum absorption in solutions of HCl in various solvents.*

Solvent	Dipole moment* e.s.u.$\times10^{18}$	Variation of HCl maximum	Relative absorption coefficients
Benzene	0.08	10 cm^{-1}	2.19
Chlorobenzene	1.52	40	2.71
Nitrobenzene	3.90	170	1.00
m-Nitrotoluene	4.20	200	1.09

* Values from P. Debye, *Polar Molecules* (Chemical Catalog Co., 1928).

depending upon the dipole moment of the solvent. The diminution of the vibrational frequency with increasing moment of solvent indicates a decrease in the effective binding force between the hydrogen and chlorine nuclei. It is possible that HCl in a polar liquid is in a state of incipient dissociation, the effect recognized by Nernst and Thomson in their early correlation between ionizing power and dielectric constant of solvents. On this hypothesis, the decrease of the effective force constants is due solely to dipole interactions. However, the changes in vibrational frequency produced by aromatic solvents are greater than those predicted by West and Arthur[4] on the basis of results obtained with solvents of another type. This indicates that the chemical nature of the solvent is also an important factor in determining the state in which HCl exists in solution. Fairbrother[8] in his studies of dipole moments finds that the moment of HCl apparently increases from 1.08×10^{-18} e.s.u. in the gaseous state to 1.30×10^{-18} e.s.u. in benzene solution, while the solvent ethyl bromide leaves the HCl moment unchanged. It is thus probable that dissolved HCl enters into associational complexes with certain solvents but remains unassociated with others. The formation of complexes would greatly modify the spectra of both solvent and solute, but changes in the spectrum of the solvent would be difficult to observe because of the masking effect of the vastly greater number of undistorted absorbing units. It is probable that both dipole interaction and the formation of complexes are involved in producing the observed effects.

The writer wishes to express his appreciation to Dr. E. K. Plyler for the use of his laboratory facilities and for his discussion of the manuscript and to Miss Estelle McClees and Mr. G. C. Kyker for their assistance in certain parts of the experimental work.

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[8] F. Fairbrother, J. Chem. Soc. **43** (1932); J. Chem. Soc. 1541 (1933).

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A Mass-Spectrographic Analysis of the Ions Produced in HCl Under Electron Impact

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An investigation has been made by a mass spectrograph of the ions formed in HCl under electron impact. The following ions were observed: HCl^+, HCl^{2+}, H^+, Cl^+, Cl^{2+}, Cl^{3+}, Cl^{4+}, Cl^{5+}, and Cl^-. When He and Ne were used as calibrating gases, the following appearance potentials were determined: HCl^+, 12.9±0.2 volts; HCl^{2+}, 35.7 ±1.0; H^+, 18.6±0.3 and 28.4±0.3; Cl^+, 17.2±0.5 and 21.2±0.5; Cl^{2+}, 45.7±0.3; Cl^{3+}, approximately 160; Cl^-, approximately 1.6 volts. The efficiency of ionization curves were of the usual form. From the ratio of the peak heights of HCl^{35} to HCl^{37} the abundance ratio Cl^{35}/Cl^{37} was found to be 3.07±0.03. Cl^{39} if present was less than 1/20,000 of Cl^{35}.

INTRODUCTION

It is the purpose of this paper to present the results of a mass-spectrographic study of the ions formed in HCl under electron impact and to correlate these results as far as possible with other available data.

The mass spectrograph used in the investigation was the same as that employed by Tate, Smith, and Vaughan.[1] It should be recalled that in this apparatus the ions are formed in a homogeneous beam of electrons of controlled energy and are subsequently analyzed by a 180° magnetic analyzer. The analyzed ion current is

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

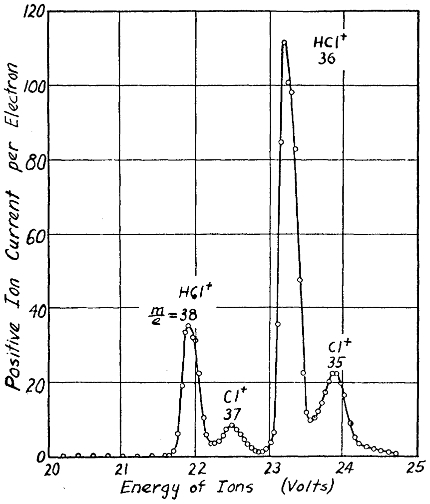

FIG. 1. Typical mass spectrum found in the region of HCl^+. Accelerating voltage applied to electrons, 100 volts. Magnetic field, 1175 gauss.

measured by a vacuum tube amplifier described by Distad and Williams.[2] As the mass spectrograph is designed primarily for the study of polyatomic gases, a differential pumping system is employed to prevent thermal dissociation products formed around the hot filament from diffusing into the ionizing region.

