NOVEMBER, 1927 PHYSICAL REVIEW VOLUME 30

# THE IONIZATION OF HCl BY ELECTRON IMPACTS

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## ABSTRACT

**Analysis of the nature of the ions formed in HCl by electron impact.**—For the purpose of supporting the Born crystal grating theory the assumption has generally been made that the observed ionization potential of HCl was a measure of the amount of energy required to split an HCl molecule into an $H^+$ and a $Cl^-$ ion. Recent indirect experiments have cast doubt on the correctness of this assumption. The work here described was undertaken to determine with the aid of a mass spectrograph, the actual products of electron impact ionization in HCl. In the first experiments, the following types of ion were observed: $H^+$, $H_2^+$, $(H_2O)^+$, $(HCl)^+$ and $Cl_2^+$. The last type, $Cl_2^+$ was only observed with high pressures and is thought to be a secondary product. It was found that the hot tungsten filament in the HCl vapor produced molecular hydrogen in quantities sufficient to account for the hydrogen ions. To be certain no $H^+$ ions were produced by impacts with HCl molecules, and also to establish the identity of the $(HCl)^+$ ions, a new apparatus was built. The resolving power obtained was sufficient to show that the peak ascribed to $(HCl)^+$ consisted, in reality, of four peaks corresponding to the ions $(Cl^{35})^+$, $(HCl^{35})^+$, $(Cl^{37})^+$, and $(HCl^{37})^+$, the isotopes being for the first time evident. The $Cl^+$ ions and the hydrogen ions were observed to decrease in number relative to the $(HCl)^+$ ions with time after each evacuation in the same manner as the $(H_2O)^+$ ions decreased. It was concluded that the water vapor coming off the walls was in some way responsible for these ions, probably aiding the production of molecular hydrogen at the filament. In test runs with pure water vapor, and with HCl after several weeks time had been given the water vapor to disappear, no hydrogen ions were observed.

In experiments with negative ions, it was found that $Cl^-$ ions were formed in numbers relatively large, chiefly near the filament. They did not require impacts of more than 3 volts for their formation, if they required impacts at all. There seemed to be no connection between the $Cl^-$ ions and the 13.8 volt ionization potential. The $(HCl)^+$ ions appeared at a minimum potential of $13.3 \pm 1.5$ volts, considered to be in agreement with the 13.8 volt value given by others. The $H^+$ ions appeared at $16 \pm 1.5$ volts, about the same voltage as is required for their appearance in pure molecular hydrogen.

The results all point to the conclusion that $W + HCl \rightarrow (HCl)^+ + e$ is the process by which electron impacts ionize this gas, and that the process $W + HCl \rightarrow H^+ + Cl^-$ does not occur. A general discussion of the breakdown of molecules is given.

FOR some years Born[1] and many others, notably Grimm and Herzfeld,[1] have made profitable use of thermochemical cycles to calculate unknown properties of various substances from other known properties of the same

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[1] The most recent surveys of the field are given by M. Born, Problems of Atomic Dynamics, M. I. T., Cambridge, Mass. (1926), pp. 168–171; and by J. Franck and P. Jordan, Anregung von Quantensprüngen durch Stösse, p. 278. See also K. T. Compton and F. L. Mohler, Critical Potentials, Bull. Nat. Res. Council, vol. **9**, No. **48** (1924), pp. 112–114. Some of the original references are: Haber, Verh. d. D. Phys. Ges **21**, 750 (1919); M. Born, same, **21**, 13 and 679 (1919); H. G. Grimm, Zeits. f. Phys. Chem. **102**, 113, 141, and 504 (1922); H. G. Grimm and K. F. Herzfeld, Zeits. f. Physik **19**, 141 (1923).

or similar substances. Such work had its inception in the success of the well known electrostatic theory of crystal ionic lattices, due chiefly to Born,[1] which made it possible to calculate the grating energy $U$ needed to separate all of the ions of a crystal to infinity. This quantity in the cycle of Fig. 1, together with the known heat of combination $Q_{\mathrm{NaCl}}$ of solid sodium and gaseous chlorine, the heat of sublimation $S_{\mathrm{Na}}$ of sodium, the heat of dissociation $D_{\mathrm{Cl}}$ of chlorine gas, and the ionization potential $I_{\mathrm{Na}}$ of sodium, permitted the calculation of $E_{\mathrm{Cl}}$ the electron affinity of gaseous atomic chlorine. Evidently then if this last quantity could be derived by an independent method it would furnish a desirable experimental check of the fundamental crystal grating theory and of the validity of conclusions based on such thermochemical cycles.

$$\begin{tikzcd}
{[\mathrm{Na}] + \tfrac{1}{2}(\mathrm{Cl}_2)} \arrow[r, "Q_{\mathrm{NaCl}}"] & {[\mathrm{Na\,Cl}]} \\
(\mathrm{Na}) + (\mathrm{Cl}) \arrow[u, "S_{\mathrm{Na}}", "+D_{\mathrm{Cl}}"'] & (\mathrm{Na}^+) + (\mathrm{Cl}^-) \arrow[u, "U_{\mathrm{NaCl}}"'] \arrow[l, "I_{\mathrm{Na}}"', "-E_{\mathrm{Cl}}"]
\end{tikzcd}$$

FIG. 1

The possible existence of an "electron affinity spectrum"[2] gave promise that a direct measurement of the affinity might be made in a way analogous to the spectroscopic determination of ionization potentials. So far, however, no spectrum has been discovered which is certainly (or even probably) due to electron affinity.[3] There remained for the calculation of $E_{\mathrm{Cl}}$ only another cyclic method which is shown in Fig. 2. In this cycle the quantities $Q_{\mathrm{HCl}}$, $D_{\mathrm{H}}$, and $D_{\mathrm{Cl}}$ were known approximately. $I_{\mathrm{H}}$ was, of course, known both from spectra and from ionization potential experiments. The further assumption had to be made that $X_{\mathrm{HCl}}$ was identical with the ionization potential measured in the electron impact experiments of Foote and Mohler,[4] Knipping,[5] and MacKay.[6]

$$\begin{tikzcd}
\tfrac{1}{2}(\mathrm{H}_2) + \tfrac{1}{2}(\mathrm{Cl}_2) \arrow[r, "Q_{\mathrm{HCl}}"] & (\mathrm{H\,Cl}) \\
(\mathrm{H}) + (\mathrm{Cl}) \arrow[u, "D_{\mathrm{H}}", "+D_{\mathrm{Cl}}"'] & (\mathrm{H}^+) + (\mathrm{Cl}^-) \arrow[u, "X_{\mathrm{HCl}}"'] \arrow[l, "I_{\mathrm{H}}"', "-E_{\mathrm{Cl}}"]
\end{tikzcd}$$

FIG. 2

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[2] J. Franck, Zeits. f. Physik **5**, 428 (1921).

[3] J. Franck and P. Jordan, Anregung von Quantensprüngen durch Stösse, pp. 279, 280.

[4] P. D. Foote and F. L. Mohler, J. Am. Chem. Soc. **42**, 1832 (1920).

[5] P. Knipping, Zeits. f. Physik **7**, 328 (1921) corrected according to J. Franck, Zeits. f. Physik **11**, 155 (1922).

