

CLXXXIV.—*The Atomic Weight of Chlorine.*

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THE results of recent researches on the atomic weight of chlorine furnish a good illustration of the uncertainties inherent in all atomic weight determinations. The values obtained in any one investigation agree closely among themselves, and vary regularly about a mean. The mean values from different methods of experiment, however, are often much more divergent than the errors of measurement would lead one to expect. The following table exemplifies these statements, and shows clearly that some of the values are affected by small constant errors:

Atomic Weight of Chlorine. O = 16.

Obtained by	Ratio measured.	H =	H =	Probable error.
Dixon and Edgar ¹	H:Cl	1·0076.	1·00787.	±0·0019
Edgar ²	Cl:H and Cl:HCl	35·463	35·471	±0·0019
Noyes and Weber ³	H:Cl and H:HCl	35·462	35·470	±0·0008
Richards ⁴	AgCl:Ag, NH ₄ Cl:AgCl, and AgNO ₃ :Ag	35·461	35·469	—
Guye and Fluss ⁵	Cl:O	35·452	35·461	±0·0008
„ „ Ter-Gazarian ⁶	Density of HCl and critical constants ...	35·457	35·456	very small
		35·466		—
		35·461	35·461	—

¹ *Phil. Trans.*, 1905, **205**, 169.² *Phil. Trans.*, 1908, *A*, **209**, 1.³ *J. Amer. Chem. Soc.*, 1908, **30**, 13.⁴ *J. Amer. Chem. Soc.*, 1909, **31**, 6.⁵ *J. Chim. phys.*, 1908, **6**, 795.⁶ *Compt. rend.*, 1906, **143**, 1233.

Since the atomic weight of chlorine is one of the fundamental values on which the atomic weights of a large number of the

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elements depend, it is of great importance that it should be known with a high degree of precision. A careful examination of the results of recent investigations by Brauner (Abegg's *Handbuch*, II., i, 185) has led him to the conclusion that 35.458 is to be regarded as the most probable value, yet from the figures just quoted it seems by no means certain that the higher value 35.470 may not, after all, be a nearer approximation to the truth. In order to obtain further evidence, we have studied the question from a physico-chemical standpoint, and the present research contains an account of the determination of this constant by methods which are essentially different from those employed either by Dixon and Edgar, Noyes and Weber, Richards and his colleagues, or by Guye and Fluss. The work consists of a detailed study of hydrogen chloride, and falls into three parts, which comprise:

1. A revision of the density of the gas.
2. Its volumetric analysis.
3. A determination of the form of the pv isothermal at 0° , between the pressure limits 780 and 150 mm.

PART I.—*The Density of Hydrogen Chloride.*

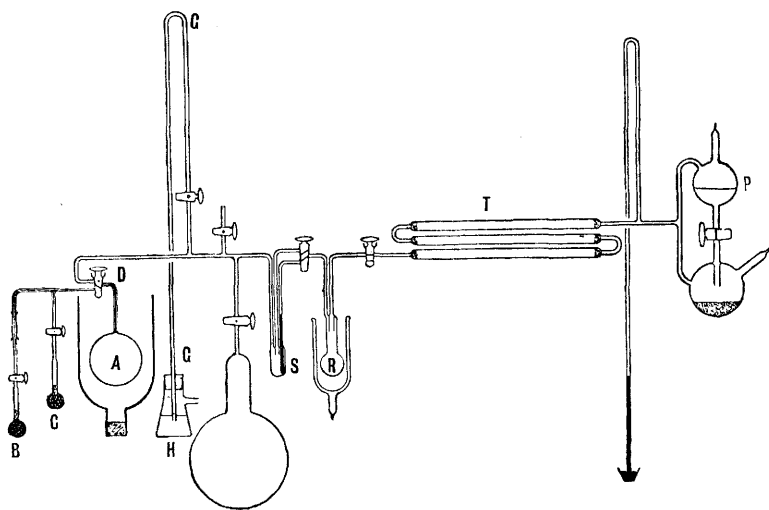
Comparatively few determinations of the density of this gas have been made. Leduc (*Ann. Chim. Phys.*, 1898, [vii], 15, 1) deduced from his experiments the value 1.6407 grams for the weight of a normal litre of the gas. Later, Guye and Ter-Gazarian (*Compt. rend.*, 1906, 143, 1233) obtained from four determinations the mean result 1.6398, which agrees well with the value 1.6397 resulting from six experiments carried out by one of us a few months later (*Proc.*, 1907, 23, 119). For reasons which will be given subsequently, we consider the latter value distinctly too large.

In our experiments the gas was weighed after it had been condensed on cocoanut charcoal. The weighing bulb had a capacity of about 20 c.c. The bulbs in which the volume of the gas was measured had a capacity of about 450 c.c. One bulb was made of soda-glass, and the other of transparent, vitreous silica. The latter was attached to the rest of the apparatus by means of a capillary glass-silica connexion, the two portions of the connexion being cemented together with paraffin wax. The bulb and connexion were made by Messrs. Johnson and Matthey for this research.

The method in all particulars is the same as that previously used by one of us for the determination of the density of nitric oxide (Gray, *Inaug. Diss.*, Bonn, 1907, "Ueber das Atomgewicht des Stickstoffs"). The details are best followed from Fig. 1. A is the volume-bulb, which could be put in connexion either with

the vessels used for storing and purifying the gas or with the charcoal absorption bulb *B*. The gas in *A* was kept at 0° by means of a bath of ice and distilled water. *A* was filled to a pressure slightly above atmospheric, and the excess of gas was allowed to escape through the sulphuric acid gauge *GG*. Complete adjustment of the gas pressure was effected by lowering the flask *H*; the standard barometer was then read, and the stopcock *D* turned off. The transference of the measured volume of gas from *A* to the weighed absorption bulb *B* was brought about by slowly cooling *B* by means of liquid air, and by opening the taps *D* and *E*. Before this operation was commenced, it was necessary to free

FIG. 1.



the capillary connexion tubes from air. This was accomplished by a ten minutes' immersion of the second charcoal-bulb *C* in liquid air. At the conclusion of an experiment, the absorption bulb *B* was detached, cleaned, and suspended from the balance-beam, and weighed after an interval of an hour. Meanwhile the empty bulb *A* was refilled, and the cycle of operations repeated. After two experiments, the absorption bulb *B* was heated, and the condensed gas removed by means of a filter-pump. After 900 c.c. of gas had been absorbed by the charcoal, the pressure inside bulb *B* did not exceed a few cm. of mercury at room temperature, so that an even larger volume of hydrogen chloride could obviously have been condensed and weighed in the 20 c.c. bulb.

With regard to the actual measurements little need be said. As can be seen from the following data, the volumes of the two bulbs were easily determined with a high degree of accuracy by weighing them full of boiled distilled water in the usual way. The bulbs were filled with water at 0°, and weighed at room temperature. A small glass bulb temporarily sealed on to the capillary stem provided space for the expansion of the water as the temperature rose from 0° to that of the balance case. A set of weights ranging from 1 kilogram to 1 milligram was used throughout the research, and their relative values were ascertained by Richards' method (*Zeitsch. physikal. Chem.*, 1900, **33**, 605).

We did not require to know the absolute values of the weights, since they only served to counterpoise water and gas filling the bulb under measured conditions. The effect on the density bulb of a variation in the buoyancy of the air was eliminated in the usual way by employing a counterpoise. In calculating our results, all weighings were corrected for the deviation of the face values of the weights from their true relative values in air, and also for the air displacement of the weights. In calculating the density results which we announced in a previous note (*Proc.*, 1908, **24**, 215), we made the perhaps not unnatural mistake of assuming that a correction was necessary for the difference between the air-displacement of platinum and brass, an assumption which would have been logical if the original calibration had been carried out in a vacuum. We overlooked the fact that this adjustment was made automatically when the weights were compared with each other in air, and that consequently the same correction for air-displacement must be made for both metals. This mistake appreciably alters our final density, and we take this opportunity of pointing out the existence of an error in the values already published.

Volumes of the Bulbs at 0°, all corrections made.

	Glass bulb.		Silica bulb.
I.	465.857 c.c.	457.419 c.c.
II. After a three months' interval.....	465.855 ,,	After heating to redness.....	457.422 ,,

The charcoal absorption bulb *B* was weighed on a long-beam Oertling balance, and the probable error of weighing was not greater than 0.03 milligram. It was counterpoised in the usual way by a bulb of nearly the same capacity, surface, and mass. On account of the small volume of this bulb, and the small variation in internal pressure due to the absorbed gas, the correction for change in buoyancy on exhaustion was of a negligible order. The

height of the mercury column of the standard barometer was referred to a glass scale, and read by means of a telescope and micrometer eye-piece to 0.03 mm. The temperature of the barometer column could be measured to within 0.2°. The absolute distance between two fixed points on the glass scale was ascertained for us at the Standards office through the kindness of Major Macmahon. A second scale used in some of the measurements was compared with an "invar" meter recently recalibrated at the National Physical Laboratory. For the loan of this standard, and for the use of the necessary reading instruments, we desire to thank Professor Trouton and Mr. Eumorphopoulos, of University College.

The Preparation of Pure Hydrogen Chloride.

The gas was prepared in three ways:

1. From sulphuric acid and sodium chloride.
2. From sulphuric acid and ammonium chloride.
3. From silicon tetrachloride and water.

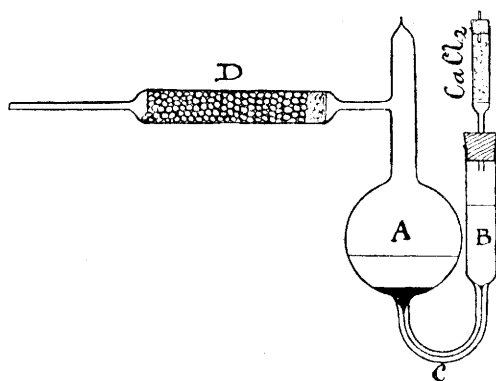
The sulphuric acid was prepared by the contact process, and proved to be very pure. The sodium chloride was prepared by precipitating from its aqueous solution, by means of gaseous hydrogen chloride, a very pure sample of the salt obtained from Messrs. Hopkin and Williams. The sodium chloride was subsequently recrystallised twice from water, and a careful examination failed to detect traces of other halogens. The ammonium chloride was purified after the method of Stas (*Œuvres complètes*, 1, 373). The salt was recrystallised twice from water, and the separation of the mother liquor was facilitated by the use of a centrifugal machine. The silicon chloride was obtained from Kahlbaum, and contained no free chlorine and no bromine compounds.

