is to point out the particular relationship between surface tension and compressibility, and to call attention to the fact that we are working further upon this relationship and other relationships concerning other allied properties of substance.

We are greatly indebted to the Carnegie Institution of Washington for generous aid in this research.

Summary.—(1) In this paper are given a number of new results on the compressibility, surface tension, boiling point, specific gravity and the vapor pressure at 20° of a number of organic substances.

(2) It is shown that approximate relationships exist between some of these quantities, particularly that as a rule substances with large surface tension possess small compressibility.

(3) This relationship is discussed briefly from the point of view of the theory of compressible atoms.

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THE ATOMIC WEIGHT OF CHLORINE.

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The ratio of the atomic weights of oxygen and of chlorine is one of extreme importance, on account of the number of atomic weights based either directly or indirectly upon the atomic weight of chlorine.

During the last few years alone, since the determination of the ratio silver to chlorine by Richards and Wells,[1] the atomic weights of a considerable number of the common elements have been determined, basing them on the value of chlorine. These values have been calculated on the oxygen basis, assuming that the ratio silver: oxygen:: 107.93: 16 is correct. Guye and Ter-Gazarian[2] have called attention to a possible source of error in the chlorate ratio of Stas, correction for which would bring the value of silver down to 107.89. The newly accepted value, 14.01 for nitrogen also points to the lower value of 107.89. Very nearly at the close of this work conclusive evidence has been presented by Richards and Forbes[3] and by Richards and Jones[4] that the value, 107.93 for silver is too high. The only direct comparison between hydrogen and chlorine which we have is that of Dixon and Edgar.[5] In this determina-

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[1] This Journal, **27**, 459.

[2] Compt. rend., **143**, 411.

[3] This Journal, **29**, 808.

[4] *Ibid.*, **29**, 826.

[5] Phil. Trans., **205**, 169. Series A., Chem. News, **91**, 263. The determinations by Deutsch (Dissertation, 1905) in the laboratory of Professor Guye, were scarcely of sufficient accuracy to be considered as atomic weight determinations

tion hydrogen was made to burn in an excess of chlorine. The hydrogen was weighed absorbed in palladium and the chlorine in the liquid form in a glass bulb. The hydrogen and chlorine were caused to unite in a large globe of glass containing a small quantity of water to absorb the hydrochloric acid formed. Corrections were applied for the quantity of chlorine remaining uncombined by titrating the amount of iodine liberated by it from a solution of potassium iodide. A further correction was applied for the amount of chlorine used up in liberating oxygen from water, by determining the amount of oxygen set free.

The fact that there was only one such direct determination of the ratio between chlorine and hydrogen, together with the opportunity afforded of carrying out the determination with hydrogen prepared in the same apparatus used for generating the hydrogen in the recent determination of the ratio of hydrogen to oxygen, made a new determination seem to be worth while.

The method we have used, besides being a direct comparison between hydrogen and chlorine, involves the principle of complete synthesis with the determination of the weights of all the substances reacting and of the reaction products formed. Briefly stated, the method consists in weighing the hydrogen absorbed in palladium, and the chlorine in the form of potassium chlorplatinate. The hydrogen is passed over the heated potassium chlorplatinate from which it removes chlorine to form hydrochloric acid. The hydrochloric acid formed is condensed in a third section of the apparatus and weighed. We have thus the weight of hydrogen used, the weight of chlorine removed, and the weight of hydrochloric acid formed. In this manner two series of ratios, each independent of the other, are obtained.

Working in this manner and with hydrogen prepared under the same conditions and at the same time as that used in the determination of the ratio hydrogen to oxygen by one of us, we believe that we have very favorable conditions for bridging the gap

$$\mathrm{Ag} \longrightarrow \mathbf{Cl} \asymp \mathbf{H} \longrightarrow \mathrm{O}.$$

Purification of Materials and Weighing.

Hydrogen.—The hydrogen used in these experiments was prepared and purified in the same manner as described in a previous paper on the atomic weight of hydrogen.[1] The gas was taken from the generating apparatus at intervals covered by the period of the work on hydrogen. Consequently all remarks concerning its character and purity as used in the hydrogen-oxygen ratio apply to these determinations. As in that work so in this, two methods of generating the hydrogen were employed. In the last series of determinations the hydrogen was obtained by the electrolysis of a solution of barium hydroxide.

Platinum.—The platinum used in the preparation of potassium chlorplatinate was originally obtained in the form of platinum sponge. The preliminary purification consisted in dissolving this in aqua regia and evaporating to remove nitric acid. The separation from other platinum metals was carried on according to the method of Schneider and Seubert as described in Graham Otto's Lehrbuch.[1]

The solution of chlorplatinic acid was boiled for half an hour with excess of caustic soda, acidified and the platinum precipitated as potassium chlorplatinate. The chlorplatinate so obtained was reduced with sodium formate. The platinum black was then heated with dilute hydrochloric acid to remove iron and washed until it commenced to go through as colloidal platinum. It was then redissolved and the process repeatedly gone through until the mother-liquors from the chlorplatinate precipitation were practically colorless and free from other platinum metals. As the same platinum was continually used and underwent a large number of successive solutions and reductions during the preliminary work, it seems safe to assume that it was sufficiently pure.