[6] C. A. MacKay, Phil. Mag. **46**, 828 (1923); Phys. Rev. **23**, 553 (1924).

With the data available several years ago for the several quantities in the cycles referred to, the agreement of the two resulting values for $E_{Cl}$ was sufficiently good to be accepted generally as a confirmation of theory. However, the best revised values at present available for the same quantities lead to considerably different values for $E_{Cl}$. Moreover, recent experiments of Barker and Duffendack[7] and of Mohler[8] have cast strong doubt on the validity of the assumption that $X_{HCl}$ is identical with the ordinary measured ionization potential. These experiments indicated that the process of impact ionization did not involve any dissociation of the molecule and left the alternative probability that the positive ions produced were $(HCl)^+$ ions. There is, of course, no reason to expect that the energy required to produce an ion of this type is the same as that required to produce $H^+$ and $Cl^-$.

The desirability of a direct experimental investigation of the nature of the ions produced by electron impact in HCl vapor was obvious. The present paper describes such an investigation using the method due principally to Smyth by which the gas ions resulting from electron impact are subjected to electromagnetic analysis before their presence is detected.

## FIRST EXPERIMENTS[9]

*Apparatus and method.* The experimental tube and auxiliary apparatus at first used (at Princeton) were those described by Smyth[10] and employed by him for a study of ionization in hydrogen, and later by the writer[11] for a similar study with argon. The method of procedure was exactly the same as that described in the papers referred to. The tube worked best with gas pressures in the ionization chamber ranging from 0.003 to 0.05 mm, such pressures being generally higher than those used in later experiments. It was found that the HCl vapor attacked the oxide coating necessary for platinum filaments but tungsten filaments were quite satisfactory and were used throughout.

The HCl vapor was prepared by dropping conc. $H_2SO_4$ into strong aq. HCl. The gas was dried by bubbling through two bottles of $H_2SO_4$ and final storage over $P_2O_5$. From time to time the stored gas was frozen in a liquid air trap and the initial and final products of the subsequent evaporation were discarded. The usual method of slowly admitting the gas into the exhausted tube through a fine capillary was employed without difficulty. The only differences in operation between HCl and more inert gases was traceable to surface effects on the walls of the vacuum system. Some of these were inconvenient but did not constitute insuperable obstacles. For example, when the HCl was first admitted most of it was adsorbed on the walls. It was only

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[7] E. F. Barker and O. S. Duffendack, Phys. Rev. **26**, 339 (1925).

[8] F. L. Mohler, Phys. Rev. **26**, 614 (1925).

[9] H. A. Barton, Phys. Rev. **25**, 890 (1925) A.

[10] H. D. Smyth, Phys. Rev. **25**, 452 (1925); see also Proc. Roy. Soc. **A102**, 283 (1922); **A104**, 121 (1923); **A105**, 116 (1924); and Jour. Franklin Inst. **198**, 795 (1924).

[11] H. A. Barton, Phys. Rev. **25**, 469 (1925).

after 20 or 30 minutes that anything like an equilibrium was reached and a steady pressure maintained in the space.

*Results and conclusions.* Fig. 3 shows mass spectra typical of those obtained in all of the early experiments. The peak of lowest *m/e* value in the range covered by the run of Fig. 3(a) is undoubtedly due to water, either $(OH)^+$, $(H_2O)^+$, or both. This peak was always the most marked of all in runs taken soon after evacuation. However, as the tube stood for some hours continually exhausted, the water peak diminished relative to the others. It is probable that the water vapor came from adsorbed layers on the glass and metal walls of the tube and that this supply was gradually used up.

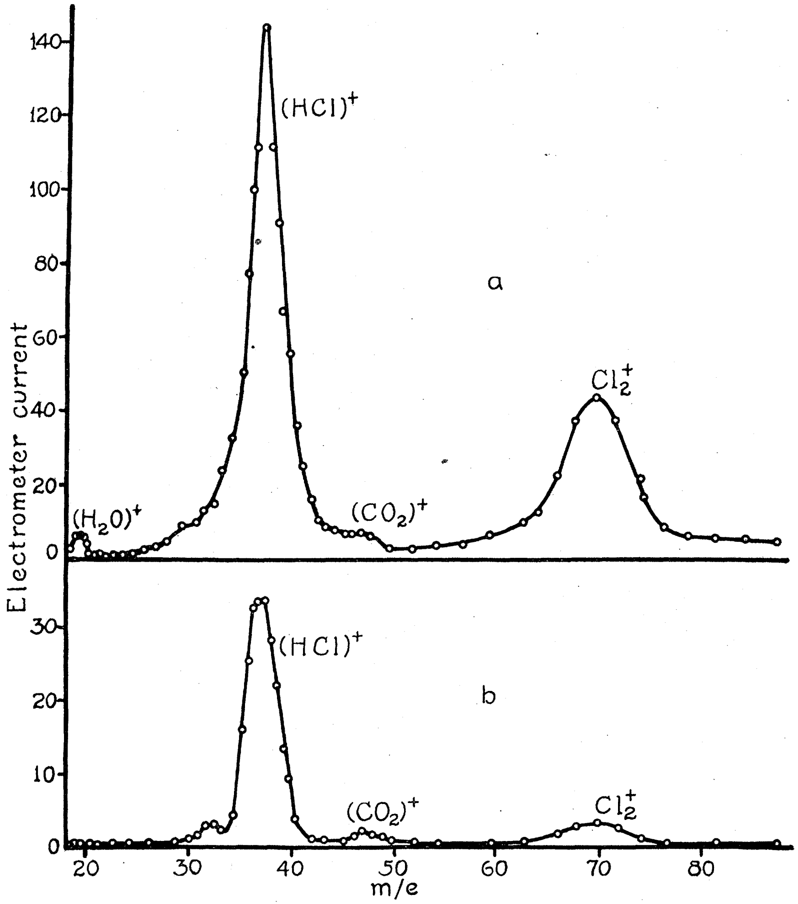

Fig. 3. Typical mass spectra. The pressure in Case (a) was 0.035 mm and that in Case (b), 0.013 mm.

The ions of about twice the mass of water shown by the second peak in Fig. 3(a) were assumed to be $(HCl)^+$ ions although it could not be proved that they were not partly or entirely $Cl^+$ ions. The resolving power was not sufficient to separate the isotopes $(HCl^{35})^+$ and $(HCl^{37})^+$.

A smaller peak of $m/e$ approximately equal to 45 is possibly $(CO_2)^+$, present because stop-cock grease and de Khotinsky joints were used. This peak, when detectable at all, was always small compared to the $(HCl)^+$ peak.

The peak of largest $m/e$ is due to ions having a mass about twice that of HCl. $Cl_2^+$ is suggested, although the mass could not be determined accurately enough to distinguish $Cl_2^+$ from some such possible composition as $(H_2Cl_2)^+$. Later, experiments were made with improved resolving power and a more accurate $m/e$ scale to determine the composition, but the peak was then no longer present, probably because of the lower gas pressures which had to be used. In the early experiments it was observed that the prominence of this peak relative to the others depended markedly on pressure. Except at high pressures, it was scarcely present at all, as is show by a comparison of the spectra (a) and (b) of Fig. 3, the latter taken at a pressure about a third of that of the former.