The interaction of the concentrated sulphuric acid and sodium or ammonium chloride was carried out in a high vacuum in a sealed glass vessel, *P*, of the form shown in Fig. 1 (Guye and Bogdan, *J. Chim. Phys.*, 1905, 3, 537). The salt was introduced into the lower, and the acid into the upper bulb, and the neck sealed off with a mouth blowpipe before exhaustion. The gas was dried by passage over phosphoric oxide contained in the tubes *T* in the diagram, and was then condensed to a solid in the vessel *R*. From *R* the hydrogen chloride was boiled off and condensed in the second fractionating vessel *S*; when the latter was about half full, the tap was reversed, and the gas allowed to bubble through its own liquid. In this way any impurities possessing a higher boiling point than hydrogen chloride were partly or wholly eliminated. That fraction of the gas which passed over at an early stage of the operation was judged to be the purest, and was stored for later

use in two large 5-litre bulbs, which had been previously evacuated, first by means of a Fleuss pump, and finally by means of charcoal cooled in liquid air. The impure gas was then allowed to evaporate, and the connecting tubes and fractionating vessels were freed from this residue with a Töpler pump. Before filling the density bulb, the gas was condensed out of the storage bulbs and put through another series of fractionations. As a rule, the first fraction was returned to the storage bulb in case it might contain traces of air which had been entangled or dissolved in the solid hydrogen chloride and thus escaped removal by the pump.

The preparation of the gas from silicon tetrachloride necessitated a different form of generator (Fig. 2). The distilling flask *A* was partly filled with distilled water. The silicon tetrachloride was

FIG. 2.



introduced into the cylinder *B*, which was protected by a calcium chloride tube from the entrance of moisture. *A* and *B* were connected by means of a tube *C*, which, before the introduction of water into *A*, had been filled with dry mercury. During an experiment the apparatus was immersed in a freezing-bath in order to moderate the reaction. By slightly reducing the pressure in *A*, a small quantity of silicon tetrachloride was sucked over, and the reaction started. The mixture of air and hydrogen chloride was passed through a tube *D*, packed with moistened glass beads, and then condensed in a large fractionating vessel. The air was pumped off through the Töpler pump, and the hydrogen chloride carefully fractionated in order to eliminate the last traces of the silicon tetrachloride.

Impurities in the Gas.

Two sources of contamination were discovered in the early stages of the investigation. The gas was found to react with the phosphoric oxide, forming a volatile phosphorus compound, which was decomposed by the mercury of the Töpler pump, a solid yellowish film being deposited on the glass surfaces. The production of this compound has already been observed by Richards. When the gas issuing from the phosphoric oxide tubes was led into water, the solution gave a yellow precipitate with nitric acid and aqueous ammonium molybdate. By employing phosphoric oxide distilled in a stream of oxygen, the formation of this compound was lessened. It was found, however, that the gas could be freed from this impurity by two distillations carried out in the manner described; after this treatment, the concentrated aqueous solution of hydrogen chloride contained no detectable quantity of phosphorus.

The action of the gas on the rubber-vaseline lubricant initially used for the glass stopcocks proved another source of contamination. The grease was rapidly charred, and the taps soon ceased to maintain a vacuum. At the same time, organic compounds volatile in the gas were formed, and the density of the latter increased. The substitution of metaphosphoric acid for the grease was considered, but abandoned on account of the large volume of hydrogen chloride it is capable of absorbing (Baker, *Trans.*, 1898, **73**, 422; Gutmann, *Annalen*, 1898, **229**, 3). Finally, a lubricant, consisting solely of pure paraffins, was prepared, and this proved to be without action on the gas and to be capable of rendering a carefully-ground stopcock gastight for an indefinite period.

After the gas had been kept for some time in the storage bulbs, it was found to contain traces of chlorine, and to cause phosphoric oxide to deliquesce. This was doubtless due to chemical action between the hydrogen chloride and traces of air adsorbed on the glass surfaces of the apparatus, or given off slowly from the tap-grease (Berthelot, *Compt. rend.*, 1897, **125**, 746). To eliminate the chlorine, the gas was passed over clean mercury before liquefaction (Shenstone, *Trans.*, 1897, **71**, 485). Any mercury vapour carried by the gas was, of course, condensed in the fractionating vessels, and could not find its way into the density bulb.

The crude gas from the ammonium and sodium chlorides and sulphuric acid certainly contained other impurities. The last fraction of the liquefied gas nearly always held in suspension a slight white precipitate, which volatilised less readily than the

hydrogen chloride itself. On examination of the gas resulting from the precipitate, hydrogen sulphide was discovered. Its presence was evident from the odour of the aqueous solution of the gas, and also from the formation of methylene-blue in a solution of *p*-aminodimethylaniline sulphate. The mode of its origin is, however, obscure. It is certain that neither the ammonium nor sodium chlorides nor the sulphuric acid contained sulphides, and one can only suppose that it originated from the reduction of the sulphuric acid itself during the evolution of the gas. The complete elimination of traces of hydrogen sulphide from hydrogen chloride is not easy. It might be supposed that it would be removed by mercury, but mercury does not attack perfectly dry hydrogen sulphide. Again, it might react with traces of chlorine, but in view of the absence of moisture this is also doubtful, and, moreover, chlorine was not always present. For its elimination we had to rely entirely on the fractional distillation of the liquefied gas.

With regard to the gas obtained from silicon tetrachloride and water, it is difficult to see how it could have contained any foreign gases besides a possible trace of chlorine and vapour of the tetrachloride. It was certainly purer initially than the product from the other two reactions. After the final fractionations, however, the gas from all three sources was certainly very pure. When condensed, the liquid was perfectly clear and colourless, and left no residue on evaporation. On further cooling, the liquid yielded a pure white, crystalline solid, which melted sharply at a constant and definite pressure of 100 mm. The gas was entirely free from air, for a little boiled water or a small piece of solid potassium hydroxide absorbed it completely. It contained no compound of phosphorus, and chlorine was entirely absent. The only likely impurity, in the case of gas prepared by the action of sulphuric acid on a chloride, was hydrogen sulphide. For reasons which will be given later, we are convinced that it could not have been present in sufficient quantity to influence the density results.

We noticed a curious phenomenon connected with the condensation of hydrogen chloride, which is worthy of mention. When the solidified gas was sublimed, or when the gas itself was slowly condensed at the temperature of liquid air, the crystalline product almost always exhibited a rose-pink coloration in patches. On allowing the solid to become warm, the pink colour entirely vanished before the melting point was reached. We have been unable to concentrate the coloration by either fractional distillation or sublimation of the hydrogen chloride. On the supposition that it is produced by a small trace of some highly coloured impurity, we have tried to increase its amount by adding small quantities of

other gases and vapours, for example, chlorine, iodine, bromine, nitrogen peroxide, sulphur dioxide, and hydrogen sulphide, to hydrogen chloride and condensing the mixture, but in no instance was there any visible increase of the coloration. The phosphoric oxide was not responsible for its production, for in one set of experiments sulphuric acid only was used as a desiccating agent, but the pink colour still made its appearance. It is noteworthy that Inglis (*J. Soc. Chem. Ind.*, 1906, **25**, 152) obtained a gas condensing to a red solid from the lead chamber gases of a sulphuric acid plant. The presence of a trace of moisture prevents the appearance of the colour, for we were never able to obtain it unless the gas had been previously very carefully dried. The intensity of the coloration varied in different specimens, but it did not appear to influence in any way either the density of the gas or its volumetric composition. We have, therefore, concluded that if the pink colour denotes the presence of an impurity, the latter must have been present in extremely small amount.

Adsorption of Hydrogen Chloride on Glass Surfaces.

In a research of this nature, the adsorption of the gas on the internal surface of the density bulb calls for careful consideration. We have confirmed the observation of Guye (*Compt. rend.*, 1906, **143**, 1233), that the density of the gas in a new bulb decreases with each filling, and finally reaches a minimum value which varies fairly regularly about a mean. In all probability this decrease is due to the presence on the surface of the bulb of a film of moisture which absorbs the gas in relatively large quantities; this film being partly absorbed by the charcoal in the weighing bulb, together with the gas itself, the apparent density is too great. With each successive filling the film should diminish, and the density reach a constant value. As a matter of fact, in our method of working, a limit of desiccation was certainly reached after the first few fillings, and since, throughout the whole series of experiments in the same bulb, there was never any necessity for removing the stopcock, any source of error due to the moisture film either vanished or remained at a minimum. In the absence of all avoidable moisture there was, however, a small but appreciable amount of gas adsorbed by the glass.

These conclusions are supported by the following experiments. A glass cylinder, fitted with a stopcock at either end, was connected with an adjustable mercury reservoir, and completely filled with dry mercury. On opening the upper tap, carefully dried hydrogen chloride entered and displaced the mercury; the gas

itself was then completely displaced by raising the mercury reservoir, and the upper tap was closed. On lowering the reservoir again, a vacuum was produced, and the mercury was drawn down until the meniscus fell below the lower tap. It was observed that during this operation small bubbles of gas came off from the walls of the vessel and collected in the cylinder. On taking special precautions beforehand to exclude moisture, the quantity of gas evolved in this way was visibly less. In order to make the experiment more definite, the cylinder was detached from the rubber tube connecting it with the mercury reservoir, and about 1 c.c. of a *N*/50-silver nitrate solution, acidified with a little dilute nitric acid, allowed to enter. Care was taken to avoid the presence of small mercury globules in the cylinder and tubes leading to the taps. When the cylinder had been carefully dried by a stream of pure air passed over phosphoric oxide, only a faint opalescence was produced, but the presence of a very small amount of moisture was sufficient to cause a marked turbidity in the reagent. Hence one may conclude that adsorption of the gas by well-dried glass surfaces is very small. That even this small amount of gas is taken up by cooled cocoanut charcoal is certain from the fact that on letting a little of the silver nitrate solution into the exhausted volume bulb of our apparatus at the end of each series of determinations, no trace of opalescence was ever observed. This test was fairly delicate, for blank experiments carried out with the same volume of silver nitrate solution showed that as little as 2 cub. mm. of the gas could be readily detected.

This last test also negatives the supposition that the glass was decomposed to any appreciable extent by the hydrogen chloride; had this been the case, chlorides of the bases present would have been formed and have yielded a precipitate with aqueous silver nitrate.

From the foregoing experiments, it is clear that a rigorous desiccation of the density bulb was essential if good results were to be obtained. A silica bulb was used in the later determinations, for it was very much easier to dry its interior completely. The silica bulb was heated to redness and repeatedly filled with dry air and exhausted before attaching it to the apparatus.