Potassium Chlorplatinate.—During the preliminary work it was soon discovered that the preparation of chlorplatinic acid by the use of aqua regia was unsatisfactory. The removal of nitric acid by the process of repeated evaporation was tedious and at best uncertain. To overcome this difficulty and eliminate nitric acid entirely, a process of dissolving the platinum electrolytically in purified hydrochloric acid was devised. This proved quite satisfactory and will be described in the following paper. After solution of the platinum in hydrochloric acid had been effected, the solution, which contained approximately 120 grams of platinum and measured 500 cc., was evaporated to about one-half its volume in a glass stoppered wash-bottle. At the same time a current of chlorine was passed through the boiling solution. The chlorine used for this purpose was prepared by the action of pure potassium permanganate upon chemically pure hydrochloric acid which had been previously boiled with a small quantity of permanganate to insure its freedom from bromine compounds. The solution of chlorplatinic acid thus obtained had a beautiful bright color matching almost exactly that of a 0.1 per cent. solution of methyl orange. It contained about 100 grams of hydrochloric acid in excess and after filtration and dilution to one liter was used directly for the precipitation of potassium chlorplatinate. For this purpose a solution of potassium chloride was prepared, using an excess of one-third above the theoretical quantity dissolved in one liter of water. The excess of potassium chloride as well as the excess of hydrochloric acid in the chlorplatinic acid were deemed necessary to check hydrolytic decomposition. For the same reason the precipitation of potassium chlor-

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[1] Graham Otto's Lehrbuch, 5th Ed., 4, 1153.

platinate was carried out with as concentrated solutions as practicable. The precipitation itself was carried out by pouring the platinum solution into the potassium chloride in a fine stream, the precipitate meanwhile being agitated thoroughly by a current of air. In some cases as much as four hours were spent in precipitating 300 grams of potassium chlorplatinate. The potassium chlorplatinate so obtained was of a pale yellow color, resembling precipitated sulphur, and was microcrystalline. It was filtered from the mother-liquor by means of a suction pump, washed with water and finally with alcohol and ether. After having been removed from the hardened filter, it was heated for some time in a large platinum dish on an electric air bath until the greater part of the moisture retained had been driven off. The quantity necessary for one determination was then transferred to a hard glass tube. This tube was placed in a cylindrical air bath which could be raised to a temperature of 400°. The potassium chlorplatinate was gradually raised to this temperature, a current of air, dried successively by sulphuric acid and phosphorus pentoxide passing over it continuously. The behavior of the salt under these conditions served as a criterion of its purity. At the exit of the current of gas, a wash-bottle was placed containing a drop of methyl orange. At first a small quantity of moisture and hydrochloric acid passed off. Finally, however, a point was reached where no further hydrochloric acid could be detected in the issuing gas stream. At this point the heating was stopped, usually after the chlorplatinate had been heated to 400° for about seven hours, or more. It seems that the chlorplatinate, when pure, will stand the temperature of 400° indefinitely in a non-reducing atmosphere, without suffering any change chemically. No appreciable quantity of hydrochloric acid could be detected after the hydrochloric acid and water held mechanically had once been driven off. This all, provided the salt was pure to start with. In the first trials, in which the chlorplatinate had been prepared by the use of aqua regia its behavior was entirely different. In these cases decomposition set in in the neighborhood of 250° and seemed to go on progressively throughout the whole mass of the salt.

After having been dried in this manner, the chlorplatinate was transferred to the final apparatus with little or no exposure to the air, through an opening which was sealed off after filling. In this it was subjected to final drying at 350° and evacuation, as described under the manipulations.

Potassium Chloride.—As a starting point for the preparation of pure potassium chloride, the purest commercial article obtainable was taken. This was first recrystallized from a solution made slightly alkaline with potassium hydroxide to remove traces of ammonia which were present. The salt was then redissolved in water and chlorine passed through the hot solution for several hours, after which it was concentrated and the potassium chloride allowed to crystallize out. Following this the salt was recrystallized five times from water, precipitated three times by alcohol and finally precipitated from aqueous solution by purified hydrochloric acid gas. The crystals in these various processes were separated from the mother-liquors by centrifugal drainage.

This potassium chloride certainly contained less bromine than 1 in 50,000. To test for bromine the following process, a modification of that described by Andrews,[1] was adopted.

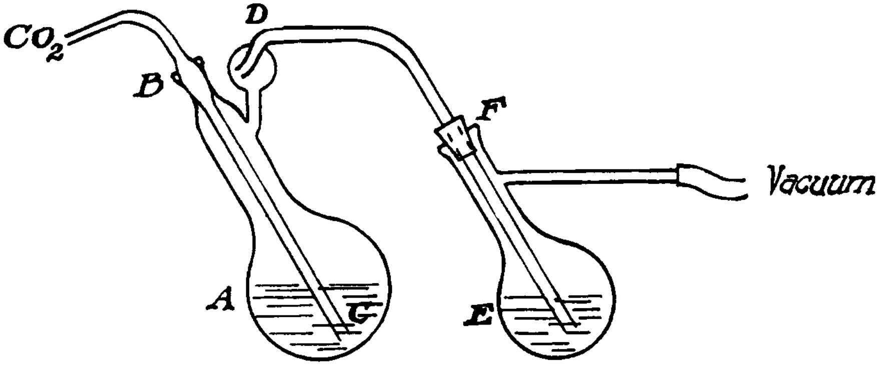

Fig. 1.