After the apparatus was baked out for several days at a temperature of 400°C, the only impurities which remained were a negligible amount of water vapor and carbon monoxide. The HCl was then permitted to flow into the tube through a capillary leak. The combined rate of leak and pumping speed were such that the pressure in the tube was less than 10^{-4} mm Hg. Liquid air was used on the traps between the mass spectrograph and the mercury diffusion pumps.

MASS SPECTRA

Fig. 1 shows a typical mass spectrum found in the region of HCl^+. It is seen that peaks are present for m/e values 38, 37, 36, and 35 corresponding to the ions $(H^1Cl^{37})^+$, $(Cl^{37})^+$, $(H^1Cl^{35})^+$, and $(Cl^{35})^+$, respectively. From Fig. 2 it is seen that the ions HCl^{2+} and Cl^{2+} are present. This figure shows also the isotopes of neon which was present in the apparatus as a calibrating gas. Fig. 3 shows the mass spectrum in the neighborhood of H^+. The trailing to the left of the peak is due to the considerable amount of kinetic energy given the H^+ ion in the dissociation process.

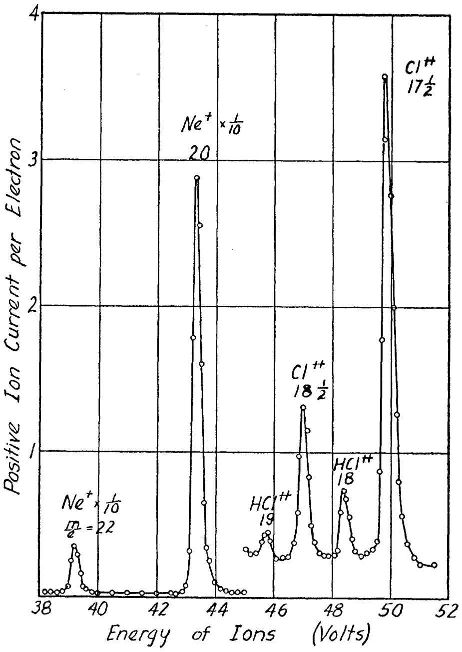

FIG. 2. Typical mass spectrum found in the region of $(HCl)^{2+}$. Accelerating voltage applied to electrons, 100 volts. Magnetic field, 1175 gauss.

In addition to the above mentioned ions, Cl^{3+}, Cl^{4+}, Cl^{5+}, and Cl^- were observed. A search was made for Cl_2^+, H_2^+, HCl^{3+}, H^-, and HCl^-, but no trace could be found of these ions.

EFFICIENCIES OF IONIZATION

In Figs. 4, 5, and 6 are shown curves for the relative efficiencies of formation of the more abundant ions as a function of electron energy.

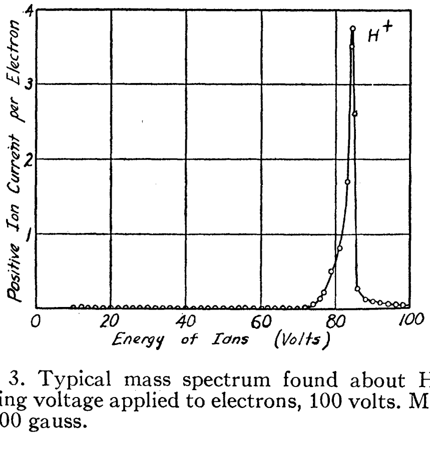

FIG. 3. Typical mass spectrum found about H^+. Accelerating voltage applied to electrons, 100 volts. Magnetic field, 400 gauss.