In our earlier density measurements, when rubber-vaseline grease was used as a tap-lubricant, it was only possible to make a small number of experiments without regreasing the bulb stopcock, and this involved the admission of moisture. For this reason, and also on account of the contamination of the gas by the grease, we consider these results untrustworthy, and they are not recorded in the final table.

In some experiments, which will be described later, we have measured the volume of gas removable from the glass surfaces in a vacuum. The method was similar to that employed in the qualitative experiments just described, but care was taken to displace the gas by the mercury at constant pressure. The bulb was made of the same glass as that used for the densities, and was kept at 0° throughout the operation. The amount of gas given off from each square cm. of surface amounted to 0.1235 cub. mm., and this quantity was constant at constant temperature and for any given initial pressure. On the assumption that this adsorbed gas exerted no pressure, we have made use of these results to correct our densities. The surface of the density bulb being 291 sq. cm., the volume of gas adsorbed by it was 0.036 c.c., and its weight 0.00006 gram, and hence the amount to be subtracted from the weight of a litre of the gas was 0.00013 gram. This correction only applied to the glass bulb, and since no direct experiments on adsorption on silica surfaces have been made, we have introduced no alteration in the measurements carried out in the silica bulb.

Another possible source of error was the solution of traces of hydrogen chloride in the grease used for the stopcocks. An attempt was made to measure this. It was found that the amount of gas dissolved by the grease on the bulb stopcock did not exceed 0.01 c.c., and since this amount of gas represents an error smaller than the mean probable error in any of the series, we have decided to neglect it.

In the following table we have applied to the numbers in the third column a small correction for the slight deviation of hydrogen chloride from Boyle's law between 760 mm. and the observed barometric height.

TABLE OF RESULTS.

Series I.

Glass bulb. Volume at 0° = 465.856 c.c. Gas from sodium chloride and sulphuric acid.

	Weight of gas condensed on charcoal : all corrections made.	Barometric pressure at 0° : London : all corrections made.	Weight of 1 litre of gas at 0° and 760 mm. in London, corrected for compressibility of HCl.
1.	0.76097 gram	756.76 mm.	1.64053 grams
2.	0.75731 "	753.38 "	1.64004 "
3.	0.75481 "	750.83 "	1.64020 "
4.	0.75968 "	755.79 "	1.63986 "
		Mean.....	1.64016 grams ± 0.00010

Series II.

Glass bulb. Gas from silicon tetrachloride and water.

	Weight of gas condensed on charcoal; all corrections made.	Barometric pressure at 0°: London; all corrections made.	Weight of 1 litre of gas at 0° and 760 mm. in London, corrected for compressibility of HCl.
1.	0.75841 gram	754.38 mm.	1.64022 grams
2.	0.75959 "	755.65 "	1.63999 "
3.	0.76169 "	757.83 "	1.63976 "
4.	0.76150 "	757.15 "	1.64083 "
5.	0.75922 "	755.14 "	1.64030 "
6.	0.76186 "	757.79 "	1.64021 "
7.	0.76194 "	757.84 "	1.64027 "
Mean.....			1.64023 grams ∓ 0.00008

Series III.

Quartz bulb. Volume at 0°=457.420 c.c. Gas from ammonium chloride and sulphuric acid.

1.	0.74622 gram	756.26 mm.	1.63950 grams
2.	0.74643 "	756.18 "	1.64013 "
3.	0.75295 "	762.87 "	1.63984 "
4.	0.75776 "	767.31 "	1.64069 "
5.	0.75762 "	767.35 "	1.64031 "
6.	0.75216 "	761.93 "	1.64017 "
7.	0.73831 "	747.85 "	1.64050 "
8.	0.73646 "	745.99 "	1.64051 "
9.	0.74316 "	752.99 "	1.63992 "
10.	0.75651 "	766.37 "	1.64001 "
Mean.....			1.64016 grams ∓ 0.00008

From the means of Series I and II, there has to be subtracted 0.00013 gram, which represents the weight of adsorbed gas given off from the walls of the glass bulb. Then the means of the three series become:

Series I	1.64003
, II	1.64010
, III (unaltered)	1.64016

The final mean calculated by the method of least squares is 1.64011 ∓ 0.00005 , and the weight of a normal litre of gas (namely, the weight of 1 litre at 0° and 760 mm., Lat. 45°) is:

$$\frac{1.64011}{1.000588} = 1.63915 \text{ gram,}$$

where 1.000588 is the factor which expresses the difference in the value of "g" between London and Lat. 45°.

On comparing the individual values in any one series, it will be seen that the maximum divergence is very much greater than the probable errors of measurement. We must say that in view of

the concordance of the results obtained by the same method with nitric oxide, a closer agreement was expected. It hardly seems likely that the discrepancies can be entirely explained by the presence of impurities in the gas, and our work on the analysis of hydrogen chloride supports this view. Moreover, in neither series is there any progressive change in weight, although the densities correspond with successive fractions of the liquefied gas. On the other hand, the agreement between the mean values of the three series leaves nothing to be desired, and in consequence of the large number of determinations, we think that our final figure is an accurate approximation to the true density of hydrogen chloride.

PART II.—*The Volumetric Analysis of Hydrogen Chloride.*

In order to deduce the molecular weight of hydrogen chloride from the value obtained for the density, it was possible to adopt several modes of procedure, involving the knowledge of either the exact volume of hydrogen yielded by two volumes of the gas, or of the relative compressibilities of hydrogen chloride and some standard gas, such as oxygen. A third method was to determine and reduce the critical constants of the gas according to the method worked out by Guye (*J. Chim. Phys.*, 1908, **6**, 795). These two latter methods involve a somewhat uncertain extrapolation, which is not the case in the first method, and for this reason we thought the most satisfactory course was first to measure accurately the volumetric composition of the gas.

On account of the deviation of hydrogen and hydrogen chloride from the gas laws, it is clear that the ratio of the densities at 0° and 760 mm. does not accurately represent the ratio of the molecular weights. If, however, the volumes occupied by chemically equivalent quantities of the two gases are known, the required ratio can at once be deduced.

The actual course of procedure was to find the volume of hydrogen obtainable from exactly two volumes of hydrogen chloride, both gases being measured in the same apparatus at 0° and 760 mm., that is, the same temperature and pressure at which the density measurements were made. In essentials the method was as follows. The two volumes of hydrogen chloride were measured successively in a constant pressure pipette, which, together with the mercury manometer column, was immersed in melting ice throughout the determination. After each filling the gas was collected in a bulb, and there decomposed by means of heated aluminium. The hydrogen produced was then returned to the measuring vessel, and since its volume was a little greater than

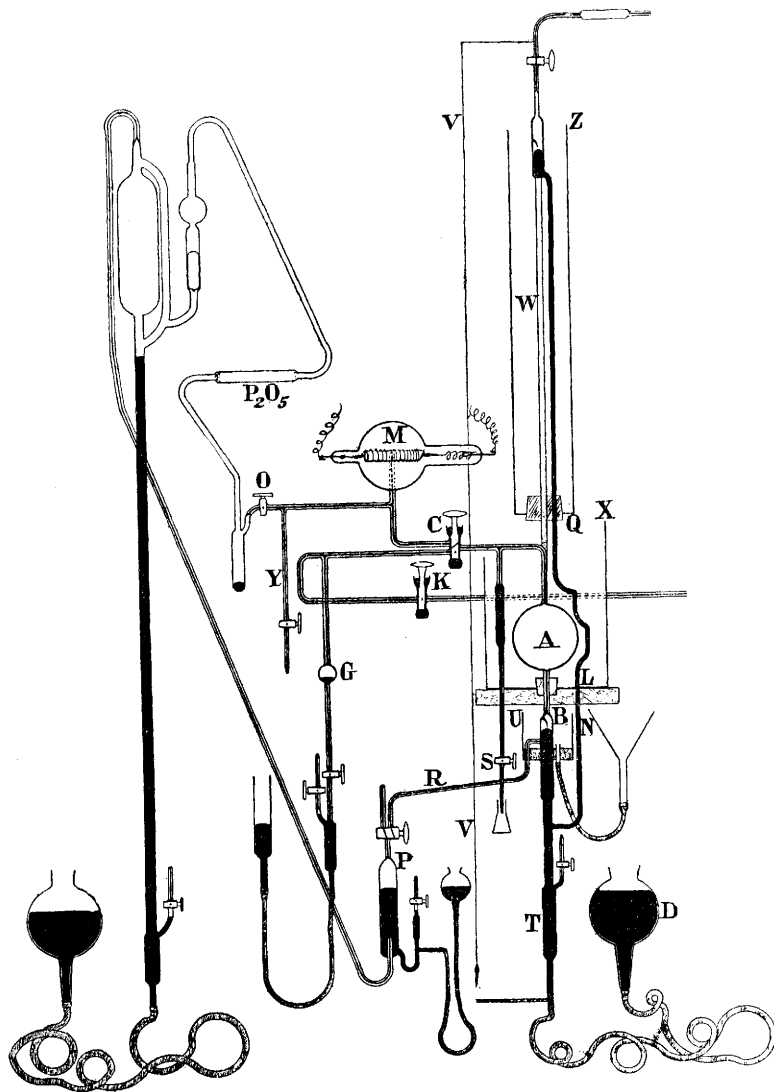
half the total volume of the hydrogen chloride, it was necessary to increase the volume of the pipette slightly in order to recover the original pressure. The accurate measurement of this small volume increment supplied the data for determining the ratio of chemically equivalent volumes of hydrogen and hydrogen chloride.

The constant pressure pipette consisted essentially of the thick-walled bulb *A* (Fig. 3) of about 300 c.c. capacity, connected below by means of a short length of capillary tubing with the dead-space *B*, and above with another capillary tube carrying a two-way stopcock *C*. The dead-space was furnished with a glass point. The upper chamber of the manometer also carried a glass point, and communicated with the lower chamber containing the dead-space as shown in the figure. The distance between the two points was maintained constant by means of a stout glass rod *W*, sealed at its upper end to the manometer head, and at its lower to the capillary tube connecting the pipette with the two-way tap *C*. For our purpose, it was not necessary to know the exact distance between the two points. It was, however, essential that this length should not differ much from 760 mm. In sealing together the two ends of the glass rod when the apparatus was being set up, special care was taken to ensure the correct adjustment of the two points, and subsequent measurement with a cathetometer proved the final distance between them to be within 0.1 mm. of the required length. It was further necessary to guard against any alteration of the vertical distance between the two points during an experiment. The whole apparatus was rigidly fixed to a heavy iron bar with a tripod base, and any vertical displacement could at once be detected by the plumb-line *VV*. By levelling the tripod it was easy to reset the plumb line, and in practice this could be done without putting any dangerous strain on the sealed glass connexions. We adopted the method of Rayleigh (*Proc. Roy. Soc.*, 1893, 53, 137) to ensure the absence of air or moisture in the manometer head. The vacuum in the latter was verified from time to time by means of a Töpler pump (not shown in figure), and a small tube containing phosphoric oxide served to retain traces of water vapour.