The flask *A* is fitted with a ground glass joint at *B* which ends in an extremely fine capillary at *C*. The side tube *D* has a trap to prevent spray from being carried over. An ordinary distilling flask is affixed to the end of this side tube with a rubber stopper in such a manner as to bring the side tube well into the bulb of the flask *E*. The flask *A* is charged with 200 cc. of distilled water, 20 cc. of N/5 potassium iodate and 20 cc. of 2 N. nitric acid. The flask *E* contains about 5 cc. of a 4 per cent. solution of potassium iodide (which must not liberate iodine upon being acidified). The flasks are then connected by means of the stopper at *F* and vacuum applied. The capillary tube which is ground into the flask at *B* is connected with a carbon dioxide generator, and after vacuum has been applied, should yield a fairly steady stream of bubbles through the liquid, so as to insure regular boiling and at the same time not appreciably to diminish the vacuum. It is desirable to have a pure neutral gas such as carbon dioxide or nitrogen passing through the capillary, since traces of reducing substances in the air used, would vitiate the results. The gas passing through the capillary, besides insuring regular boiling, acts as a diluent for the steam formed and as such checks the reaction

$$H_2O + Br_2 = 2HBr + O.$$

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[1] This Journal, **29**, 275.

The flask containing the potassium iodate and nitric acid mixture is then heated on the water bath until 100 cc. have distilled into the flask containing the potassium iodide. If the resulting distillate is colored by the presence of free iodine, the process is repeated after adding water to make up for the quantity distilled off, until a satisfactory blank is obtained. Then 3–5 grams of the potassium chloride to be tested are dissolved in a little water and added to the flask containing the iodate and the volume of the solution made up to 250 cc. again. The distillate containing the free iodine corresponding to the amount of bromine distilled over, is then titrated with a solution of thiosulphate corresponding to 1 mg. of bromine per cubic centimeter. To 5 grams of potassium chloride which had been treated until blank distillates were obtained the following quantities of bromine were added and found:

Added, 1 mg. 0.5, 0.3, 0.1.
Found, 1 mg. 0.52, 0.36, 0.12.

The potassium chloride used for precipitating potassium chlorplatinate contained less than 0.1 mg. bromine in 5 grams or 1 : 50,000. This amount, it is safe to assume, was further reduced in the preparation of potassium chlorplatinate.

Hydrochloric Acid.—The hydrochloric acid used in the preparation of pure hydrochloric acid was free from sulphuric and nitric acid. It was treated by allowing chlorine to bubble through it for one day. Following this, air was bubbled through the acid saturated with chlorine until the chlorine was expelled and the acid was again colorless. Usually the air was left passing through the acid over night, a reduction of about one-fifth in the volume of the acid, due to evaporation, taking place with the removal of the excess of chlorine. During the manipulations in preparing chlorplatinic acid, it was further subjected to the action of chlorine twice, namely, during electrolysis of the platinum and on evaporation of the platinum solution.

Chlorine.—All the chlorine used was generated by the action of pure potassium permanganate on hydrochloric acid which had been previously boiled with a small quantity of potassium permanganate.

Water.—The water used was obtained by redistilling distilled water with alkaline permanganate, rejecting the first part of the distillate until it no longer contained ammonia.

Balance and Weights.—The balance and weights were identical with those described under the atomic weight of hydrogen.[1] The air of the balance case was dried by means of a current of air as described in the previous paper. Each piece of apparatus was weighed with a corresponding counterpoise approaching it within 1 cc. in volume and 30 grams

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[1] Noyes, This Journal, 29, 1723.