Another characteristic of this peak was that when the field serving to draw the positive ions out of the ionization chamber was increased, the size of the peak decreased more rapidly than that of the others. This and the pressure characteristic mentioned indicate that the corresponding ions were due to secondary and relatively unstable associations. That is, it is supposed that when the free path was small (at high pressures) the primary ions due to the electron impacts may have come into association with neutral molecules or other ions to form heavy ions such as those observed. If, however, the primary ions were drawn more rapidly out of the high pressure space, such associations were less likely to occur. Also the associations themselves, if they were relatively unstable, were more likely to be broken up when they were drawn rapidly through the gas.

*Hydrogen ions.* In addition to the mass spectra thus far discussed, others were taken with a much weaker magnetic field so as to cover a region of smaller $m/e$ values. The only new ions found were the same as those which Smyth[10] and Hogness and Lunn[12] observed in hydrogen, namely, $H^+$, $H_2^+$, and $H_3^+$. Of these, the last were not numerous and were not studied further.

In view of the possibility that the products of electron impact in HCl were $H^+$ and $Cl^-$, the presence of $H^+$ was not surprising but that of $H_2^+$ was unexpected. It was, of course, not possible to account for $H_2^+$ ions from single HCl molecules on the basis of simple electron impacts alone. Some other process must have been responsible and it was at first thought that some of the types of ion observed, including $H_2^+$, were due to secondary effects of the sort already mentioned and discussed more fully by Smyth[10], namely, combinations or break down of primary ions. An attempt was therefore made to bring out the secondary types of ion in the present case by increasing the pressure and thus the number of encounters of the primary ions which might lead to formation of secondary ions. In Fig. 4 are curves showing the variations observed in the numbers of the several types of ion as the pressure was gradually increased to a final value nine times the original. Although the

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[12] T. R. Hogness and E. G. Lunn, Phys. Rev. **26**, 44 (1925).

hydrogen ions were relatively few, they appeared at lower pressures than did the heavy ones. This fact, in the case of $H^+$, suggested that this type of ion was a primary product and favored the process $W + HCl \rightarrow H^+ + Cl^-$ as the primary action of electron impacts in HCl.

On the other hand, the $H_2^+$ peak was even more marked at low pressures than $H^+$. This suggested that the $H_2^+$ type was likewise a primary product, which could only mean that some gas having at least two atoms of hydrogen in its molecule was available in the tube for electron impact. Water vapor and molecular hydrogen were possibilities. Further experiments pertinent to this question will be discussed presently.

Thus it seemed that the hydrogen ions were primary and the two heavier ions secondary since the latter did not appear (cf. Fig. 4) until relatively higher pressures were reached. It was difficult, however, to understand how any secondary products could be so pronounced in comparison with the primary products as these were.

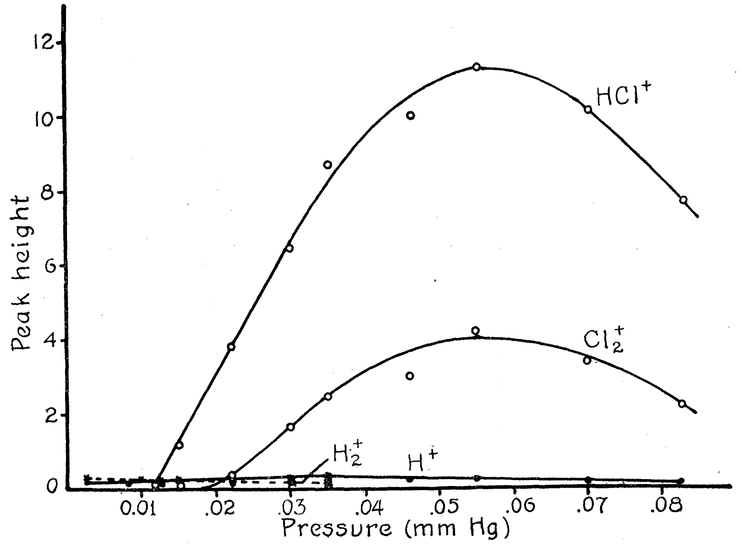

Fig. 4. Curves showing the effects of varying the pressure on the several types of ion.

*Chemical action at the filament.* To throw further light on the source of the hydrogen ions recourse was had to a somewhat different type of experiment suggested by similar work on the part of Barker and Duffendack.[7] To understand this it is necessary to recall that, during operation of the apparatus, the HCl was admitted continuously and pumped out at two places by single-stage diffusion pumps. One two-stage diffusion pump backed these up so that all of the gas fron the apparatus passed through it. The gas was then removed by a Cenco oil pump.

For the present experiment, a stop-cock was placed in the outlet tube of the two-stage pump. When this was closed the gas discharged accumulated in the small space between the pump and the stop-cock. The pressure in this space was observed with a manometer and, under ordinary conditions, rose fast enough for the increase to be measured in mm after a few minutes. The rate of rise was then observed for several different conditions as shown in the following progressive schemes, where each new condition was added to those already operative:

| Conditions | Rate of pressure rise |
|---|---|
| First Series | |
| 1. Filament off. HCl not being admitted | 8.0 mm/hr |
| 2. HCl being admitted | 75.0 |
| 3. Traps between apparatus and pumps immersed in liquid air | 5.9 |
| 4. Filament hot. | 8.9 |
| Second Series | |
| 1. Filament off. HCl not being admitted. Liquid air on traps | 5.7 mm/hr |
| 2. Filament hot | 5.7 |
| 3. HCl being admitted | 9.1 |
| 4. Filament off | 5.8 |
| 5. Filament hot | 9.1 |
| 6. 26.5 volts applied to emitted electrons | 9.5 |
| 7. Voltage off | 8.9 |
| 8. Voltage on | 9.1 |
| 9. Voltage and filament off. | 5.7 |

It will be seen that the first series of observations gave, first, a measure of the rate at which gas leaked into the apparatus or was evolved from the walls, and second, a measure of the rate of inflow of HCl. The latter rate was kept constant throughout the experiment. The third test of the series showed that the liquid air traps were effective in condensing all of the HCl, the rate of pressure rise being, in fact, slightly less than the previously measured leakage. The increased rate of the fourth test indicated that, when the filament was hot, a gas was produced which could pass through the liquid air traps without condensing and appear in the pump discharge.

The first two tests of the second series showed that the non-condensible gas was not given off by the filament in the absence of HCl. The third, fourth, and fifths tests confirmed its production by the hot filament in the presence of HCl. The remaining tests showed that very little, if any, more non-condensible gas was produced when the electrons emitted by the filament were accelerated by a voltage well above the ionizing potential.

To summarize, it is concluded from this experiment that the HCl in the presence of the hot tungsten filament underwent some chemical action resulting in the formation of a new gas not readily condensed at the temperature of liquid air. This gas was undoubtedly hydrogen and its presence is sufficient to account for all of the hydrogen ions observed. This discovery not only explained nicely the unexpected presence of the $H_2^+$ ions, but also made unnecessary any assumption as to a relationship (e. g. primary-secondary) between the hydrogen ions and the $(HCl)^+$ ions. It thus becomes possible to regard the $(HCl)^+$ ions as primary ions whose abundance increased with pressure simply because the number of HCl molecules available for impact increased. This view avoids the previous difficult assumption that secondary products could so greatly exceed primary products of ionization in number. It should be noted that the "$Cl_2^+$" ions were always fewer in number than the $(HCl)^+$ ions so that they may still be regarded as secondary products.