Sealed to the capillary between the bulb and the tap *C* was a capillary T-piece expanding into a tube of a few c.c. capacity, which terminated at its lower end in another capillary carrying a tap *S*. During the measurement of the hydrogen chloride, this side-tube, which we have called the volume-adjuster, was filled with mercury up to the top. It only came into use during the measurement of the hydrogen, and enabled the necessary increase in volume to be made.

As can be seen in the diagram, the pipette, manometer column,

FIG. 3.



bath so as to cover the cork Q , in order to keep adjacent parts of the manometer column and glass connecting rod at 0° . It was clearly impossible to surround the dead-space with melting ice

on account of the difficulty of seeing the point. To obviate this, we surrounded the dead-space by a small subsidiary bath *U*, which could be filled with a suitable liquid cooled below 0° by means of the funnel. For this purpose we used brine, and we found no difficulty in keeping the temperature within one degree of zero when the final setting was made. On account of the small volume of the dead-space (almost exactly 1 c.c.), a variation of this order did not affect the results. The mercury required for displacing gas from the pipette was contained in a reservoir *D*. An air-catch *T* guarded the pipette from any trace of leakage at the rubber junction.

Calibration of the Pipette.—The pipette was calibrated from the tap *C* to the glass point in the dead-space by means of mercury after the apparatus had been set up, and before the side-tube leading to the manometer head had been sealed on. For this purpose a stopcock on capillary tubing, which was drawn out to a fine point, was temporarily fused on to the glass tubing below the dead-space. The pipette was then filled with mercury and cooled to 0° . The whole volume of mercury from the tap *C* was run out and weighed. Mercury was introduced again until the meniscus was set to the glass point, and this quantity was then run out and weighed. In a second calibration, the required volume was obtained directly by weighing the mercury run out from the tap to the dead-space point. During the calibration, the tubing below the dead-space was wrapped in cotton-wool to prevent the temperature from changing. The actual temperature in this part of the apparatus was not of importance so long as it remained approximately constant. The initial and final temperatures recorded by a thermometer in the cotton-wool were found not to vary by more than a degree throughout the operation, a difference involving no correction on the total volume.

The mercury was weighed in four portions, and a set of platinised brass weights, ranging from 1 kilogram downwards, which had been carefully compared with each other, were used for this purpose. The same set of weights was employed for weighing the mercury withdrawn from the volume-adjuster in the measurement of the hydrogen during the analyses. In this way the volume increment was compared very exactly with the total volume of the gas, and the accurate evaluation of this ratio was all we desired to accomplish. The absolute volumes of the mercury withdrawn could have been calculated by making the usual corrections for air-displacement, and by comparing our weights with a standard set, but this was unnecessary, for in no circumstances could the required ratio have been appreciably altered by changes in atmospheric conditions during weighing.

Calibration Values.

			Temp. of cotton wool.
I.	Weight of mercury from tap <i>C</i>	4365.749 grams	2.5°
	" " " dead-space point	193.968 "	2.9
	" " " filling pipette from tap		
	<i>C</i> to point.....	4171.781 "	—
	Volume	306.850 c.c.	—
II.	Weight of mercury from tap <i>C</i> to dead- space point	4171.750 grams	1.2—2.3
	Volume	306.848 c.c.	—
	Mean	306.849 c.c.	—

Introduction and Measurement of the Gas.

The purified gas was distilled into the pipette through the taps *K* and *C* * until the points in *B* and *E* were approximately set. The tap *K* was then closed, and the final setting effected by means of the pressure-adjuster *G*; this requires no special description. By arranging the small reservoir *H* at a suitable height, and swinging the tap *J*, minute quantities of gas could be introduced into or withdrawn from the pipette. By the alternate manipulation of the pressure-adjuster and of the screw controlling a wooden clip, which compressed the rubber tubing connecting the reservoir *D* to the pipette, the two mercury menisci were set to their respective points. As Lord Rayleigh has shown, this method enables a very accurate adjustment to be made (*Phil. Trans.*, 1902, *A*, **198**, 418).

With regard to temperature, the only parts of the system not actually surrounded by melting ice were the dead-space, which was cooled in a brine-bath as described, the short piece of capillary tubing connecting the dead-space and pipette, and the short column of mercury in the manometer from *L* to *M*. On account of a slow leaking of cold water from the bath above, the temperature of these portions of the apparatus was reduced nearly to 0°.

When the temperature and pressure had been satisfactorily adjusted, the tap *C* was reversed, and the gas allowed to flow through the capillary tube leading to the previously exhausted decomposition bulb *M*. This bulb carried a silica boat slung from two stout platinum electrodes by means of silver leads; the boat was surrounded by a spiral of 30 per cent. iridium-platinum wire, which could be heated to redness by an electric current. The boat contained small pieces of pure aluminium.

In order to obviate the use of a ground joint necessitating a

* Both the taps *C* and *K*, through which hydrogen chloride passed, were lubricated with the paraffin grease described on p. 1639.

lubricant, the boat and its attachments were sealed up in the bulb before the latter was fixed *in situ*. When the two volumes of hydrogen chloride had been transferred, mercury was taken through the tap *C* and along the capillary as far as the bulb. During decomposition, the capillary leading to the pump was kept filled with mercury, previously introduced through the side-tube *Y*. This served to confine the hydrogen chloride to the bulb, and also to protect the lubricant of the tap *O* from the action of the gas. We might mention here that in our final experiments no gas but pure hydrogen was ever allowed to pass the tap *O* leading to the pump.

After decomposition, the resulting hydrogen was allowed to flow back through the tap *C* into the pipette, and the remainder taken through the pump into the collector *P*, which was sealed to the inverted end of the capillary fall-tube. From time to time the hydrogen in the collector was allowed to return by the capillary tube *R* to the pipette. As has already been indicated, the recovery of the original pressure was effected by running out mercury from the tap *S*, and so increasing the pipette volume. This volume increment was then accurately measured by weighing the mercury run out.

Decomposition of the Hydrogen Chloride.

The selection of a suitable metal for the decomposition of hydrogen chloride was a problem of some difficulty. Those metals forming chlorides reducible at a red heat by hydrogen were clearly unsuitable. For the process to take place readily, it was necessary that a clean metallic surface should always be exposed to the gas. To ensure this, the resulting chloride had to be either fusible or capable of being sublimed, or the metal had to be in the liquid state so that it could be agitated during the process.

Preliminary trials were made with the following metals: magnesium, tin, sodium amalgam, and, lastly, aluminium. With magnesium, the reaction did not start easily, and, once started, was quite uncontrollable. Molten tin reacted more gently, but with the dry gas the reaction did not proceed to completion. In the case of sodium amalgam, no decomposition whatever occurred unless the reaction vessel was appreciably moist. Even on raising the temperature to about 200°, the bright surface of the amalgam remained untarnished. In carrying out the reaction in presence of moisture, the hydrogen yield was too small. This probably is to be attributed to the fixation by the sodium hydroxide of a portion of the water, which did not then react with the amalgam.

Experiments with aluminium gave far more satisfactory results. Whilst there was no reaction in the cold, at dull redness and in

entire absence of moisture decomposition proceeded steadily and rapidly to completion. We therefore selected this metal for our final analyses.

The aluminium employed was a very pure specimen obtained from the British Aluminium Company. Analysis showed that it contained no carbon, a trace of iron, and only 0.1 per cent. of silicon. As is well known, aluminium electrodes, when subjected to the electric discharge in a vacuum tube, evolve hydrogen in appreciable quantities. The metal we used evolved a relatively small quantity of this gas, but the evolution was slow, even at bright redness in a vacuum. In order to reduce this content of hydrogen to negligible proportions, the silica boat and metal were kept at a high temperature in the evacuated bulb for several hours before a series of experiments was begun. Finally, the temperature was raised, and the aluminium just fused, which ensured the expulsion of the last traces of the gas. The silica boat was practically unattacked by the fused aluminium or by the subsequent treatment it underwent in the decomposition bulb, and its weight, even after a series of experiments, was hardly altered.*

During decomposition, the chloride volatilised as it was formed, and was deposited as a colourless, crystalline sublimate on the walls of the bulb, which were kept cold by a stream of water. The resulting hydrogen, when slowly bubbled through a silver nitrate solution, proved to contain no trace of hydrogen chloride. If, however, the aluminium chloride was first resublimed by heating the walls of the bulb, the hydrogen pumped off undoubtedly contained traces of the original gas. This showed that a certain quantity of hydrogen chloride had been retained by the sublimate; this occluded gas could not be pumped off, but was expelled during volatilisation. To eliminate this source of error, the aluminium chloride was sublimed in a vacuum after the main bulk of the hydrogen had been removed, and the small quantity of hydrogen chloride liberated was then decomposed by reheating the aluminium. This process was repeated until no more gas could be obtained. The final glowing served also to expel any gas which might have been taken up by the platinum-iridium wire on cooling in hydrogen at a high pressure.

In the earlier experiments, a wire of pure platinum was used for heating the boat, but we found that owing to the action of the aluminium vapour the wire fused after a short time and the circuit was interrupted. Renewal of the wire required the breaking and resealing of the end of the bulb, and caused much delay. By

* Original weight of boat.....	4.6715 grams	} Loss per experiment, 0.00003 gram
Weight after seven experiments	4.6712 "	
" " nine more experiments. 4.6710 "	"	

the employment of a wire containing a high percentage of iridium, drawn for us by Messrs. Johnson and Matthey, this difficulty was overcome. Frequent openings of the bulb entailed other disadvantageous consequences. The admission of moist air, even when no aluminium chloride was present, invariably led to irregular results, doubtless on account of the difficulty of drying the glass surfaces before the actual decomposition was begun. For this reason, sufficient aluminium for a series of determinations was introduced into the bulb at the start, and, with proper precautions to eliminate moisture, concordant values were usually obtainable after the first analysis.