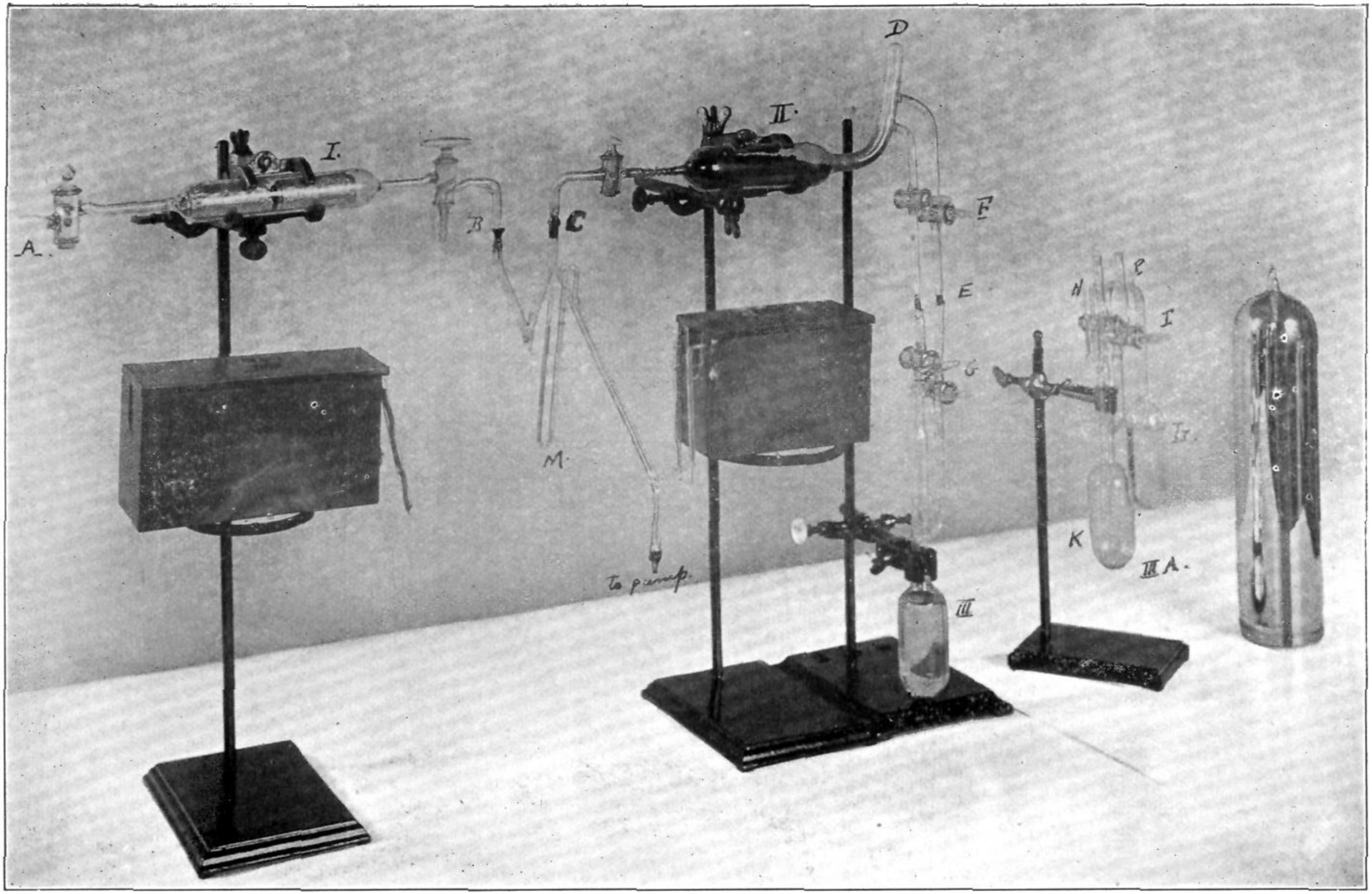

Fig. 2.

in weight. In the case of the hydrogen the counterpoise was within 0.3 cc. of the volume and 2 grams of the weight of the palladium tube.

All pieces were rinsed with distilled water after having been used in a determination. Having been wiped dry, they were suspended for some time in a desiccator through which a current of dry air was passing, before being transferred to the dry air of the balance. For the hydrogen apparatus twelve to twenty-four hours were allowed in order to attain constant surface conditions. The current of air through the balance was stopped fifteen to twenty minutes before a weighing was made. Duplicate weights were taken at intervals of an hour or more and rarely differed by more than 0.05 mg.

Weights.—The weights were calibrated to vacuum standard here in the Bureau of Standards. The small correction necessary on account of the difference in volume between the brass and platinum weights was included in a table with the corrections for the errors of the weights.

Method of Carrying Out the Determinations.

First Series.

There are three parts to the apparatus, which was prepared for a determination in the following way:

The Palladium Tube.—This consisted of a cylindrical tube with a stopcock sealed on at each end. The tube at one end was bent downwards at right angles and drawn out to a tip at *B*. Connection with the hydrogen generator was made by sealing the tip into a corresponding socket with Khotinsky cement. The three-way stopcock at *B* was opened in the position so that the small amount of air in the limb of *B* was swept out. Communication was then established between the palladium and the hydrogen generator, and hydrogen was led in until no more was absorbed. The stopcock at *A* was next opened and the hydrogen allowed to sweep through the apparatus for a short while. The stopcocks were then closed and after cleaning the apparatus it was ready for weighing. Before the apparatus was used the first time, it was repeatedly charged with hydrogen and the hydrogen driven out at 400°. After that the tube was ready for charging anew at the end of each experiment.

Chlorplatinate Tube.—This tube had the general form as shown in the accompanying photograph. The potassium chlorplatinate was introduced through the curved neck which was open at *D*. For this purpose the hard glass tube in which the chlorplatinate had been heated to 400° was connected to it by a short piece of stout rubber tubing and the chlorplatinate was shaken into the apparatus. The end *D* was then sealed off without allowing vapors from the flame to enter the tube. After this was done the apparatus was attached to the Sprengel pump and evacuated to a few thousandths of a millimeter at a temperature of 350°. This temperature was maintained for about four hours. After closing the stopcock, disconnecting and rinsing after it was cool. the apparatus was transferred to the desiccator before weighing.

Absorption Tube for the Hydrochloric Acid.—This consisted of a bulb having a volume of about 100 cc. It terminated in two tubes with stopcocks and sockets to fit the tips of the two tubes from the platinum apparatus at *E*. Fifty cc. of boiled distilled water were poured into this bulb. It was then evacuated by means of the Sprengel pump. which was protected by an extra phosphorus pentoxide tube in this case. The evacuation was continued as long as air could be removed from the apparatus or liquid. Usually it was found necessary to allow the partly evacuated apparatus to stand for a day before the last traces of air could be removed from the water. After evacuation the apparatus was rinsed and set in the desiccator for weighing. Then, the different portions of the apparatus having been weighed, they were set up as shown in the photograph. The potassium chlorplatinate and the palladium charged with hydrogen were enclosed by electrically heated air baths. These are lowered in the photograph to show the apparatus.