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

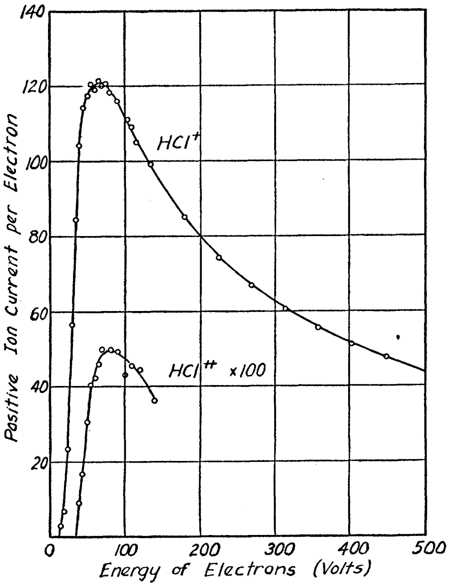

FIG. 4. Efficiency of formation of $(HCl)^+$ and $(HCl)^{2+}$ as a function of electron energy. HCl^{2+} curve carried out to only 140 volts.

The ordinates of these graphs have all been reduced to the same pressure and electron current. It is to be observed that the positive ion curves are of the usual form. The efficiency curve of Fig. 6 for Cl^- is similar in shape to the curves found for negative ions in H_2O,[3, 4] CO,[4, 5] NO,[4] and O_2.[4, 6] In order to identify definitely the negative ions fomed in HCl, Cl_2 was admitted to the apparatus as a calibrating gas. It is known that when Cl_2 is bombarded by electrons of the proper energy, Cl^- ions are formed. As the ions formed in HCl had exactly the same m/e as those found in Cl_2, it was definitely established that they were Cl^- ions.

IONIZATION POTENTIALS AND PROBABLE PROCESSES OF IONIZATION

In Table I is given a list of all the ions observed, the appearance potentials of the more abundant ones, the probable processes of formation, and the theoretical minimum electron energy required to form the ions by the assumed processes.

While the ionization potential measurements were being made, HCl, He, and Ne were present together in the apparatus. The appearance potentials of HCl were determined in reference to the ionization potentials of the calibration gases, Ne and He.

The calculated minimum energy of formation was obtained by using a heat of dissociation of HCl of 4.42 volts.[7] The energy levels of the Cl atom are taken from Bacher and Goudsmit.[8]

The appearance potential of HCl^+, 12.9 ± 0.2 volts, is in agreement with Barton's[9] value of 13.3 ± 1.5 volts.

The group of H^+ ions with the appearance potential of 18.6 ± 0.3 volts may be correlated with a dissociation process in which the chlorine atom remains unexcited. The minimum energy required for such a process would be $4.42(D_{HCl}) + 13.54(\text{I.P. of H}) = 17.96$ volts. The fact that the observed appearance potential is slightly higher than this calculated minimum indicates that the molecule must dissociate with some kinetic energy.

The group of H^+ ions with the appearance potential of 28.4 ± 0.3 volts may be ascribed to a process in which dissociation takes place with excitation of the chlorine atom. The lowest excited level in the chlorine atom is 8.89 volts

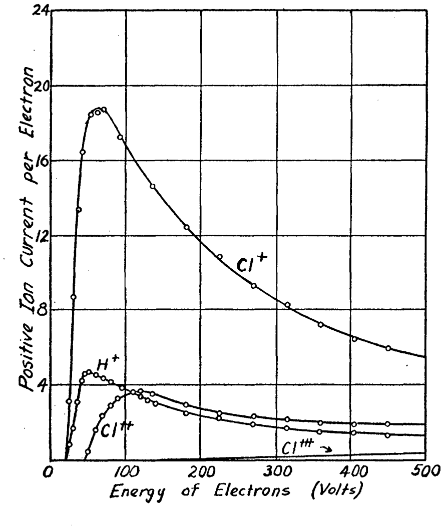

FIG. 5. Efficiency of formation of H^+, Cl^+, Cl^{2+}, and Cl^{3+} as a function of electron energy.

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[3] Lozier, Phys. Rev. **36**, 1417 (1930).

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

[5] Tate and Lozier, Phys. Rev. **39**, 254 (1932).

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

[7] Landolt-Börnstein **2**, 1489 (1923); Frank, Trans. Faraday Soc. **2**, 536 (1926).

[8] Bacher and Goudsmit, *Atomic Energy States* (McGraw-Hill Book Company, New York).