The relationship between the two pressure curves for $H_2^+$ and $H^+$ in Fig. 4 is the same as that observed in pure hydrogen by Smyth. It is likely, therefore, that the $H^+$ ions, as well as the $H_2^+$ ions, came from $H_2$ molecules. To achieve the purpose undertaken in this research, however, it was necessary to go further and establish whether or not any at all came as primary ions from HCl molecules. It was also necessary still to identify positively the ions heretofore designated $(HCl)^+$. These objects were attained in a second series of experiments carried out (at Harvard) with an entirely new appratus.

## SECOND EXPERIMENTS[13]

*Apparatus and method.* The principles involved in the operation of the new tube were exactly the same as in the old. The construction, however, was quite different. It may best be described from the scale drawing of Fig. 5. The two main vertical portions of the tube were of glass, these being fitted together by a ground joint as shown. The inner portion carried the filament supported by leads sealed through the glass, and the nickel thimble-shaped electrode shown around the filament. The outer portion was cemented to the metal part of the tube and carried at its lower end a nickel disk slitted as shown. The parts of the tube below this disk were of brass except for the iron cup-shaped piece marked *Fe* which was provided to shield the ions from stray magnetic field during their acceleration. The heavy black horizontal lines in the figure represent the walls of a length of square-drawn seamless brass tubing viewed from the side. This was closed at the ends by brass fittings soldered to it. At the left the fitting was merely an outside square flange providing a surface to which a brass closing plate could be cemented with de Khotinsky cement for easy removal. At the right the outward extension of a square plug was turned to receive a glass tube (not shown) joined with cement.

The two sockets on top of the box thus formed were turned from brass and soldered to the surface of the box after holes had been drilled in the latter at $S_2$ and $S_3$. In the right socket the iron cup supported the brass slit jaws. The screw holes were large enough so the cup as a whole could be turned slightly and the jaws could be adjusted for any slit width up to 1 mm. A similar arrangement was provided in the left socket except that a brass disk replaced the iron cup. A brass tube was soldered into a hole in the side of the right socket and cemented at its outer end to a glass tube not shown.

All joints were soldered except those marked *W* which were cemented, usually with de Khotinsky cement. In some cases a German cement called Picein was used and proved more satisfactory for glass to metal joints which were difficult to heat.

The broken line within the brass box shows a cross section of two thick blocks of soft iron so placed as to extend effectively the pole pieces of the electromagnet toward one another inside the tube. The air gap between the inner faces of these blocks was about 3/8″ long.

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[13] H. A. Barton, Phys. Rev. **29,** 44 (1927); Nature, **119,** 197 (1927).

The nickel electrode labelled $G$ was used to set up the field $V_1$ accelerating the electrons from the filament. This electrode could have been made of gauze but it was found that the shielding it provided against the stray field of the magnet was of great advantage. The electrons passed through the open slit. Ions were drawn down by the small field $V_2$ and those passing through $S_1$ fell through the analyzing field $V_3$ · $V_2$ was usually six volts while $V_3$ was varied from 100 to 360 volts. The magnetic field was kept constant during a run. For various purposes magnetic field strengths of from 600 to 5500 gauss were employed.

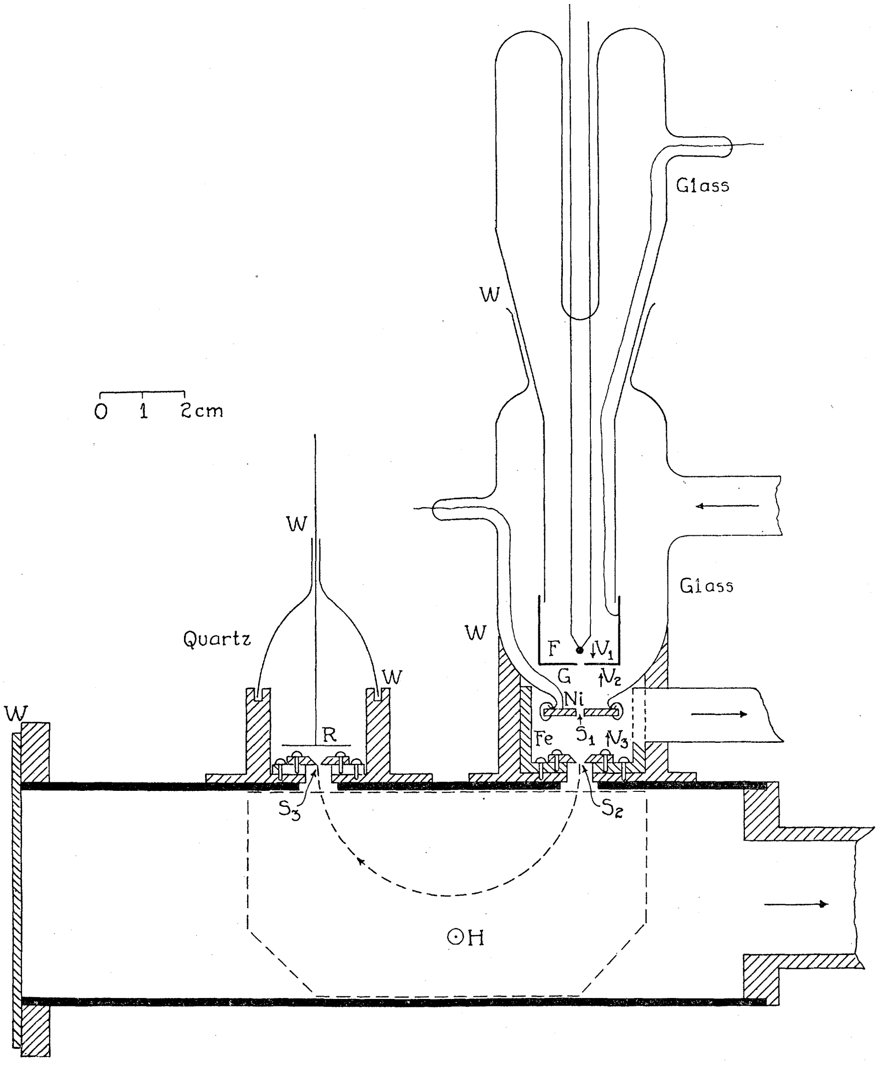

Fig. 5. Second apparatus.

This tube differed from that of Smyth previously used in that the ions passed through two instead of three slits before entering the magnetic field. This increased the number of ions getting through, and consequently, the overall sensitivity of the apparatus. Great care was taken to adjust slits $S_2$ and $S_3$ parallel to one another and perpendicular to the line joining them. A cross hair microscope mounted on the carriage of a lathe facilitated the making of this adjustment, the box being clamped to the lathe bed. The high resolving power attained was doubtless due to the care taken in this respect.

A second difference from the previous tube lay in the fact that smaller pressures had to be used for most satisfactory results. This was probably due to the greater width of slit $S_1$ which made impossible the maintenance of a low pressure in the analyzing portion of the tube if the pressure in the ionization chamber was high. However, the wide slit permitted more ions to pass through thus contributing to the sensitivity.