The tip *B* of the hydrogen tube and *C* of the chlorplatinate tube were connected with each other and with the Sprengel pump by means of a T-tube. The two tips from the chlorplatinate tube were connected to the two corresponding sockets of the absorption tube. These joints were made with Khotinsky cement.[1]

The joints were perfectly tight and no leakage was ever discovered. After the three parts of the apparatus had thus been connected with each other and with the vacuum pump. the connections were evacuated. The gas in the two connecting limbs at *E* was removed by opening the stopcocks at *F* and pumping the gases out over the chlorplatinate. which had meanwhile been brought to a temperature of about 300°. When every part of the apparatus had been evacuated to a few thousandths of a millimeter, as shown by the McLeod gauge attached to the pump, connection with the pump was cut off. The stopcock of the hydrogen apparatus at *B* was then opened and gradual heating of the hydrogen tube commenced. Then the stopcock at *C* was opened very gradually and the hydrogen admitted to the chlorplatinate. Next, the four stopcocks communicating with the absorption tube were opened. This was done very gradually to prevent a sudden rush of gas into the absorption tube and consequent carrying over of the finely divided potassium chlorplatinate. In doing this. the stopcocks were opened in such order that communication was first established through the tube entering the chlor-

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[1] P. G. Nutting, of this Bureau, has supplied us with a cement of the same character, which seems to answer the purpose as well as the Khotinsky. It is made by fusing together equal parts by volume, of rosin and pure rubber.

platinate apparatus at the lower level. Following this, communication was established by means of the adjoining tube. The purpose of the double connection between the chlorplatinate and the absorption tube was to prevent stagnation of the gas current between the two parts of the apparatus. A little hydrogen was always carried along with the hydrochloric acid toward the absorption apparatus. This would tend to accumulate and block the current. By making the level of the second tube somewhat higher than that of the first, the tendency of the hydrogen to rise would cause a direct and continuous flow. Actually, this arrangement proved entirely satisfactory.

The apparatus remained in this condition for several hours. The temperature of the palladium tube generating the hydrogen was allowed to rise slowly at such a rate that the pressure in the apparatus was kept at or below one atmosphere. This pressure was measured by means of a small mercury manometer *M* which formed a part of the connecting T-tube *B C*. The closed end of the manometer contained a little air. By this means it was possible to measure any pressure from zero to more than one atmosphere with a light manometer 8-10 cm. in length.

When it was deemed that a sufficient quantity of hydrogen had been evolved from the palladium tube the stopcock *B* of this part of the apparatus was closed and the palladium allowed to cool off. The temperature of the tube containing the chlorplatinate was allowed to rise to 350°. At the same time the absorption tube, which had been cooled by ice during the earlier part of the experiment was now cooled to —20° by a mixture of ice and dilute sulphuric acid. The hydrogen remaining in the apparatus upon cutting off the palladium tube was continuously converted into hydrochloric acid and removed as such by the water. This could be followed by means of the manometer *M* previously mentioned. After two or three hours the manometer had reached the lowest point which it would indicate. At this point the stopcocks *G* of the absorption tube were closed. The conditions prevailing at this moment were as follows:

The chlorplatinate tube still contained an excess of potassium chlorplatinate and was at a temperature of 350°.

The absorption tube was at a temperature of —20°. The residual pressure throughout the apparatus was very low.

Under these conditions but a very minute quantity of hydrogen could have escaped conversion into hydrochloric acid. To determine this, connection with the Sprengel pump was again established and that part of the apparatus between the stopcock *B* of palladium tube and the stopcocks *G* of the absorption tube was evacuated to the best vacuum obtainable by the pump, usually a few thousandths of a millimeter. The gas pumped out was collected in a eudiometer and analyzed. In analyzing the gases their volumes were read at a pressure of about one-sixth to one-seventh of an atmosphere, making accurate determination possible. Thus the volume of 1 cc. under these conditions represented less than 0.02 mg. of hydrogen.

The residual gas having been pumped out of the apparatus, all stopcocks were closed and the apparatus taken apart. All traces of the cement adhering to the glass where the various pieces had been joined were carefully removed. The pieces were then rinsed with distilled water, when sufficiently cool, wiped dry and transferred to the desiccator. The following day they were weighed. The determination itself required about eight hours, of which about two hours were used for the evolution of hydrogen and about three hours for the pressure to drop from atmospheric to practical zero.

Second Series.

Before giving the results obtained by the first series it may be just as well to turn to the manipulations giving the second set of values. They are essentially the same as in the first series with this difference: the hydrochloric acid generated was condensed as a solid by cooling with liquid air and connection with all other parts of the apparatus was cut off before it was absorbed by water. The point in view was this: During the period of absorption of the hydrochloric acid it might be possible that a transfer of water would take place from the absorption apparatus to the chlorplatinate apparatus and remain there in spite of the fact that there was not only a difference of 370° in temperature between the two parts but also a very high vacuum. This would cause the apparent amount of chlorine transferred to appear lower than the real. Or there was the possibility of the water vapor reacting with the material in the chlorplatinate tube. To eliminate these possibilities the reaction was so carried on that the chlorplatinate was at no part of the determination in contact with water vapor.

Further, this series differs from the first in that the hydrogen used was generated from a solution of barium hydroxide, the hydrogen in the first series being obtained from a sulphuric acid electrolyte. The absorption apparatus in the second series (which simply took the place of the water absorption tube) was constructed as follows:

The bulb *K* was designed for the condensation of the hydrochloric acid and had a volume of 100 cc. It terminated in a neck from which led two exit tubes provided with the stopcocks *H* and *I*. The stopcock at *I* was provided with two perforations so that communication could be established either between the chlorplatinate tube and *K* or between the two bulbs *K* and *L*. The bulb *L* had a volume of 70 cc. and contained the water for the absorption of the hydrochloric acid. Below *H* a miniature mercury manometer was affixed. This was found absolutely necessary in order to follow the conditions of pressure during the transfer of the solid hydrochloric acid in *K* to the water in *L*. Indeed, previous to the attachment of this device to the apparatus every determination was lost either by the bursting of the apparatus or the blowing out of the stopcocks. By making the air space above the mercury of capillary tubing, while the remainder was about 1½ mm. in bore, satisfactory readings could be obtained both at normal and reduced pressures and there was no danger of the mercury being sucked out of the manometer.