From the foregoing description, it can be seen that in this apparatus the errors of measurement of the volume of the gas were reduced to a minimum. There was no appreciable uncertainty in the temperature of the manometer column, and the pressure was constant within the small limits defined by the accuracy with which the mercury surfaces could be set to the two points. The internal diameter of the glass tubing of which the reading portions of the manometer were constructed was about 15 mm. The capillary depression was consequently very small, and its influence on the pressure setting must have been quite negligible on account of the method of adjustment of the meniscuses. Further, it was repeatedly proved that the gas could be circulated through the apparatus and retransferred to the pipette with hardly any perceptible change in volume. Before the final determinations recorded in this paper, we spent more than two months in testing the apparatus. We frequently made the experiment of passing a measured volume of hydrogen prepared from hydrogen chloride into the decomposition bulb, heating the aluminium for a long period, and then measuring the gas again in the pipette. In absence of moisture, the two measurements never differed by more than one part in ten thousand, and in many cases a concordance of one part in twenty thousand was attained. In the actual analysis of hydrogen chloride, many unforeseen sources of error made their appearance, and these will now be briefly considered.

Impurities in the Hydrogen Chloride.

In discussing the purity of the gas with which the density determinations were made, we pointed out that a rigorous fractionation of the liquefied hydrogen chloride was necessary in order to remove traces of hydrogen sulphide from gas generated from sulphuric acid and a chloride. The results of the volumetric analysis indicated still more clearly the need of the same precaution, since an amount of this impurity, insufficient to affect the density,

had a marked influence on the volume ratio. That we finally succeeded in eliminating hydrogen sulphide is shown by the fact that nearly identical results were obtained by analysis of gas from silicon tetrachloride and water, and from phosphoric acid and ammonium chloride, sources which admitted of no possible contamination with this impurity.

Although the gas prepared from silicon tetrachloride and water had given excellent density results, a fresh preparation for the volume ratio apparatus was not so satisfactory. The difficulty of separating by fractionation some impurity the nature of which we were unable to determine soon led us to discontinue experiments with this particular sample of gas. From the lower-boiling fractions, we obtained one result which we have included in our final series, but the higher-boiling fractions gave values differing from each other by as much as one part in 2500, and were hence neglected. It was judged sounder to check our results by the analysis of gas from a fresh source rather than prepare another sample from silicon tetrachloride and water. Accordingly, we selected the interaction of phosphoric acid and ammonium chloride as likely to yield a pure product. The phosphoric acid (Kahlbaum, sp. gr. 1.7) contained no sulphates, no organic matter, no lower acids of phosphorus, and only a small trace of nitric acid, as shown by the brucine test. The ammonium chloride was a sample of very pure salt supplied by Merck, and contained no organic bases. It was recrystallised twice from boiling water, and the perfectly clear solution was then evaporated to dryness in the flask in which the reaction was afterwards carried out. The greatest care was taken to avoid the entrance of dust or other organic impurities. No corks were used, and evaporation was effected by the passage of a stream of pure dry air over the surface of the solution while the flask was heated on a water-bath. When the salt was perfectly dry, phosphoric acid was introduced, the neck of the flask sealed off, and the side-tube fused on to the rest of the apparatus. The reaction, which was carried out in a vacuum, proceeded steadily on gentle warming. The residue left in the flask after the reaction was always perfectly white. From its method of preparation, this specimen of hydrogen chloride must have been very pure. The liquefied gas, however, was subjected to the same series of distillations before storage as the less pure gas from other sources, and was fractionally distilled into the pipette immediately before analysis.

Among the list of impurities already discussed, we should include traces of sulphur dioxide and carbon dioxide, which might have been formed by the action of sulphuric acid on dust particles in

the reaction vessel. The existence of the former of these gases—which would have been easily separated by fractionation—is incompatible with that of hydrogen sulphide, small quantities of which were known to be present in the early stages of purification. Owing to its physical and chemical properties, traces of carbon dioxide would have escaped recognition or separation, but the presence of appreciable quantities would certainly have been detected, as the density and the volume ratio results would have been affected in opposite senses. Assuming that the carbon dioxide would have been completely reduced by the aluminium in the decomposition bulb, the volume ratio would have been low, whereas the density would have been high. The following table shows the effect of 0.1 per cent. by volume of various impurities on the density and volume ratio respectively:

	Density.	Volume of hydrogen from two volumes of hydrogen chloride.
Pure hydrogen chloride.....	1.6392	1.0079
0.1 per cent. H_2S	1.6391	1.0089
0.1 „ air	1.6383	1.0085
0.1 „ $SiCl_4$	1.6423	1.0069
0.1 „ CO_2	1.6396	1.0069
0.1 „ SO_2	1.6405	1.0069
0.1 „ HBr	1.6412	1.0079

It is easy to see that most impurities would have changed the results of the volumetric analysis and the densities in opposite directions and by different amounts. The fact that constant values for both sets of measurements were obtained with gas from different sources furnishes the best criterion of its purity and of the accuracy of our final numbers.

Adsorption of Hydrogen Chloride on the Glass Surfaces.

This phenomenon has already been discussed in Part I. A correction was made for the gas adsorbed on the walls of the density bulb and subsequently removed by the charcoal. In the same way the displacement by mercury of the hydrogen chloride from the pipette in the volume-ratio apparatus left on the walls a layer of adsorbed gas, which had to be taken into account, for had it not been removed it would certainly have escaped from the walls when the bulb was filled with hydrogen. In this case, however, it was unnecessary to measure and allow for this gas, since it could be got rid of without difficulty. In order to avoid any variation in the quantity of gas adsorbed, each volume of hydrogen chloride was transferred from the pipette to the decomposition bulb at approximately constant pressure. This was achieved by a suitable regulation of the tap *C* and of the position of the reservoir *D*, and

by carrying out the decomposition of the first volume of hydrogen chloride before the introduction of the second. As soon as the second volume of gas had been displaced, the tap *C* was shut and the reservoir *D* lowered. The adsorbed gas escaped from the walls into the vacuous pipette, and on taking the mercury up again was collected in the capillary. From here it was removed into the fractionating train by forcing the mercury through the other bore of the tap *C*. By repeating this operation twice, the adsorbed gas was reduced to a negligible quantity. In most experiments we adopted the further precaution of washing out the pipette with hydrogen from a previous determination.

Impurities in the Hydrogen.

The purity of the hydrogen obtained from the volume analysis was tested in various ways. The gas had no odour, and, as has already been mentioned, contained no trace of hydrogen chloride. The absence of hydrocarbons was proved by exploding with oxygen, when no carbon dioxide was found. Traces of silicon compounds, such as silicon tetrachloride, silicochloroform, or silicon hydride, might conceivably have been derived from the small quantity of silicon in the aluminium. Of these, silicon tetrachloride or silicochloroform would have been detected in the same manner as hydrogen chloride when the hydrogen was bubbled through silver nitrate solution. Silicon hydride, being very unstable, would hardly have escaped decomposition in the bulb. Further, on exploding the hydrogen with oxygen, any silicon compounds present would have left a residue of silica, and this was never observed.

In order to test for the presence of nitrogen, about 150 c.c. of the hydrogen were exploded with pure oxygen, until the volume was reduced to less than 1 c.c. This residue, after being dried over phosphoric oxide, was taken into a vacuum tube and examined spectroscopically. At low pressures no nitrogen could be detected, and there was only a very faint indication of its presence when the pressure was raised. This amount was negligibly small, and could not have influenced the results.

Numerical Results.

Since the volume, pressure, and temperature of the hydrogen chloride and the pressure and temperature of the resulting hydrogen were fixed and constant, the weight of the mercury run out of the volume-adjuster was a direct measure of the increase in volume, no corrections being required.

Volume of Hydrogen Chloride, 306.849×2 c.c. in all cases. Volume of Hydrogen, $306.849 + x$ c.c.

Source of gas.		Weight of mercury run out (in grams).	Increment volume x (in c.c.).	Volume of hydrogen from two volumes of hydrogen chloride.
NaCl and H_2SO_4 ...	Exp. 1	33.25	2.446	1.00797
NaCl and H_2SO_4 ...	„ 2	33.16	2.439	1.00795
NH_4Cl and H_2SO_4 ...	„ 3	32.98	2.425	1.00790
NH_4Cl and H_2SO_4 ...	„ 4	32.97	2.425	1.00790
NH_4Cl and H_2SO_4 ...	„ 5	32.57	2.396	1.00781
$SiCl_4$ and H_2O	„ 6	32.50	2.390	1.00779
NH_4Cl and H_3PO_4 ...	„ 7	32.85	2.416	1.00787
NH_4Cl and H_3PO_4 ...	„ 8	33.30	2.449	1.00798
Mean				1.00790
Maximum deviation, 1 in 5000.			Probable error, ∓ 0.000017 .	

We now have all the requisite data for calculating the atomic weight of chlorine.

If D_{HCl} represents the weight of a litre of hydrogen chloride at 0° and 760 mm., Lat. 45° , and D_H represents the weight of a litre of hydrogen under the same conditions, and if the ratio of the volumes of hydrogen and hydrogen chloride, which at 0° and 760 mm. contain equal number of molecules, is denoted by R , then the molecular weight of the gas in terms of $O=16$ is given by the expression :

$$\left\{ \frac{D_{HCl}}{D_H} \cdot \frac{2}{R} \right\}. \quad \text{Atomic weight of hydrogen.}$$

Assuming Morley's value for the weight of the litre of hydrogen under standard conditions, namely, 0.089873 gram, and also his value 1.00762 for the atomic weight of this element on the oxygen standard, the molecular weight of hydrogen chloride is obtained on substituting our experimental values in the above expression :

$$\frac{1.63915}{0.089873} \cdot \frac{2}{1.00790} \cdot 1.00762 = 36.467.$$

and the atomic weight of chlorine = **35.459**.

This value is in close agreement with the values found by Dixon and Edgar, namely, 35.463, and by Edgar, 35.461, who also based their calculations on Morley's atomic weight of hydrogen, but differs by 1 part in 3500 from that found by Noyes and Weber, namely, 35.452, whatever value is assigned to hydrogen. It should be pointed out here that our result, unlike Dixon and Edgar's, is dependent not only on the atomic weight, but also on the density of hydrogen. We have selected Morley's value for this constant as being the most trustworthy, and our selection seems justified by

the results of the measurement of the compressibility of hydrogen chloride which we now proceed to describe.