The auxiliary apparatus was very much like that used in the first experiments. So also was the experimental procedure. The feathered arrows in Fig. 5 indicate how the gas flowed through the tube. The use, at each outlet, of a diffusion pump designed rather for speed than for high vacuum avoided the necessity of providing a third diffusion pump for backing, the discharge being taken directly by a Cenco oil pump.

The receiving electrode $R$, made of brass, was supported by quartz for efficient insulation. In the previous apparatus, the lead from the receiving electrode to the electrometer was sealed through the glass walls of the tube with the result that the electrical leakage over the glass surface during very humid weather was sufficient to prevent operation. In the new apparatus this lead touched nothing but carefully cleaned quartz, the improvement thereby effected being so marked that weather conditions never had the slightest effect on the operation of the electrometer.

For further more detailed description of apparatus of this sort, as well as of its uses and operation the reader is referred to the papers cited.[10, 11, 12]

## RESULTS AND CONCLUSIONS FROM SECOND EXPERIMENTS

Preliminary mass spectrum runs with the new apparatus showed definitely only the two principal peaks of those present in previous runs like those of Fig. 3. Thus the water and $(HCl)^+$ ions were again in evidence but the peak supposed to be due to $Cl_2^+$ was absent. Nothing more than a doubtful trace of this type of ion was ever observed with the new tube. This is in accord with the previous suggestion that such ions were secondary products and therefore required for their appearance greater pressures than were used in the new apparatus.

*Identity of principal ions.* One of the chief results of the second experiments has to do with the nature of the principal peak, supposed due to $(HCl)^+$. After considerable adjustment of conditions the resolving power of the apparatus was developed to a maximum and curves such as those in Fig. 6 finally obtained. The figure shows two typical mass spectra covering the small range occupied by the heretofore unresolved principal peak. It will be seen that there are visible certainly three and probably four component peaks whose relative spacing, as calculated from the $V_3$ values at which they were obtained, indicates that the mass of each successive ion exceeded that of the previous by the mass of one hydrogen atom. The accuracy of the experiment was not sufficient to be sure that the $m/e$ scale is correct as shown or should be displaced one or two units to the right or left. The nature of the peaks themselves, however, leaves little chance for error in identifying the corresponding ions. The known abundance-ratio of approximately 3:1 for the isotopes of chlorine, $Cl^{35}:Cl^{37}$, appears between the first and third, and between the second and fourth ions (reading from left to right) and hence identifies these pairs as isotopes of the same ion respectively. With this established it is obvious that the heavier ion (second and fourth peaks) is the more abundant. It can hardly be doubted that this ion is $(HCl^+)$ and the less abundant ion $Cl^+$. All of this confirms the placing of the $m/e$ scale in Fig. 6 and justifies the previous supposition that the heretofore unresolved peak consisted principally of $(HCl)^+$ ions.

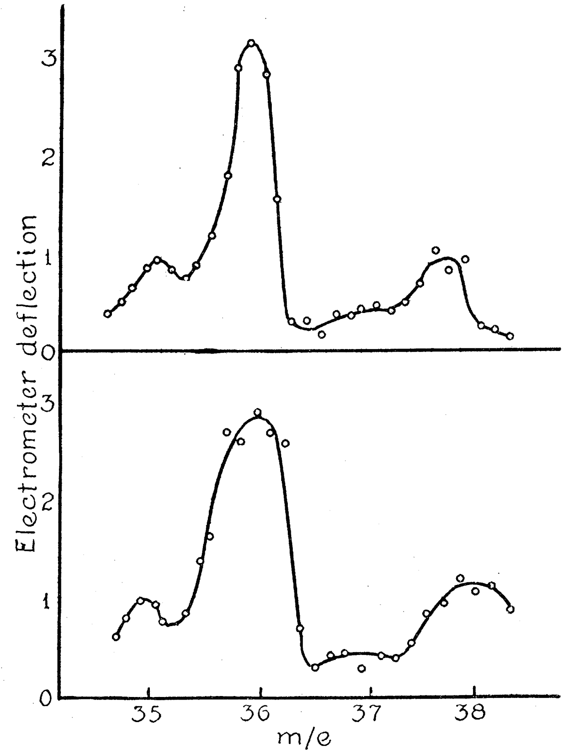

Fig. 6. Typical mass spectra with high resolution. The range covered is that of the principal peak in Fig. 3. The ions here are shown to be $(HCl)^+$ and $Cl^+$, each having the expected two isotopes; thus, from left to right, the peaks represent $(Cl^{35})^+$, $(HCl^{35})^+$, $(Cl^{37})^+$, and $(HCl^{37})^+$ ions respectively.

Parenthetically it is worth mentioning that this is the first quantitative determination of the abundance-ratio of the chlorine isotopes. That is, it is free of the assumption necessarily made in calculating the same ratio from the chemical atomic weight that no other isotopes exist. However, Aston's[14] work left little doubt of the correctness of this assumption and the present work likewise supports it. The average ratio observed by the writer was 2.8:1 agreeing, within the rather broad limits of experimental error, with the calculated ratio 3.35:1.

*Hydrogen ions.* Examination was again made of the low mass ions present and $H^+$ and $H_2^+$ ions found as before. Again the $H_2^+$ ions were usually the more abundant of the two. Several different investigations of the effect of varying pressure were made, one of these being shown in Fig. 7. In all cases, the result was the same as that found before, namely, that the $(HCl)^+$ ions increased with pressure and the hydrogen ions remained sensibly constant. Owing to the resolution of the main peak it was now possible at low pressure to compare the $Cl^+$ ions with the $(HCl)^+$ ions. This comparison was limited as the pressure became higher (about 0.002 mm) because the scattering of the positive ion beam destroyed the resolving power and the peaks were no longer separated. One set of mass spectra taken at five different pressures from 0.0004 to 0.0023 mm indicated roughly that the $(HCl)^+$ and $Cl^+$ ions

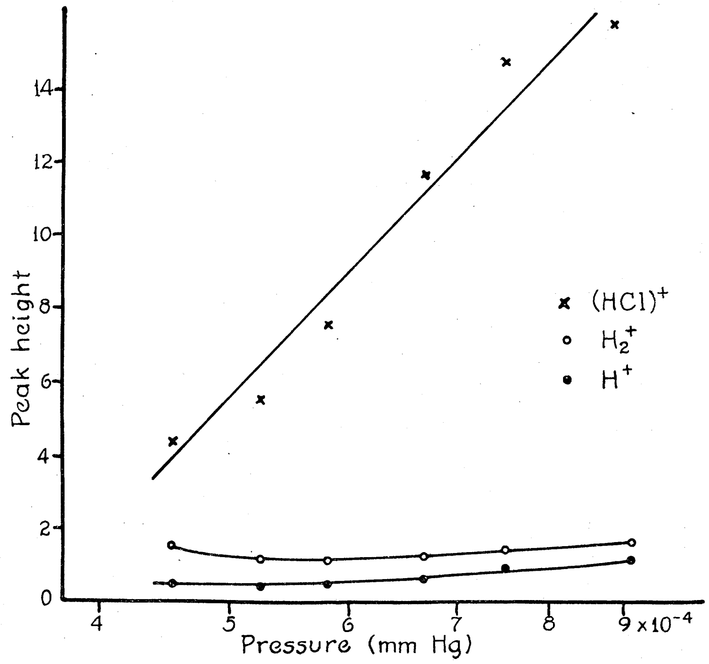

Fig. 7. Curves showing the effects of varying the pressure in the second experiments. Compare with Fig. 4.