To prepare the apparatus for weighing, somewhat more than 50 grams of water were filled into *L* through a small opening at *P*. The water was then boiled and when all air had been expelled the opening at *P* was sealed off. The whole apparatus was then evacuated with the Sprengel pump, the last traces of air being removed from *L* by opening the stopcock *I* momentarily until the limit of the pump was reached. Rinsing, drying and desiccation then completed the preparations for weighing as usual. The apparatus was then put together and prepared for the determination in precisely the same manner as in the first series with the one difference that the absorption apparatus *III A* was now connected at *E* instead of the absorption tube *III*. Communication with the water bulb *L* was entirely cut off during the first part of the determination. The condensation bulb *K* was plunged in liquid air at the beginning and kept at the temperature of boiling air throughout the determination.

In opening the stopcocks to obtain communication between the various parts of the apparatus very great care had to be exercised, as the first rush of gases into the chilled condensation bulb often carried some of finely divided chlorplatinate with it. In a few cases it was not possible to avoid this. Since this chlorplatinate remained in the condensation bulb *K*, its amount could be found at the end of the determination and a suitable correction applied.

After communication had been established between the hydrogen tube, the chlorplatinate tube and the condensation tube, the hydrogen tube was cautiously heated so as to obtain a constant and steady rise in temperature. Somewhat more care was necessary in this series, as there seemed to be a greater tendency for the pressure in the hydrogen apparatus to fall below that of the remaining parts. This would result in the finding of hydrochloric acid in the palladium tube at the end of the experiment. Suitable corrections were made for this and will be spoken of with the other corrections. When the hydrogen tube had reached a temperature of from 150° to 160°, it was judged that the requisite amount of hydrogen had been evolved. The stopcock from the hydrogen tube was then closed. Any temperature above 150° sufficed for the reduction of the chlorplatinate by the hydrogen, but at the end the temperature of the chlorplatinate tube was run up to 400°. The condensation bulb was kept fully submerged in liquid air. After the supply of hydrogen had been turned off, the pressure in the apparatus gradually sank until all hydrogen had been used up and all hydrochloric acid condensed. The conditions then were: excess of the chlorplatinate at 350° to 400°; the hydrochloric acid at about −180° and a small fraction of a millimeter residual pressure. The stopcocks of the condensation tube were then closed and the residual gases in the remaining parts of the apparatus pumped out.

The condensation tube was then separated from the remaining parts of the apparatus and the transfer of the hydrochloric acid to the water commenced. The water bulb *L* was plunged into ice water and the condensation bulb *K* removed from direct contact with the liquid air but not entirely beyond the cold vapors. As soon as the pressure of the hydrochloric acid had risen to a small part of an atmosphere, communication was established with the cold water in *L*. After some hydrochloric acid had been absorbed by the water the bulb *L* was cooled by ice and dilute sulphuric acid instead of by ice alone. With the aid of occasional shaking of the absorption bulb the last of the condensed hydrochloric acid was finally absorbed by the water. With cautious manipulation the pressure in the apparatus did not rise above one-half atmosphere during the transfer and remained at a few millimeters at the close. The stopcock *I* between *K* and *L* was then closed, and the apparatus was cleaned, rinsed, wiped and set aside to be weighed. The determinations of the second series required about ten hours from beginning to end. About two hours were consumed in transferring the solidified hydrochloric acid from the condensation to the absorption bulb. The solidified hydrochloric acid resembled snow in appearance and the greater part of it was absorbed by the water without passing into the liquid state. Towards the end of the transfer, when the absorption became less rapid, the remaining hydrochloric acid would liquefy attended by a sudden rise in pressure. Shaking of the absorption tube immediately reduced the pressure and caused the liquid hydrochloric acid to solidify to a glassy solid.

Errors and Corrections.

Hydrogen.—If there were any errors due to a contamination of the hydrogen, they are not apparent. The hydrogen was prepared and purified with all possible precaution. It was repeatedly tested for impurities in the work on hydrogen and oxygen and none or only negligible quantities found.[1]

Two corrections on the weight of hydrogen were found necessary. The first of these was the amount of hydrogen remaining in the chlorplatinate tube at the end of the determination and pumped out with the

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[1] Noyes, This Journal, **29**, 1724.

residual gases to be analyzed. In eight cases out of the twelve this correction was applied, the maximum being 0.11 mg., the minimum 0.01 mg. and the average 0.047 mg. The determinations affected are 1, 2, 4, 5, 6, 7, 11 and 12. The second correction was due to hydrochloric acid in the palladium tube. Under certain conditions, when the current of hydrogen from the palladium tube was not sufficiently rapid, hydrochloric acid found its way back into the palladium tube, either by diffusion or by being drawn back. Correction for this was readily applied. After having been weighed, the hydrogen apparatus was charged for the succeeding determination. The tube was fitted with a stopcock at both ends, as may be seen in the photograph. After the palladium had been saturated with hydrogen the stopcock farthest from the hydrogen generator was connected to a Liebig flask containing water colored by a drop of methyl orange. The stopcock at *A* was opened while the hydrogen generator was kept going and the hydrogen bubbled through this water before escaping. If the presence of hydrochloric acid made itself known, the palladium was heated to 160° to expel the larger part of the hydrogen it had absorbed and with it any hydrochloric acid present. It was then allowed to cool with a current of hydrogen passing through it and finally filled again at normal temperatures. The hydrochloric acid absorbed by the water was then titrated by N/10 sodium or barium hydroxide. The real weight of the hydrogen was greater than the apparent loss of the tube by the weight of hydrochloric acid found. This correction was applied in determinations 1, 3, 4, 10 and 11 varying between 0.35 and 9.26 mg. and averaging 4.8 mg.