[9] Barton, Phys. Rev. **30**, 614 (1927).

above the ground state. Thus, the minimum energy required to form $H^+ + Cl$ (excited) would be $4.42(D_{HCl}) + 13.54$(I.P. of H)$+8.89 = 26.85$ volts. The discrepancy between this value and the observed appearance potential may be explained either in one or both of two ways: (1) The dissociation takes place with a large amount of kinetic energy, or (2) The chlorine atom is excited to some higher level or levels than the one considered.[10]

The group of Cl^+ ions with the lower appearance potential is probably formed by a dissociation into H (normal)$+Cl^+$ (normal). The calculated minimum energy required for this process is within experimental error equal to the observed appearance potential.

It has not been possible to correlate definitely the second group of Cl^+ ions with any known process. Neither the hydrogen atom nor the Cl^+ ion can be excited since this would require an appearance potential larger than the one observed. A possibility that suggests itself is that the lower group of Cl^+ ions come from the stable $HCl^+(^2\Pi)$ potential energy curve, while the second group arises from the corresponding repulsive curve. The difference in the appearance potentials is a measure of the difference in the kinetic energy given the dissociation products by the two processes. The fact that r_e for HCl (normal) is nearly equal to r_e for $HCl^+(^2\Pi)$[11] militates against this explanation. Another possible explanation is that both groups of Cl^+ ions arise from repulsive potential energy curves and that the second group comes from a higher or steeper curve. Such unstable potential curves might exist for each of the triplet states of $Cl^+(^3P)$.[12]

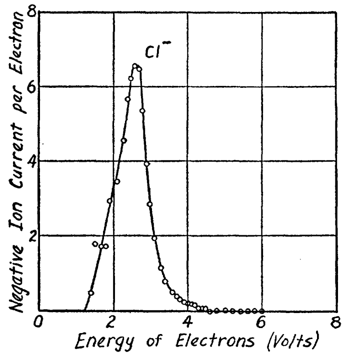

FIG. 6. Efficiency of formation of Cl^- as a function of electron energy.

TABLE I. *Summary of experimental results.*

Ion observed	Appearance potential (volts)	Probable process	Calculated minimum energy required (volts)
HCl^+	12.9 ± 0.2	$HCl \rightarrow HCl^+$	
HCl^{2+}	35.7 ± 1.0	$HCl \rightarrow HCl^{2+}$	
H^+	18.6 ± 0.3	$HCl \rightarrow H^+ + Cl$	17.96
	28.4 ± 0.3	$HCl \rightarrow H^+ + Cl(^4P)$	26.85
Cl^+	17.2 ± 0.5	$HCl \rightarrow H + Cl^+$	17.38
	21.3 ± 0.5	$HCl \rightarrow H + Cl^+$	
Cl^{2+}	45.7 ± 0.3		
Cl^{3+}	160 (approximately)		
Cl^{4+}			
Cl^{5+}			
Cl^-	1.2 (approximately)	$HCl \rightarrow H + Cl^-$	0.7

It should be noted that in Barton's work on HCl[9] the formation of H^+ and Cl^+ ions was a function of the water vapor present in the experimental tube. This made it uncertain whether these ions were formed by simple collisions between electrons and HCl molecules. In the present work, since the tube could be baked out, only a minute trace of water vapor was present, while the HCl gas was dry.[13] The fact that no H_2^+ or Cl_2^+ ions were observed showed that dissociation products were not getting into the ionizing region and that the H^+ and Cl^+ ions did not come from H_2 and Cl_2 molecules respectively. Barton's failure to observe some of the ions found in this work may be easily explained by the fact that his apparatus was not so sensitive as that used here.

ISOTOPE RATIO

From the ratio of the peak heights of HCl^{35} to HCl^{37} the abundance ratio of the chlorine isotopes was calculated to be $Cl^{35}/Cl^{37} = 3.07 \pm 0.03$. The value for this ratio as calculated from the atomic weight is 3.10. This may be regarded as a very satisfactory check. Kallman

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[10] Two other possibilities of excitation of Cl exist: it could be in either the ^2P state or in the $^4P^0$ state. (See reference 8.)

[11] Jevons, *Report on Band Spectra of Diatomic Molecules* (The Physical Society, London).