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[14] Aston, Isotopes, pp. 65, 66.

increased with pressure without changing their relative ratio. This range is so small that no certain conclusions can be drawn.

*Factors governing the relative numbers of the several types of ion.* It was noticed that the abundance of the $Cl^+$, $H_2^+$, and $H^+$ ions relative to the $(HCl)^+$ ions varied markedly from day to day without apparent regularity. On recapitulation of several months work, however, it was discovered that the governing factor was the length of time since the system had last been open to the air. For example, the only two runs showing the $Cl^+$ nearly as high as the $(HCl)^+$ peak were taken shortly after evacuation. The effect was much more marked in the case of the hydrogen ions as may be seen from the comparison in Fig. 8. The first set of curves was taken not more than three hours after the apparatus had been closed up and pumped down. The second set was taken about 24 hours later, the tube having been kept evacuated meanwhile. Conditions of pressure, electron current, etc. were the same except that in the second set of observations the potential $V_1$ was higher. This would not have affected the ratio of the peak heights materially.

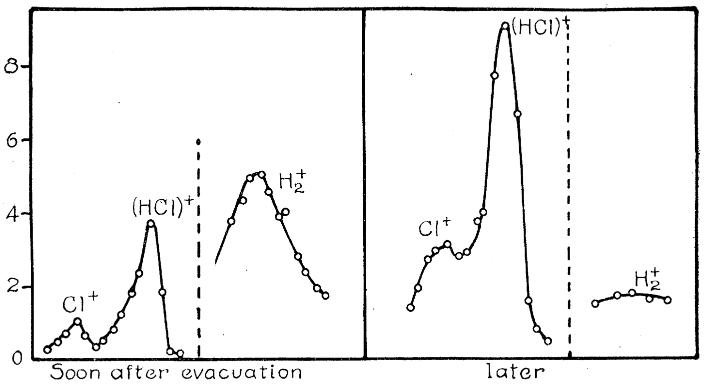

Fig. 8. Comparison of relative number of ions 3 hours and 27 hours after the tube was closed and evacuated.

As was to be expected, the peak ascribed to $(H_2O)^+$ also decreased with time as the adsorbed water vapor on the walls of the tube was used up. It took weeks for this peak to become really small, owing probably to the fact that it was not possible to bake the tube out. The similar behavior of the hydrogen peaks is not thought to be due to adsorbed hydrogen since it is difficult to understand how a new supply could be obtained every time the air was let in. The conclusion reached is that the hydrogen ions depend on the presence of water vapor, and this is probably related to the earlier conclusion that both a hot filament and the presence of HCl were necessary for the production of hydrogen gas.

It was important to test these conclusions both because of their own interest and because of the uncertainty the presence of hydrogen ions introduced in the experimental quest for the true impact ions from HCl. Two of the three conditions apparently concerned in the production of hydrogen or hydrogen ions in these experiments could be controlled. Thus, it was possible to observe the ions produced (1) from residual water vapor with the HCl shut off, and (2) from HCl alone after the apparatus had stood for weeks until practically all the adsorbed water had disappeared. Such observations were made and, as was expected, in both cases the hydrogen ions were absent or so few in number as to be difficult or impossible to detect.

*Conclusions from positive ion experiments.* It will be seen at once that the latter of these two observations partly answered the purpose of the research. That is, it showed that in pure HCl, under low pressure conditions favorable for the appearance of primary ions, $H^+$ ions were not observed. The $Cl^+$ ions, on the other hand, could not be so easily disposed of as they were never entirely absent even though dependent somewhat on the presence of water vapor. It can be said that the $Cl^+$ peaks were small relative to the $(HCl)^+$ peaks under all of a variety of conditions of gas pressure, electron current, and voltage of impact. Thus the $(HCl)^+$ ions stood out as the only type of primary positive ion certainly produced by electron impact in HCl vapor.

It should be noted that the accelerating voltages applied to the electrons were never raised in these experiments beyond about 75 volts. The conclusion just stated, and all others also, must be accordingly limited. A study of the effect of impacts by very fast electrons was not within the scope of the work undertaken.

## NEGATIVE IONS

With the electric fields $V_2$ and $V_3$ and the magnetic field $H$ all reversed, both the first and second tubes could be used as mass spectrographs for negative ions.[15] The appearance of such ions on the receiving electrode was manifested by a motion of the electrometer needle in the negative direction.

*Identity.* In both early and later experiments, it was found that whenever HCl was present in the tube negative ions could be obtained in numbers usually large relative to the number of positive ions observed. The ions had about the mass of the chlorine atom and, with the second tube, were resolved into two isotopes of about the proper separation and ratio of abundance. A typical negative ion mass spectrum is shown in Fig. 9. It is to be noted that only two peaks appear instead of the four observed with positive ions. As in the case of the positive ions, the $m/e$ scale was not known with sufficient accuracy to distinguish between $Cl^-$ and $(HCl)^-$. Aston,[14] however, found that negative ions were formed, under the conditions of his experiment, by chlorine atoms only, and not at all by HCl molecules. It would be very surprising if, in the present experiments, the result were completely reversed —even though conditions of pressure and applied voltage were different from those in Aston's discharge tube. The location of the $m/e$ scale in Fig. 9 is based on the assumption here implied.

*Source of the negative ions.* In view of the purpose of the present research, it was essential to determine the necessary conditions for the production of these negative ions. It would take a disproportionate amount of space to describe in detail the experiments that were carried out to this end. Briefly,

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[15] H. A. Barton, Phys. Rev. **26**, 360 (1925).

it is obvious that negative ions of one definite mass must, when the magnetic field is fixed, fall through just the right voltage to describe a semicircle of the prescribed radius and so be detected. By comparing this voltage, which was known to within three or four volts, with the fields $V_1$, $V_2$, and $V_3$, it was possible to determine quite accurately in what part of the tube the observed ions originated. In fact, by varying $V_3$ the whole high pressure space of the tube (between the filament and slit $S_1$) could be explored and the relative number of ions from the different regions determined. Once determined, the sources could be checked by arbitrarily varying the fields $V_1$ and $V_2$ and observing how much $V_3$ had to be changed to compensate for such variations. Ions coming from the filament, for example, appeared at a new $V_3$ value if either $V_1$ or $V_2$ were changed. Ions from the grid were not effected by any change in $V_1$.