PART III.—*The Compressibilities of Oxygen and Hydrogen Chloride*

It has been shown by D. Berthelot and Rayleigh that at sufficiently low pressures all gases should strictly follow Boyle's law, and that their relative densities should be exactly proportional to their molecular weights. The actual measurement of gaseous densities at low pressures is unnecessary, for the normal densities can be reduced to the corresponding values for perfect gases from a knowledge of the gaseous compressibilities. Thus, if D_1 represents the normal density of a gas, and A_{10}^1 the mean coefficient of com-

pressibility between 1 and 0 atmospheres, then $D_1(1 - A_{10}^1)$ represents the density the gas would have under normal conditions if its behaviour on compression from very low pressure to 1 atmosphere were theoretically perfect. That is to say, the ratio of the molecular weights of different gases is exactly equal to the ratio of the densities:

$$D_1(1 - A_{10}^1) : D_2(1 - A_{20}^1) : D_3(1 - A_{30}^1), \text{ etc.}$$

The compressibility coefficient represents the deviation per atmosphere of a gas from Boyle's law between the pressure limits 0 and 1 atmosphere, and is defined by the expression:

$$A_{10}^1 = \frac{p_0 v_0 - p_1 v_1}{p_0 v_0 (p_1 - p_0)},$$

where v_1, v_0 represent the volumes occupied by the same mass of gas under pressures p_1, p_0 , at constant temperature. The densities $D_1(1 - A_{10}^1)$, $D_2(1 - A_{20}^1)$, etc., are called by D. Berthelot limiting densities.

The variation of gases from Avogadro's law may be conveniently expressed in terms of density per unit pressure. If the weight of a certain mass of gas is W grams, and if it occupies at 0° a volume V litres under a pressure of p atmospheres, its density per unit pressure is W/pv . The value taken by this expression when $p=1$ atmosphere represents the normal density, and the value when p is very small, the limiting density. At pressures intermediate between 0 and 1 atmosphere the same mass of gas will occupy the volumes v_1, v_2 , and v_3 , and exert the pressures p_1, p_2 , and p_3 , and the densities per unit pressure will be:

$$\frac{W}{p_1 v_1}, \quad \frac{W}{p_2 v_2}, \quad \text{and} \quad \frac{W}{p_3 v_3}.$$

For a perfect gas it is clear that these values will be equal, for pv is independent of the pressure, but for those gases which are more compressible than theory demands, pv increases as the pressure falls and the density per unit pressure diminishes. On the other hand, for gases like hydrogen and neon, the converse is true, and the limiting densities are greater than the normal densities.

The ratio of the limiting densities of two gases in this terminology is:

$$\frac{D_1}{D_2} = \frac{W_1}{p_0^1 v_0^1} \cdot \frac{p_0^2 v_0^2}{W_2},$$

where W_1 and W_2 represent any weights of two different gases in grams, and $p_0^1 v_0^1$, $p_0^2 v_0^2$ the values in litre atmospheres of the corresponding pv products of these weights at very low pressures. Consequently, if the molecular weights of the two gases are represented by M_1 and M_2 , and the molecular weight M_2 is known, the value of M_1 is given by the expression:

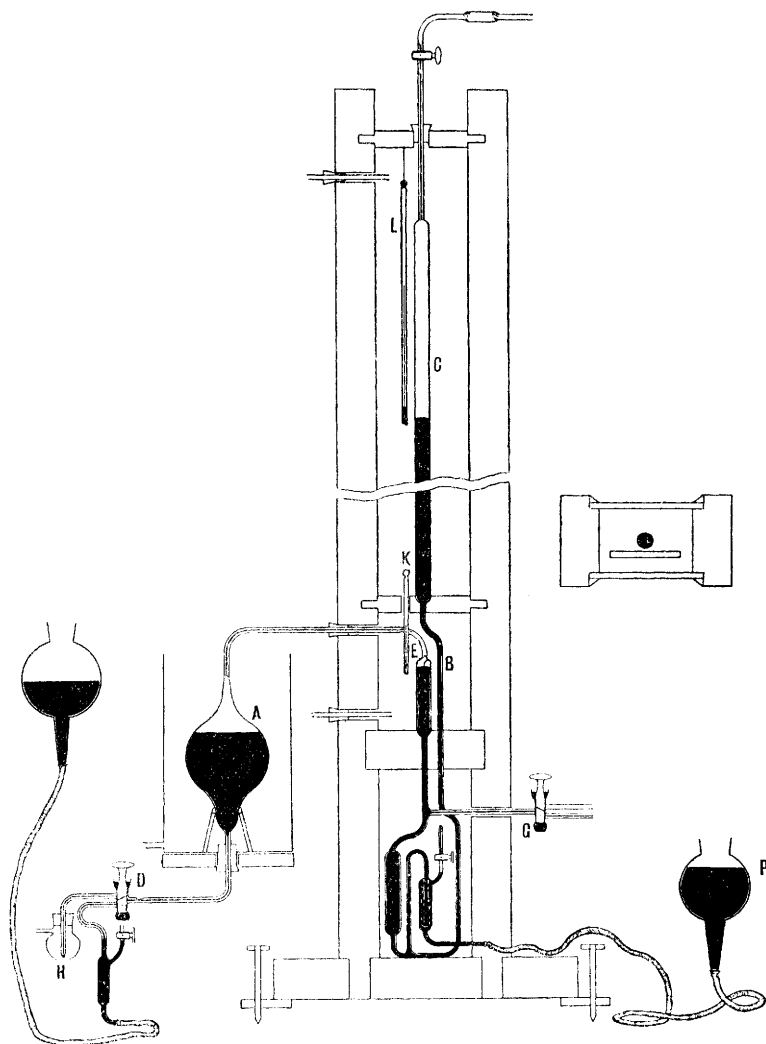
$$M_1 = M_2 \cdot \frac{W_1}{p_0^1 v_0^1} \cdot \frac{p_0^2 v_0^2}{W_2}.$$

It is, therefore, evident that the measurement of the exact molecular weights of gases by the method of limiting densities resolves itself into the accurate determination of the factor $p_0 v_0$. The whole problem, then, is to determine with the necessary precision the variation of pv between the pressure limits 0 and 1 atmosphere.

There are two ways in which pv can change with changing pressure. The variation per unit pressure may remain constant down to very low pressures, or the variation of pv may decrease. It is, however, very difficult to decide experimentally whether dpv/dp ever becomes zero, because as the pressure falls the measurement of p becomes less and less accurate. At very low pressures a gas may apparently obey Boyle's law; that is to say, if the volume be doubled, the pressure may appear to be exactly halved, but on account of the slight absolute change of p , the variation of pv may escape detection. For this reason, it is difficult to say from the researches of Rayleigh on the behaviour of gases at low pressures whether dpv/dp remains constant from one atmosphere down to very low pressures, or whether its value decreases as the pressure falls. All methods of determining the value of $p_0 v_0$ involve an extrapolation from regions where pv measurements are experimentally practicable. It is, therefore, essential to determine the lie of the pv isothermal in these regions as exactly as possible. In making the necessary extrapolation in order to calculate the exact molecular weights, most investigators have assumed either that pv is a linear function of p between the

limits 1 and 0 atmospheres, or that the slight curvature of the isothermal can be calculated from theoretical considerations (Guye, *J. Chim. phys.*, 1908, **6**, 769, and D. Berthelot, "Sur les Ther-

FIG. 4.



momètres à gaz"). The first assumption is very probably correct for the permanent gases, but for the more compressible gases, such as hydrogen chloride, the true form of the isothermal can only be

satisfactorily ascertained by the experimental determination of a large number of points. In their researches on the compressibilities of ammonia and sulphur dioxide, Jaquerod and Scheuer made only three measurements of pv at pressures of 800, 400, and 200 mm. respectively, and extrapolated to zero pressure by means of a parabolic formula. The values they obtained in this way for the molecular weights of the two gases were distinctly too low, and it seems possible that the true form of the isothermal escaped recognition on account of the small number of points.

Another factor which has been neglected by all investigators in this connexion is the variation in the amount of gas adsorbed by glass surfaces with varying pressure. In the present investigation we have endeavoured to settle as accurately as possible the pv isothermals of oxygen and hydrogen chloride by determining a large number of points, and in the case of hydrogen chloride we have taken into account the adsorption effect.

A series of pressure and volume measurements were made between the pressure limits of 860 and 150 mm. Our results for oxygen confirm those of previous investigators, and show that the isothermal at 0° is a straight line within the limits of measurement. In the case of hydrogen chloride, the isothermal shows a distinct curvature, which becomes more marked as the pressure decreases.

The apparatus (Fig. 4) consisted essentially of a bulb *A*, connected with a dead-space *B* and manometer *C*. The effective volume of the bulb *A* could be varied by withdrawing mercury from the tap *D*. The bulb, which was made of thick glass, had a capacity of about 550 c.c., and was filled with mercury to a mark *E* on the capillary immediately above the dead-space. The pressure contraction of the bulb was measured by completely exhausting it, filling it with mercury cooled to 0° to a mark on the capillary stem, and then determining the change in volume with changing pressure by the movement of the meniscus along the graduated capillary. The results were expressed in a graph, from which the necessary volume correction for any given pressure could be read.

Experimental Numbers.

Pressure.	Volume to be subtracted from volume of gas.
760 mm.	0.000 c.c.
600 "	0.006 "
550 "	0.008 "
350 "	0.014 "
40 "	0.025 "

At the end of the compressibility measurements, we made experiments to see whether the weight of mercury in the bulk caused any

distortion involving alteration of volume. This was done by weighing out mercury and at the same time sucking in water through the upper capillary. The volumes corresponding with the successive quantities of mercury removed were compared with the volumes of water weighed in. Only a very small and negligible alteration in volume due to distortion was observed.

The dead-space and manometer were made from carefully selected lead glass barometer tubing, which had an internal diameter of about 17 mm. The use of lead glass tubing, on account of its freedom from bubbles and striæ, allowed the position of the meniscus to be determined with very great accuracy. In making the dead-space, special care was taken to avoid heating the glass immediately opposite the point. After many unsuccessful attempts, a dead-space possessing a volume of only 1.275 c.c. was obtained, and when it was placed in front of a glass scale and viewed through a low power microscope, no distortion of the scale lines in the vicinity of the point could be detected.

Dead-space and manometer were immersed in a bath with two plate glass sides, and a stream of water kept the temperature constant. Inside the bath and immediately in front of the manometer column was suspended a glass millimetre scale, to which the distance between the two mercury menisci was referred. The scale, which was 1200 mm. long, was made by the Société Gènevoise. The lines were of the order of 0.002 mm. in thickness, and required careful illumination to render them visible. For measuring fractions of a millimetre, we used a telescope fitted with a Hilger micrometer eye-piece, which enabled an accuracy of 0.01 mm. to be obtained. The length of scale over which readings were taken (960 mm.) was compared with an "invar" standard, and found to be 0.044 mm. too long at 16°. The scale was further calibrated in 30 mm. lengths by means of a reading microscope and standard screw reading to 0.001 mm., and a table of deviations drawn up. The maximum correction for irregularity of the scale was 0.03 mm.