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

[13] As a second precaution to insure dryness of the gas, CO_2 snow was kept on a trap in the gas reservoir.

and Lazareff[14] found the ratio to be 3.24. Aston[15] found values between 3.0 and 3.1.

Becker,[16] Hettner and Bohme,[17] and Kallman and Lazareff[14] have given evidence for the existence of Cl^{39}. On the other hand, Ashley and Jenkins,[18] and Hardy and Sutherland[19] have been unable to find Cl^{39}. From the present investigation it is concluded that Cl^{39}, if present, exists to less than 1 part in 20,000 compared to Cl^{35}.

The writers wish to express their appreciation to Professor John T. Tate for his interest and advice in connection with this experiment. The HCl gas was furnished by D. L. Fuller, C. P. Roe, and R. E. Peck of the School of Chemistry, University of Minnesota.

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[14] Kallman and Lazareff, Zeits. f. Physik **80**, 237 (1933).

[15] Aston, *Mass Spectra and Isotopes* (Longmans, Green & Co., New York).

[16] Becker, Zeits. f. Physik **59**, 583 (1930).

[17] Hettner and Bohme, Zeits. f. Physik **72**, 95 (1931).

[18] Ashley and Jenkins, Phys. Rev. **37**, 1712 (1931).

[19] Hardy and Sutherland, Phys. Rev. **41**, 471 (1932).

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Collisions of Alpha-Particles with Sulphur Nuclei*

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More than 700,000 thorium C and C′ alpha-particle tracks have been photographed with a stereoscopic camera in a Wilson chamber filled with a mixture of hydrogen sulphide and hydrogen. A range-velocity curve for sulphur recoil atoms has been constructed by plotting the measured ranges (reduced to standard air) against the calculated velocities for 60 selected alpha-particle sulphur collisions. This curve is discussed and compared with the results of other workers. A possible relationship has been noted between the range-velocity curves of atoms having similar electronic configurations. No collisions indicating possible sulphur disintegrations were observed. Several low energy collisions were noted which were apparently lacking in coplanarity, but this effect is explained as being due to small deflections suffered by the recoil nucleus shortly after the collision. The calculated distances of closest approach are compared with the radius of the sulphur nucleus as given by Pollard and Brasefield. The methods of measurement and calculation employed have been checked by applying them to collisions with protons.

I. INTRODUCTION

SINCE the pioneer experiments of Blackett and others, the Wilson cloud chamber has become of great importance in the study of nuclear reactions. No accurate interpretation of the energy changes in these reactions can be made, however, unless it is possible to deduce the velocities of the recoiling particles from their observed ranges. The relationship expressing the velocity as a function of the range of the particle cannot as yet be obtained from theory for heavy nuclei owing to the complexity of these atoms, and the construction of such a curve is of necessity an experimental problem.[1] Previous experiments by Blackett,[2] Blackett and Lees,[3] Feather,[4] and Eaton[5] have established such curves for several elements. However, it is important that such information be extended as far as possible in order that a general empirical relationship may be established which will apply to all atoms.

The element sulphur was selected in this work for the following reasons:

First, a stable gaseous compound of sulphur, hydrogen sulphide, can be obtained, enabling this element to be studied conveniently in the cloud chamber, and the form of the range-velocity curve can therefore be determined.

Second, in addition to increasing the general information on the subject of range-velocity curves the form of the sulphur curve is of particular interest in the study of the following nuclear reaction

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* Part of a dissertation presented to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy.

[1] Calculations made by W. E. Duncanson, Proc. Camb. Phil. Soc. **30**, 102 (1933–34), and by G. Mano, J. de phys. et rad. [7] **5**, 628 (1934), using the theoretical expressions of Bethe and Bloch, have yielded results in good agreement with experiment for the range-velocity relations of alpha-particles and protons of moderately high energies. Unfortunately, however, the assumptions made in the derivation of these formulae preclude their application to particles having the low energies considered here.

[2] P. M. S. Blackett, Proc. Roy. Soc. **A102**, 294 (1922); **A103**, 62 (1933).

[3] P. M. S. Blackett and D. S. Lees, Proc. Roy. Soc. **A134**, 658 (1932).

[4] N. Feather, Proc. Roy. Soc. **A141**, 194 (1933).

[5] W. W. Eaton, Phys. Rev. **48**, 921 (1935).