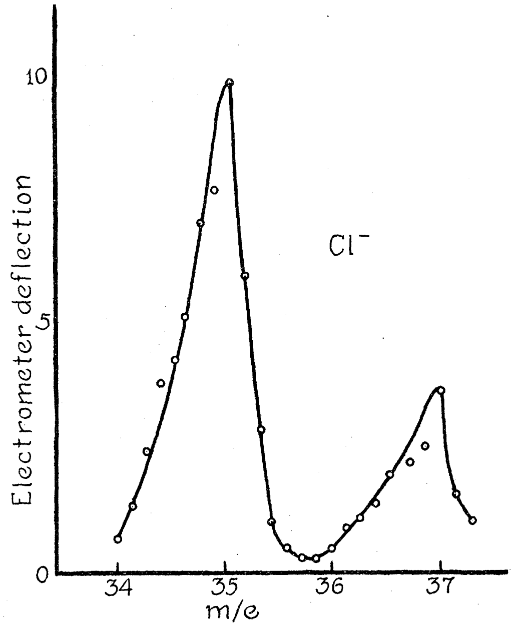

Fig. 9. Typical negative ion mass spectrum.

By such methods it was found that in the first tube negative ions were produced only in two places, either near the filament or near the grid. In the second tube, negative ions were never observed from any place except the region of the filament. Several differences between the tubes must account for this. In the second, the copper grid $G$ was replaced by a nickel electrode with a single slit. Also lower gas pressures were used. It is possible that the ions from the grid were formed on the near (filament) side and then diffused or were drawn through the mesh. In the nickel electrode the one slit offered, perhaps, less opportunity for such a process. However, neither this nor any other explanation occurring to the writer appears wholly satisfactory.

An important result of the work with negative ions was the discovery of the fact that they could be obtained with $V_1$ and $V_2$ both very small. These fields provided the total gradient through which an electron could fall in the region of high gas pressure. It is obvious, therefore, that if electron impacts were needed at all for the formation of negative ions, they had only to supply quite small amounts of energy. Ions were observed, in one case, when the electrons could have fallen through not more than two volts in all.

*Conclusions from negative ion experiments.* One clear and important conclusion can be drawn namely, that negative ions can be formed in HCl without electron impacts of more than two or three volts energy. Further, there is no evidence that the presence of electrons of energy equal to or greater than the ionization potential of HCl adds to the number of negative ions formed. In fact, in the present experiments, there were fewer ions when the electrons moved at greater speeds. Thus, there is here no support for the existence of the hypothetical process of ionization indicated by the formula: $W+\mathrm{HCl}\rightarrow\mathrm{H}^++\mathrm{Cl}^-$ while there is certain evidence that negative ions occurring in HCl can be accounted for in another way. Just what this way is in detail remains a speculation. One strong possibility was suggested by Mohler,[8] namely, that the negative ions are formed by the capture on the part of isolated Cl atoms of slow moving electrons. This hypothesis serves best to explain the ions near the filament where the concentration of slow electrons must have been relatively great. The ions arising near the grid may have been formed by attachment of electrons reflected by or ejected from the wires. The previously mentioned conclusions as to dissociation and reaction at the filament provide an explanation of the presence of isolated chlorine atoms in the tube.

## PERTINENT NEGATIVE RESULTS AND CONCLUSIONS THEREFROM

For the sake of completeness, a careful search was made for other negative ions. None were observed. In particular, no $\mathrm{H}^-$ or $\mathrm{H}_2^-$ ions were observed at a time when, as usual, $\mathrm{Cl}^-$ ions were appearing in large numbers.

The production of $\mathrm{Cl}^-$ ions at the filament suggested the possibility that $\mathrm{H}^+$ ions were likewise so produced. Tests of this were made under conditions judged to be favorable from the abundance of $\mathrm{Cl}^-$ ions. To do this, it was necessary to reverse $V_1$, keeping $V_2$, $V_3$, and $H$ of course, directed for positive ions. Such a search was made on several occasions and no $\mathrm{H}^+$ ions were observed. Similarly, no ions of the approximate mass of the HCl molecule appeared. It may therefore be stated with a fair degree of certainty that no positive ions of mass within the ranges examined were produced in detectable numbers by reaction at the filament.

This result is contrary to the hypothetical process: $\mathrm{HCl}\rightarrow\mathrm{H}^++\mathrm{Cl}^-$, whether by slow impact or thermal dissociation. It does not distinguish between the two processes:

1. $e+\mathrm{HCl}+$impact of little energy$\rightarrow\mathrm{H}+\mathrm{Cl}^-$
2. $\mathrm{HCl}\rightarrow\mathrm{H}+\mathrm{Cl}$ by reaction or thermal dissociation, $\mathrm{Cl}+e\rightarrow\mathrm{Cl}^-$ by attachment.

It is evident from the same result that in the production of the molecular hydrogen found to be formed in the apparatus, $H^+$ is not a necessary intermediate product.

## Ionization Potentials

Aside from the fact that a knowledge of ionization potentials is worth while for its own sake, it was desirable in the present experiments to ascertain what type (or types) of ion was associated with the previously determined ionization potential, 13.8 volts.

*Method of determination.* The procedure followed in determining the ionization potential of any type of ion may be either that of Smyth or the more rapid one of Hogness and Lunn. In the case of the former[10] mass spectrum runs are made over the range in which the ion appears, using successively decreased values of $V_1$. The value of $V_1$ at which the peak corresponding to the ion in question disappears is the ionizing potential. By plotting the peak heights against the $V_1$ values, the customary type of ionization potential curve is obtained (cf. Fig. 10*b*). Usually it is sufficient to employ the method of Hogness and Lunn[12] in which $V_3$ is set where the electrometer current is a maximum. $V_1$ is then varied and the electrometer current taken as a measure of the peak height (and therefore of the number of ions) at each value of $V_1$. Such a curve as that of Fig. 10*a* is thereby obtained directly. In the present experiments, the $H^+$ ions were studied with the first apparatus according to Smyth's method. The $(HCl)^+$ ions were studied with the second apparatus using the method of Hogness and Lunn, tests having confirmed its applicability.

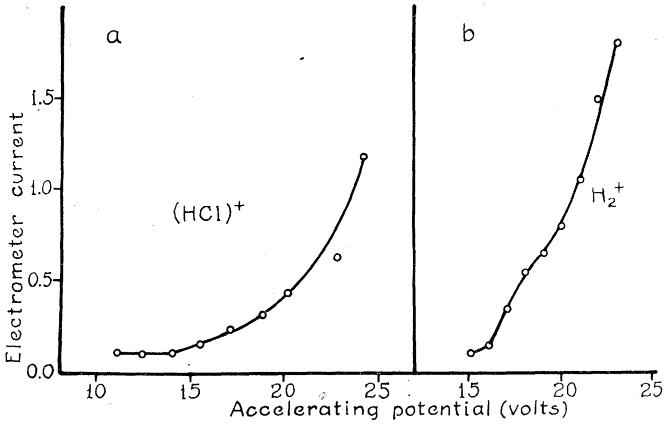

Fig. 10. Typical ionization potential curves.