EXPERIMENTAL.

The oxygen was prepared by heating pure potassium permanganate, and was purified and dried by passage over soda-lime and phosphoric oxide. It was finally liquefied and distilled into the bulb. The hydrogen chloride was prepared and purified in the way already described. Before the final filling, the bulb was repeatedly exhausted and washed out with the gas to be experimented with. It was then filled with mercury rather beyond the mark *E* on the capillary above the dead-space, and the whole cooled to 0°. The gas entered the dead-space through the side-tube *G*,

and when the pressure had risen to atmospheric, the final adjustment of the meniscus to the mark on the capillary was made by means of the tap *D*. By making this final adjustment at atmospheric pressure we obviated the necessity of applying a correction to the original volume of the gas for the contraction of the bulb on exhaustion. The next step was to allow mercury to run out of the tap *D* into a weighed bottle *H* until the effective volume of the bulb was of the required magnitude. The quantity of gas in the bulb and dead-space could then be adjusted, so that when the mercury meniscus was set to the glass point the pressure was of the order desired. By working in this manner, the initial volume of the gas was given directly by the volume of the mercury at 0° withdrawn from the bulb, plus the volume of the dead-space.

Before reading the pressure of the imprisoned gas, we waited for some time after the temperature of the water in the manometer bath had ceased to vary. After a constant temperature gradient had been attained, there was usually a small difference of the order of 0.1° between the water surrounding the dead-space and the water at the top of the bath. The temperature of the water was ascertained by means of two thermometers, *K* and *L*, inside the bath, one fixed close to the dead-space point, and the other adjustable to the level of the upper mercury meniscus. At low pressures the thermometers showed an almost perfect agreement, since they were closer together. The temperature of the bath remained constant for long periods, and since the mean temperature was certainly known to within 0.05° , the maximum error on the length of the mercury column due to uncertainty of temperature was less than 0.01 mm.

The reduction of the temperature of the bulb and its contents to 0° was necessarily slow, but by observing whether the mercury meniscus in the dead-space remained set, it was easy to see when equilibrium had been established. To avoid uncertain correction, that part of the capillary tube which was outside the bath, and connected the bulb and dead-space, was also immersed in melting ice contained in a metal gutter.

Before making a pressure reading, the mercury meniscus in the dead-space was always brought exactly in contact with the point by means of a screw clamp compressing the rubber tubing connecting the reservoir *P* with the dead-space and manometer column. The distance of a line on the scale from the set meniscus was verified immediately before and after each reading, as it was found that the position of the scale was subject to minute variations. Except that we always adjusted our mercury meniscus exactly to the glass point, our method of reading was the same in all particulars as the method described by Travers, Senter, and Jaquero

in their research on the coefficients of expansion of helium and hydrogen. On account of the relatively large diameter of the mercury meniscus, the point and its mirror image were visible through the telescope, so that an exceedingly accurate setting was possible; further, the correction for capillarity was reduced to negligibly small dimensions.

The initial pressure having been determined, successive quantities of mercury were withdrawn from the bulb and weighed, and the pressures corresponding to the new volumes read. As can be seen from the diagram, mercury would cease to flow from the tap *D* after the pressure in the manometer had fallen to about 500 mm. At this stage, mercury was withdrawn by attaching the side-tube of the small flask *H* to a filter pump. When nearly all the mercury had been removed from the bulb, the process was reversed, and a series of readings taken with rising pressure.

The results in the following table are stated with all corrections made. The latter comprise:

For volume.

1. Reduction of the volume occupied by the gas in the dead-space to 0°.
2. Contraction correction of the bulb.
3. Reduction of the apparent weight of mercury to the vacuum standard.

For pressure.

1. Correction for the total error in the scale at the temperature of reading.
2. Correction for irregularity of ruling in the scale.
3. Reduction of the corrected manometric height to 0°.

In order to show how the corrections were applied, we append a full calculation of the results of one experiment taken at random from our note-book.

Oxygen.

Series I.

<i>p</i> (in mm.).	<i>v</i> (in c.c.).	<i>pv</i> .	Smoothed <i>pv</i> .
763·52	182·864	139620	139629
711·07	196·373	139635	139638
612·56	227·980	139651	139656
564·46	247·440	139670	139665
499·93	279·400	139680	139677
447·18	312·393	139696	139687
384·52	363·300	139696	139696
348·83	400·456	139691	139705
313·57	445·585	139722	139712
284·77	490·603	139709	139717

Series II.

p (in mm.).	v (in c.c.).	pv .	Smoothed pv .
875.99	158.611	138942	138940
849.32	163.605	138953	138945
826.60	168.106	138956	138949
778.09	178.587	138957	138956
738.03	188.304	138974	138962
690.64	201.212	138965	138970
609.03	228.204	138983	138983
560.45	248.010	138997	138992
515.32	269.724	138994	139000
409.56	339.420	139013	139018
372.85	372.842	139014	139024
337.27	412.177	139015	139031
309.58	449.115	139037	139035
280.52	495.651	139040	139040
256.73	541.616	139049	139044

Series III.

866.99	64.874	56245	56249
785.76	71.597	56258	56255
607.97	92.570	56280	56267
547.05	102.863	56271	56272
488.03	115.302	56271	56276
426.36	131.996	56278	56280
365.61	153.959	56289	56285
322.83	174.367	56291	56288
282.72	199.102	56290	56290
252.53	222.920	56294	56293
226.33	248.730	56295	56294
204.30	275.575	56300	56296
188.54	298.563	56291	56298
185.87	302.916	56303	56298
171.66	327.945	56295	56299
169.39	332.375	56301	56299
157.48	357.468	56294	56300

Calculation of pv at 0° from experimental results (last in Series III).

Volume of Gas.

Volume of gas in bulb at previous reading, all corrections made		328.807 c.c.
Weight of mercury run out.....	373.25 grams	
Correction for air displacement of mercury ...	+0.03 ,,	
Increase in effective volume of bulb	373.28	= 27.456 ,,
	13.5955	
Volume of dead-space	1.275 c.c.	
Temperature of gas in dead-space	11.00°	
Volume of gas in dead-space at 0°	$\frac{1.275 \times 273}{284}$	= 1.226 ,,
Contraction of volume of bulb under diminished internal pressure, namely, 158 mm.		-0.021 ,,
Total volume occupied by gas at 0°		357.468 c.c.

Pressure of Gas.

Lower Meniscus.—Mean of two series of readings taken before and after reading upper meniscus:

	Micrometer readings.	Millimetre.	Scale readings.
Distance from mercury meniscus set to point in dead-space to scale-line 5 above it	92, 89, 89, 91,	0.70	5.00 - 0.70 = 4.30
	91, 89, 89		
	Mean = 90		
	(128 micrometer divisions = 1 mm.)		

Upper Meniscus:

Distance of upper meniscus below scale- line 163	111, 113, 112 Mean = 112	0.88	163.00 - 0.88 = 162.12
Uncorrected manometric height	162.12 - 4.30	=	157.82 mm.
Correction for total error in scale	0.044 × 158 960	=	+ 0.007
Contraction of scale from 16° to 11°	0.000009 × 5 × 158	=	- 0.007
Correction for irregularity of scale ruling		=	- 0.021
Correction of observed manometric height from 11.05° to 0°		=	- 0.320
Corrected manometric height		=	157.48 mm.

Therefore, $pv = 157.48 \times 357.468 = 56294$.

The experimentally found values of pv for each series were plotted on squared paper on an open scale against the corresponding pressures, and it was found that the points were evenly distributed about a straight line. Various lines were ruled, until one was obtained which was judged to approximate most closely to the positions of the largest number of points. The deviations of the points from this line were read off and summed. This process was repeated, if necessary, with a fresh line until the algebraic sum of the deviations approached zero. From the final line the smoothed values for pv given in column 4 were obtained. From the table it can be seen that, although a few of the points diverge appreciably, yet the majority deviate only slightly from the smoothed values, and the position of the final line, on account of the number of points, is fixed with a high degree of accuracy.

From the three series, the corresponding values of p_0v_0 and p_1v_1 are readily obtained:

Series.	p_0v_0 .	p_1v_1 .
1	139769	139628
2	139087	138959
3	56311	56256

The limiting densities are given by the expression:

$$D_{\text{lim.}} = \frac{W}{p_0v_0},$$

where W equals the weight of gas in grams, and p_0v_0 is expressed in litre-atmospheres.

But $W = \frac{D_{\text{norm.}} \cdot p_1 v_1}{p_1}$, where $D_{\text{norm.}}$ is the weight of a litre under standard conditions, $p_1 v_1$ is in litre-atmospheres, and $p_1 = 1$. Substituting $D_{\text{lim.}} = \frac{D_{\text{norm.}} \cdot p_1 v_1}{p_0 v_0}$, which is independent of the units in which pv is expressed, the limiting density of oxygen, assuming for the weight of a normal litre, lat. 45°, the value 1.42900 grams, is:

Series 1	1.42756
„ 2	1.42768
„ 3	1.42760
<hr/>	
Mean, taking into account the number of observations in each series.....	1.42762

The compressibility coefficient A_0^1 from each series is:

Series 1	-0.001009
„ 2	-0.000920
„ 3	-0.000977
<hr/>	
Mean	-0.000964

The pv measurements in the case of hydrogen chloride were obtained in a precisely similar way to those just described, but in calculating out the results, a further correction was applied for adsorption of the gas on the walls of the bulb. The maximum volume of gas adsorbed at 0° and 760 mm. was determined in the bulb itself, which for this purpose replaced one of the glass cylinders shown in Fig. 5. Afterwards the variation of the quantity of gas adsorbed with varying initial pressure was measured in the apparatus about to be described, and these experiments, in conjunction with the experiment in the bulb, enabled the requisite corrections for all pressures to be applied to the compressibility measurements.