Chlorine from the Loss of the Platinum Tube.—The purity of the chlorine entering into the composition of the chlorplatinate has been spoken of. The maximum amount of bromine in the ingredients used seems to have been 1 in 50,000. The resultant error in the weight would be half of this, since 35.5 grams are replaced by 80, or 1 : 100,000. There seems to be ample justification for considering this point beyond question.

The only other impurities which could possibly affect the results were volatile products in the platinum or elements capable of producing volatile products such as ammonia, water, hydroxyl or oxygen. The method of preparation seems to preclude the possibility of the presence of ammonium salts. The potassium chloride was especially treated to free it from these. Following this there was repeated treatment with chlorine in hot solution. The final heating of the chlorplatinate to 400° over an extended period of time must have caused the destruction and removal of any ammonium compounds which had escaped previous treatment.

The three following impurities, water, hydroxyl or oxygen in the platinum salt, were somewhat more difficult of treatment. It is known that potassium chlorplatinate hydrolyzes in aqueous solution. With this point in view the precipitation of potassium chlorplatinate was carried out in concentrated solutions with both an excess of potassium chloride and hydrochloric acid, and the mother-liquor was removed as soon as practicable. It was shown that by heating sufficiently long at 400°, all occluded hydrochloric acid could be removed, the chlorplatinate being perfectly neutral after this treatment. This served as indirect evidence that the water was also removed. The agreement between Series 1 and 2 may be considered as additional evidence on this point. In the first series the chlorplatinate had opportunity to become saturated with water vapor at the temperature of 350° during the course of the experiment. In the second series it was in equilibrium with solid hydrochloric acid at —180°. Now hydrochloric acid with its well-known affinity for water vapor may be considered as a very perfect drying agent. Yet the difference between the two series is 1 in 10,000. One hundred and twenty grams of potassium chlorplatinate were used. The presence of 0.05 per cent. moisture in this salt would have raised the atomic weight of chlorine found from 35.184 to 35.244.

Further, in the second series it was noticed that if the condensation tube for the hydrochloric acid was allowed to contain a trace of moisture before the determination was begun this would remain as a trace of aqueous hydrochloric acid after the gas had been transferred from this part of the apparatus to the absorption bulb, the temperature during this transfer remaining, of course, below zero. If, however, the condensation tube was perfectly dry to start with, no such trace of aqueous hydrochloric acid remained, that is, no water had been carried over from the chlorplatinate.

A final test of the chlorplatinate was made for water, hydroxyl or oxygen. One hundred grams of potassium chlorplatinate were treated exactly as for a determination. The chlorplatinate was heated to 400° in a current of dry air, transferred to the apparatus used in the determinations and then evacuated at 350°. Next, pure hydrogen was led over the chlorplatinate until it was completely reduced. The hydrochloric acid formed was led through a narrow U-tube surrounded by a mixture of solid carbon dioxide and alcohol (—78°). Finally, the whole apparatus including the U-tube was evacuated, the final conditions being, 350° in the chlorplatinate tube, —78° in the U-tube and several thousandths millimeters pressure. Upon weighing, the U-tube had shown an increase in weight of 0.9 mg. or 1 in 30,000 on the hydrochloric acid formed.

A number of corrections on the weight of the chlorplatinate tube were necessary. The first of these was necessary on account of the traces of air or nitrogen found in the chlorplatinate tube at the end of the determination. These corrections were found necessary in Experiments 4, 5, 6, and 7, their magnitude being 0.35, 0.76, 0.25 and 2 mg. This air may have been occluded by the chlorplatinate, or it may have come from the water of the absorption tube. It was immaterial how this correction was applied as it lay within the limits of the experimental errors, the maximum correction being 1 : 10,000.

In the second series it sometimes happened that with the most cautious manipulation, chlorplatinate was blown over into the condensation bulb at the beginning of the experiment. After the hydrochloric acid had been absorbed by the water and the apparatus weighed, this chlorplatinate was removed by dissolving in water and weighing first as potassium chlorplatinate and then again as potassium chloride + platinum, after reduction. This correction was applied in Experiments 8, 9 and 11, the amounts being 2.03, 15.0 and 36.5 mg. The apparent loss of the chlorplatinate tube was of course diminished by these quantities.

Hydrochloric Acid.—From the agreement of Series I and II it seems reasonable to assume that no errors were introduced by using water as the absorbing agent for the hydrochloric acid.

The corrections on the apparent gain of the absorption tube were of the following nature: First, the apparent gain was increased by the hydrochloric acid found in the palladium tube and by the hydrochloric acid pumped out from the chlorplatinate tube. The former has been spoken of under hydrogen. In Experiments 1, 6, and 7, there were found 1.27, 0.8 and 0.15 mg. of hydrochloric acid, respectively, in the gases pumped out.