*Results.* Table I shows the ionization potentials for $H^+$ and $(HCl)^+$ which were estimated from curves like those of Fig. 10. The assigned weights are based on the sensitivity, the ordinate of each curve at $V_1 = 20$ volts being taken as a measure of the sensitivity of the apparatus during that particular determination. Making an allowance of 1.5 volts for the

TABLE I

*Ionization potentials for* $H^+$ *and* $(HCl)^+$

| $H^+$ion. | | | $(HCl)^+$ion. | | | | | |
|---|---|---|---|---|---|---|---|---|
| Run | I. P. | Wt. | Run | I. P. | Wt. | Run | I. P. | Wt. |
| 2–13 | 16 | 7 | 11–26 | 13.7 | 7 | c | 14.0 | 3 |
| 2–20 | 18 | 4 | 11–27a | 14.0 | 4 | d | 13.0 | 15 |
| 3–24 | 15.5 | 12 | b | 12.4 | 4 | 12–2 | 14.0 | 4 |
| 3–25 | 15.5 | 8 | 12–1a | 13.2 | 3 | 12–7 | 13.0 | 10 |
| 3–28 | 16 | 5 | b | 13.7 | 7 | | | |
| Weighted mean | | 16.0 | | | | Weighted mean | | 13.3 |

uncertain initial velocity of the electrons, contact e.m.f., and voltage drop along the filament, the observed ionization potentials were:

For $H^+$: $16 \pm 1.5$ volts
For $(HCl)^+$: $13.3 \pm 1.5$ volts

The former is the same as that given by Smyth[10] and by Hogness and Lunn[12] for $H^+$. The fact that it agrees with the results of these authors working with pure hydrogen is strong additional evidence that the $H^+$ ions, in the present experiments, came from $H_2$ and not HCl molecules.

The result for the $(HCl)^+$ type of ion is, within the limits of experimental error, the same as the ionization potential of HCl measured by Foote and Mohler,[4] Knipping,[5] and MacKay.[6] There can hardly be any doubt that it was this type of positive ion that they detected.

Attempts were made to determine the minimum potential required for the appearance of the $Cl^+$ ions but these were unsuccessful, partly because the $Cl^+$ ions were few in number and partly because the peaks were never quite free of overlap from the $(HCl)^+$ peaks.

## GENERAL CONCLUSION

In effect, several different experiments have been carried out in the work which has been described. It has been shown that these led to several conclusions each partially answering the original question as to the physical significance of the ionization potential of HCl. It is now possible to bring these together to form the following principal conclusion derivable from the work as a whole: With electron impacts of energy greater than the ionization potential of HCl, 13.8 volts, and not more than 75 volts, the only primary type of positive ion certainly formed is $(HCl)^+$. There is, further, no evidence that $H^+$ or $Cl^-$ ions are formed as primary ions by impacts of such energy upon HCl molecules. There is evidence that $H^+$ ions are not so produced. We are forced, therefore, to discard the process:

$$W + \mathrm{H\,Cl} \longrightarrow \mathrm{H}^+ + \mathrm{Cl}^-$$

for the alternative process:

$$W + \mathrm{H\,Cl} \rightarrow (\mathrm{H\,Cl})^+ + e$$

Thus the similar conclusions of Barker and Duffendack[7] and of Mohler[8] are directly confirmed. It is evident that the use of the ionization potential of HCl for the value of $X$ in the thermochemical cycle of Fig. 2 is not justified.

## DISCUSSION

The withdrawal of the support which the supposed identity of $X$ and the ionization potential of HCl gave to the crystal grating theory cannot be regarded as serious in view of the many successes of the latter. In the main it must be right. The present work tends chiefly to focus attention on the physical ways in which a molecule can be broken up. There is no evidence that a single isolated neutral molecule can be split into *ionized* parts by any direct process. On the other hand, Franck and Blackett[16] have shown that, in hydrogen at least, the molecules can be dissociated into *neutral* atoms by electron impact. Furthermore, a great deal of evidence exists to the effect that light absorption may also lead to dissociation of molecules, both polar and non-polar, into neutral atoms. This matter had been investigated by Franck[17] and others and needs no additional discussion here.

When we say that the products of dissociation effected by such agencies are never ions, it is necessary to avoid cases where the molecule is first ionized as a whole and then dissociates. Birge and Sponer[18] have found instances of this sort. But then we are dealing with the dissociation of an ion and, of course, one or more of the dissociated products must carry the electron deficiency. The same is the case with electron impacts. Smyth[10] and Hogness and Lunn[19] have found several molecules which, after they are ionized as a whole, may break down into simpler ions or ions and atoms.

It must now finally be emphasized that the present work adds HCl to the list of molecules for which the primary ion produced by electron impact is the undissociated molecular ion. Included in this list are all of the molecules thus far investigated.[20] This suggests the rather far reaching generalization

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[16] P. M. S. Blackett and J. Franck, Zeits. f. Physik **34**, 389 (1925).

[17] J. Franck, Trans. Faraday Soc. **63**, **XXI**, Part 3 (1925); Zeits. f. Phys. Chem. **120**, 144 (1926); J. Franck, H. Kuhn, and G. Rollefson, Zeits. f. Physik **43**, 155 (1927); J. Franck and H. Kuhn, Zeits. f. Physik **43**, 164 (1927); see also the references given in the last two papers.

[18] R. T. Birge and H. Sponer, Phys. Rev. **28**, 259 (1926).

[19] T. R. Hogness and E. G. Lunn, Phys. Rev. **26**, 786 (1925); **27**, 732 (1926); **28**, 849 (1926) A; **30**, 26 (1927).

[20] This statement requires a little explanation. Hogness and Lunn[19] found that in the case of oxygen, $O^+$ ions were produced by electron impacts as well as $O_2^+$ ions. The abundance-ratio between the two types was independent of the pressure so it was not possible to classify them as primary and secondary in the sense that $H^+$ and $H_3^+$ could be classified as secondary to $H_2^+$ ions in hydrogen. In the latter sense, secondary ions mean those produced subsequently only through encounter of the primary ions with other particles. In the case of oxygen we now assume that $O^+$ was still produced subsequently from $O_2^+$, the difference being that here no encounter was needed, the breakdown being spontaneous. Thus, there is no necessary contradiction to the statement that the ion immediately produced by impact is always the undissociated molecular ion. The same may be said of the $N^+$ and $O^+$ ions from NO[19]. The early work of Semenoff and Kondratjeff also appeared to contradict the general statement here made. They have recently revised their conclusion, however, so that their results are no longer in conflict. (Zeits. f. Physik **39**, 191 (1926), see footnote 2.)

that an electron impact can alter only the electron arrangement of a molecule, and that any alteration in the relative position of the nuclei occurs subsequently because of the changed internal force-fields of the new arrangement rather than through any direct action of the impact itself. A sort of mechanical correspondence principle suggests the reasonableness of such a generalization. That is, an electron is of such small mass that it could not, in a classical collision with a nucleus, very much alter the motion of the latter. It would, however, alter the motion of an electron it struck. We may take this by correspondence over into quantum mechanics and obtain immediately the suggested generalization.

Such a view of electron impacts is practically identical with the view of quantum absorption by a molecule advanced by Franck[17] and supported by Blackett,[16] Dymond,[21] Birge and Sponer,[18] and Condon.[22] The writer ventures to suggest that with molecules, even more than with atoms, the similarity of quantum absorption and electron impact is beautifully illustrated.

It is a pleasure to acknowledge the valuable suggestions and assistance tendered in connection with the work of this paper by Professor E. C. Kemble of Harvard University and Professors K. T. Compton and H. D. Smyth of Princeton University.

Jefferson Physical Laboratory,
Harvard University,
July 29, 1927.

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[21] E. G. Dymond, Zeits. f. Physik **34,** 553 (1925).

[22] E. Condon, Phys. Rev. **28,** 1182 (1926).