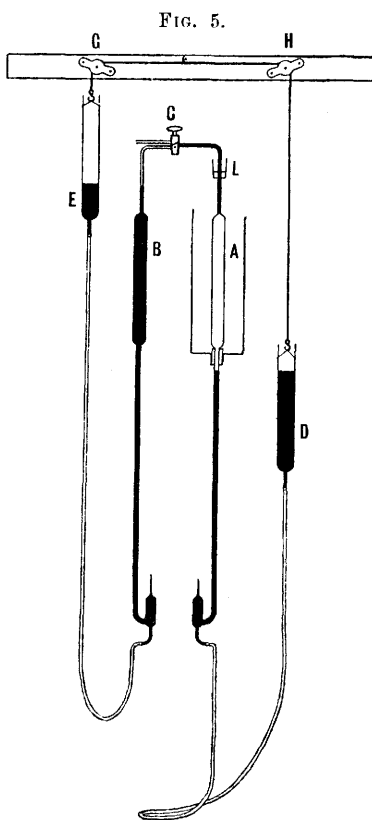
The principle of the method was to expose the surface of a dry glass cylinder to hydrogen chloride at a definite temperature and pressure, and then to displace the gas at constant pressure by mercury. The adsorbed gas remained on the glass below the surface of the mercury, and was subsequently removed by lowering the mercury and producing a Torricellian vacuum in the cylinder. Finally, the volume of the adsorbed gas was measured in a capillary tube.

The apparatus (Fig. 5) consisted of two cylinders, A and B , of about 300 sq. cm. internal surface, connected with each other through a two-way stopcock C . The cylinders could be filled with mercury from the reservoirs D and E , which were attached to a

cord running over the pulleys *G* and *H*. This system of adjustment enabled one to transfer the gas from one cylinder to the other at constant pressure. The cylinder *B* was not used in the measurements, and merely served as a reservoir for the collection of the displaced gas. The measuring cylinder *A* was surrounded with ice and water contained in a tin-bath, and the capillary tube *K*, which was carefully calibrated, was used for the measurement of the volume of the adsorbed gas.

Before the hydrogen chloride entered the apparatus, the greatest care was taken to ensure the complete absence of moisture. The gas was left in contact with the glass for twenty-four hours, and then displaced into the cylinder *B* at constant pressure. The tap *C* was then turned off, and a short length of the mercury thread in the calibrated capillary was frozen by means of solid carbon dioxide contained in the paper vessel *L*. This was necessary, because the gas dissolved in the grease of the tap, and was afterwards slowly evolved in a vacuum. The mercury was next lowered so as to produce a vacuum, into which the adsorbed gas escaped. On allowing mercury to refill the cylinder, this gas was collected and measured in the capillary, and was afterwards removed through the tap *C*.

The mercury thread was then frozen again, and by repeating the operations described, a further quantity of gas was collected and measured. This process was continued, allowing definite intervals of time for the adsorbed gas to accumulate, until the volume obtained became negligibly small. The measured volumes of gas were afterwards plotted against the times during which the surface remained exposed to a vacuum. By making measurements at different pressures, we obtained a series of curves from which the total volumes of gas adsorbed at various pressures



could be read. The logarithms of these volumes were finally plotted against the corresponding pressures, and the corrections to be applied to the volumes in the compressibility measurements were read from the curve so obtained.

Variation of Adsorption with Pressure.

Experiments in cylinder *A* ; surface 300 sq. cm. $T=0^{\circ}$.

Pressure.	Volume of adsorbed gas at 0° and 760 mm.
0	0.0000
218 mm.	0.0034 c.c.
317 "	0.0045 "
547 "	0.0070 "
730 "	0.0104 "

The experiments in the bulb yielded for the same initial pressure a larger volume of gas per unit area. This was almost certainly due to a difference in the state of the surface of the glass, since the other experimental conditions were the same. The total quantity of gas adsorbed at a pressure of 782 mm. of mercury and at 0° was 0.047 c.c., and the surface was 320 sq. cm. In correcting our results, we have adopted the value obtained in the bulb itself, and for lower pressures we have multiplied the values from the cylinder experiments by a factor to correct them to this standard.

It should be stated here that experiments on the amount of adsorption of hydrogen and air were also made in this apparatus. With hydrogen the amount of gas adsorbed was barely detectable. Air was adsorbed to a greater extent, but the value obtained was very much smaller than that in the experiments with hydrogen chloride. These results are of interest, since they show that the gas was really adsorbed and not imprisoned in minute cavities in the glass surface.

Before correcting the results, one other factor had to be taken into account. Since the quantity of gas adsorbed is directly proportional to the surface, it was necessary to know how the surface of the bulb exposed to the gas varied as the mercury was withdrawn. For this purpose, we assumed that the bulb was spherical, and we calculated the surface for the corresponding volumes. The nature of the correction will be clear from the following figures, taken from the correction table in our note-book:

Pressure of gas.	Surface of glass exposed.	Volume of adsorbed gas at 0° and at observed pressure : to be added to measured volume of gas.
829 mm.	68 sq. cm.	0.0098 c.c.
314 "	122 "	0.0172 "
158 "	193 "	0.0341 "

As the glass surface increased and the pressure fell, the absolute amount of gas adsorbed also increased, since the surface effect more than counter-balanced the effect of diminishing pressure. The actual alteration of the form of the curve on applying this correction was very small.

The following table of results for hydrogen chloride is given with all corrections made:

Hydrogen Chloride.

p (in mm.).	v (in c.c.).	pv .	Smoothed pv .
829.50	66.012	54757	54757
761.09	72.023	54816	54802
734.65	74.626	54824	54820
720.78	76.072	54831	54829
604.71	90.815	54917	54903
558.67	98.334	54936	54932
515.35	106.642	54958	54958
468.21	117.432	54983	54986
424.66	129.525	55004	55010
384.13	143.259	55030	55034
347.70	158.343	55056	55054
314.29	175.233	55074	55072
289.39	190.331	55080	55084
264.53	208.286	55098	55097
243.40	226.401	55106	55107
223.95	246.117	55118	55116
207.68	265.447	55128	55125
193.41	285.016	55125	55132
180.24	305.898	55135	55138
157.57	349.978	55146	55148

On plotting pv against the corresponding pressures on the same scale as the oxygen, we found that a line drawn through the points had a slight but distinct curvature, which was more marked in the low pressure region. That is to say, the variation of pv per unit pressure decreases as the pressure falls, and the rate of decrease is greater at lower pressures. It seems probable that a compressibility curve of this type may be characteristic of all gases which at 0° lie below their critical points, and, if this is so, D. Berthelot's principle, when properly applied, should give as accurate results for the liquefiable as it does for the permanent gases (Guye, *J. Chim. phys.*, 1908, **6**, 792).

In drawing the most probable line through the points, exactly the same procedure was followed as in the case of oxygen. Two points in the high pressure region were obviously inaccurate, and less weight has been assigned to them than to the other points. On account of the slight curvature, extrapolation to zero pressure seemed at first sight an uncertain process. Afterwards, when the general lie of the curve had been fixed by means of a spline, graphic extrapolation over the comparatively short length of 157 mm. gave values for p_0v_0 differing only slightly from each other. After many

trials, we decided that the fairest extrapolation was obtained with the curve cutting the pv axis at 55213. The value of p_1v_1 , also taken from this curve, proved to be 54803, so that the value given by the results for

$$\frac{p_0v_0}{p_1v_1} \text{ is } \frac{55213}{54803} = 1.00748,$$

and the limiting density of hydrogen chloride is

$$\frac{D_{\text{norm.}} \cdot p_1v_1}{p_0v_0} = \frac{1.63915}{1.00748} = 1.62698 \text{ grams per litre at } 0^\circ \text{ and } 760 \text{ mm.}$$

The molecular weight of hydrogen chloride in terms of oxygen is, therefore,

$$\frac{D_{\text{lim. hydrogen chloride}}}{D_{\text{lim. oxygen}}} \cdot 32 = \frac{1.62698 \times 32}{1.42762} = 36.469,$$

and the atomic weight of chlorine, $36.469 - 1.0076 = 35.461$.

If the validity of the assumption underlying the principle of limiting densities be admitted, this result affords valuable confirmatory evidence of the correctness of the atomic weight of chlorine obtained by volumetric analysis. The two values, 35.459 and 35.461, only differ by 1 part in 18,000. They both depend, however, on the density of hydrogen chloride, and any uncertainty in it would affect them equally. The former value, as is evident from the method of calculation, is further influenced by any error which would change the ratio atomic weight of hydrogen: density of hydrogen, but the latter number is practically independent of the O: H ratio, for the molecular weight of hydrogen chloride yielded by the compressibility results is expressed directly in terms of the oxygen standard. The close agreement is mainly brought about by the concordance of the results of the volumetric analysis and those of the pv measurements. Thus, if $+0.00054$ be taken as the coefficient of compressibility of hydrogen per atmosphere at 0° (the mean of the results of Rayleigh, Jaquero, and Scheuer and Chappuis), the ratio of the volumes of hydrogen and hydrogen chloride containing equal numbers of molecules is:

$$\frac{1 + 0.00054}{1 - 0.00748} = 1.0081,$$

whilst volumetric analysis gave 1.0079.

The final value for the atomic weight of chlorine yielded by these investigations is, therefore,

$$35.460. \quad \text{O} = 16.$$

An arithmetic mean of all recent determinations ($O=16$; $H=1.00762$) gives the same result.

Dixon and Edgar	35.463
Edgar	35.461
Noyes and Weber	35.452
Richards and colleagues	35.457
Guye and Fluss	35.466
Guye and Ter-Gazarian.....	35.461
Gray and Burt	35.460
Mean	35.460

Consequently, it may be stated with a considerable degree of certainty that the higher numbers which result from the use of Noyes' value for the atomic weight of hydrogen, namely, 1.00787, are distinctly too great, and that the value advocated by Brauner is a close approximation to the true atomic weight of chlorine.*

In conclusion, we desire to express our appreciation of the kindly interest Sir William Ramsay has taken in the research, and to thank him for his advice and criticism. Also we wish to thank Mr. H. S. Patterson and Mr. H. Page, who analysed some of the samples of aluminium, and Mr. W. N. Morley and Mr. A. C. Dunningham, who helped us in some of the compressibility measurements.

Part of the expense of the work was defrayed by a grant from the Royal Society, and we here record our indebtedness to the Government Grant Committee, without whose assistance this investigation could not have been made.

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* During the correction of the proofs of this paper, a research by Scheuer on the density of hydrogen chloride has appeared (*Compt. rend.*, 1909, **149**, 599). According to this he obtains for the weight of a normal litre of the gas the value 1.6394 grams. This only differs from our present figure, namely, 1.6392 grams, by 1 part in 8000. Possibly this small discrepancy may be due to the different method employed by us to correct for the gas adsorbed by the walls of the bulb.

We have already referred to the error affecting the results which we published in a preliminary note (*Proc.*, 1908, **24**, 215).