In Experiments 8, 9, and 11, the gain of the absorption tube was diminished by the amount of the chlorplatinate blown over. The corrections were 2.03, 15.0 and 36.5 mg.

The final check on correctness of manipulation, freedom from leaks and other losses was found in the checking of the sum of the weights of the hydrogen and chlorine with the weight of the hydrochloric acid. In the preliminary experiments of both series, discrepancies were found until the details of the determination had been mastered. On this account and on account of other known errors the preliminary determinations were rejected entirely.

Results.

The values obtained are given in the following tables. The weights represent those found after all corrections had been applied. The second part of Experiment 5 was lost.

The value as found for the atomic weight of chlorine is 35.184 with a probable error of ±0.0013. The value obtained for the molecular weight of hydrochloric acid is 36.184 with a probable error of ±0.0012. The combined average of both sections of the two series is 35.184 with a probable error of ±0.0008. This is, of course, on the basis of hydrogen

	Hydrogen.	Chlorine.	Hydrochloric acid.	At. wt. Cl.	Mol. wt. HCl.
1	0.25394	8.93293	9.18695	35.177	36.178
2	0.28004	9.85590	10.13259	35.195	36.183
3	0.51821	18.23468	18.75359	35.188	36.189
4	0.67631	23.79587	24.47123	35.186	36.185
5	0.58225	20.48158	....	35.177	....
6	0.47989	16.88423	17.36310	35.184	36.182
7	0.64132	22.55816	23.20054	35.175	36.176
			Average of Series I,	35.183 and	36.181
8	0.81608	28.71691	29.53167	35.188	36.187
9	0.83194	29.28055	30.11207	35.195	36.195
10	0.39074	13.74926	14.14078	35.187	36.188
11	0.75560	26.58427	27.33926	35.183	36.182
12	0.77518	27.26746	28.04110	35.177	36.175
			Average of Series II,	35.186 and	36.185
			Total average,	35.184(3)	36.183(7)

On the oxygen basis this value becomes 35.452 if H = 1.00762[1] and 35.461 if H = 1.00787.[2] The values for silver calculated from Richards' ratio and these two values are, respectively, 107.87 and 107.89.[3]

The mean values must be considered as most probable at the present time. These are **35.457** for chlorine and **107.88** for silver.

In eleven experiments 6.41925 grams of hydrogen were united with 225.86017 grams of chlorine and yielded 232.27288 grams of hydrochloric acid. The values obtained from these figures are 35.1846 and 36.1838.

	H + Cl.	HCl.	Difference.
1	9.18687	9.18695	+0.00008
2	10.13594	10.13259	—0.00335
3	18.75289	18.75359	+0.00070
4	24.47218	24.47123	—0.00095
6	17.36412	17.36310	—0.00102
7	23.19948	23.20054	+0.00106
8	29.53299	29.53167	—0.00132
9	30.11249	30.11207	—0.00042
10	14.14000	14.14078	+0.00078
11	27.33982	27.33926	—0.00056
12	28.04264	28.04110	—0.00154
	232.27942	232.27288	—0.00654

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[1] Morley's value.

[2] Noyes' recent value.

[3] The value calculated from the results of Dixon and Edgar in the same manner are 35.463 or 35.472 for chlorine and 107.90 or 107.93 for silver. The mean values, 35.467 and 107.91 must be considered, for the present as the most probable which can be calculated from their work. The values for silver are calculated from the results of Richards and Wells, who found that 100 parts of silver gave 132.867 parts of silver chloride, This Journal, **27**, 525.

It may be interesting to note the discrepancies between the weights of hydrogen and chlorine and the hydrochloric acid formed in the individual experiments.

In these eleven experiments there were seven with an apparent loss of weight and four with an apparent gain, the total loss being 1 in 35,000.

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PREPARATION OF CHLORPLATINIC ACID BY ELECTROLYSIS OF PLATINUM BLACK.

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In the work[1] on the atomic weight of chlorine it was necessary to prepare considerable quantities of chlorplatinic acid free from nitric acid. When using aqua regia to dissolve platinum, considerable difficulty was experienced in removing the last traces of nitric acid by evaporation. When working with as much as 100 grams of platinum, the oft-repeated evaporation to dryness of the solution becomes exceedingly tedious and even at best, yields uncertain results. If the evaporation is carried on with strong hydrochloric acid considerable quantities of material become necessary, while with the use of water there is danger of hydrolytic decomposition of the chlorplatinic acid and consequent contamination of the chlorplatinate with hydroxychlorplatinates.

The process here described overcomes these difficulties and yields a pure solution of chlorplatinic acid. The platinum is prepared for electrolysis by dissolving platinum scraps or platinum sponge in aqua regia. The excess of acid is removed either by neutralization or evaporation, and the platinum solution is reduced by zinc or an alkaline formate, preferably the latter. The solution is decanted from the precipitated platinum, which is then warmed with a little dilute hydrochloric acid to remove iron. The platinum is then transferred to the electrolytic apparatus, the washing of the precipitated platinum being completed in this apparatus, which is constructed as follows:

It consists of a cylindrical tube about 4 cm. in diameter and 35 cm. long, which ends in a narrow glass tube, about 4 mm. bore, which is given the form of a siphon. The anode is a thin disk of sheet platinum which just fits into the tube and is perforated with numerous small pinholes. A small piece of platinum wire is welded to the disk and carried through the glass tube by means of sealing glass. The other end of the platinum wire ends in a glass tube which is carried to the top of the ap-

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[1] Noyes and Weber: See preceding article.