PHYSICAL PROPERTIES OF CHLORINE AND OF ITS AQUEOUS SOLUTIONS

THE PHYSICAL PROPERTIES OF CHLORINE AND OF ITS AQUEOUS SOLUTIONS WITH A VIEW TO THE ELUCIDATION OF THE EQUILIBRIA EXISTING IN THE LATTER

A THESIS

BY

ARCHIBALD STEWART ROSS, M.A.

Submitted to the Faculty of Graduate Studies and Research of McGill University in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Department of Chemistry.

Montreal, Canada. April, 1937.

THE PHYSICAL PROPERTIES OF CHLORINE AND OF ITS AQUEOUS SOLUTIONS WITH A VIEW TO THE ELUCIDATION OF THE EQUILIBRIA EXISTING IN THE LATTER

FOREWORD

The writer expresses here his warm appreciation of Dr. O. Maass as research director, teacher and friend. Without his kindly encouragement and assistance this thesis would not have been completed.

The writer also expresses appreciation for suggestions from Dr. E. W. R. Steacie and for optical apparatus loaned by Dr. F. Fitz-Osborne.

Acknowledgment is hereby made to the National Research Council of Canada of a Bursary, and to the Corporation of McGill University of a Demonstratorship and an Assistantship in the Department of Chemistry.

TABLE OF CONTENTS

GENERAL INTRODUCTION

1. Nature of the Problem 1

PART I. The Density of Chlorine Gas.

1. Survey of the Literature 4
2. Introduction to the Method . . . 27
3. Experimental Details 33
4. Experimental Results 47
5. Discussion of the Results . . . 54

PART II. The Solubility of Chlorine in Water.

1. Survey of the Literature 1
2. Introduction to the Method . . . 37
3. Experimental Details 39
4. Experimental Results 48
5. Discussion of the Results . . . 64

SUMMARY

BIBLIOGRAPHY

LIST OF FIGURES

Figure 1 . . . . To Follow Page 33, Part I.

Figure 2 . . . . To Follow Page 35, Part I.

Figure 3 . . . . To Follow Page 37, Part I.

Figure 4 . . . . To Follow Page 53, Part I.

Figure 5 . . . . To Follow Page 39, Part II.

Figure 6 . . . . To Follow Page 63, Part II.

INTRODUCTION

1. The Nature of the Problem

Considerable work has been done in this laboratory on the properties of certain of the common gases, and the survey already includes viscosities, densities, and the solubilities and conductivities of the aqueous solutions. Not only are these investigations of theoretical interest but they have contributed much valuable data to the arts and crafts of industrial practice. For the example, the gas densities and aqueous solubilities of carbon dioxide determined by Maass, Cooper (2), and Morgan (12) are embodied in the comprehensive monograph of Quinn and Jones (13) as the best existing data. The intensive researches of Maass (9)(10), Campbell (1), Morgan (12), Cooper (3), Gurd (7), Gishler (4)(5)(6), and Stewart (15)(16), on such properties of sulphur dioxide as the viscosity, the gas density, the aqueous solubility and conductivity, and the reaction equilibria with lime and with wood pulp and cellulose, have been of direct commercial value to industry.

Up to the present, chlorine and its aqueous solutions have not been studied in this laboratory. This thesis describes the initial step in a series of investigations by means of which the technique and experience gained in the earlier studies will be applied to the elucidation of the chlorine and hypochlorite equilibria. The present increase in the use of chlorine as a bleaching agent for wood pulp is an indication of the importance of the work. In 1925, 32,500 tons of chlorine were used in the United States for bleaching pulp. In 1935, 146,000 tons were used and it is estimated that 300,000 tons will be required in the near future to take care of the increased demand for bleached kraft pulp (8) (14). Not only are the equilibria in aqueous solutions obscure but Mellor (11) quotes C. von Meyer as saying in 1889, "Bleaching powder has been the subject of numberless researches made with the object of arriving at its constitution and it may be said that in spite of all these efforts there is no other substance of equally simple composition regarding whose nature and composition so much doubt prevails".

A casual survey of the literature on bleaching powder is sufficient to show that the important factor which has been treated inadequately hitherto is the concentration of the gas phase. Accordingly the present method of attack is well adapted to resolving the inconsistencies existing in the data and the thorough investigation of the properties of the aqueous solutions should furnish data having both theoretical significance and practical value. That such a common substance as chlorine has not been examined from this point of view is surprising. Little data are available on the density of the gas itself. Vapour pressures of its aqueous solutions are only recorded in the extreme case where the solid phase appears and even there the accuracy of the recorded values is problematical. The published conductivities of the aqueous solutions are valueless. Probably the extraordinary chemical activity of the gas is responsible for the sparsity of the quantitative measurements which have been made. The difficulties encountered on the latter score have been no small hindrance to the prosecution of the present work.

PART I

THE DENSITY OF CHLORINE GAS

1. Survey of the Literature

Possibly the earliest recorded determination of the density of chlorine gas was made by Davy (6). In a discussion of the properties of muriatic acid gas, he stated that 100 cubic inches at normal temperature and pressure weighed 74.5 grains or had a density of 2.38 compared to 1.00 for ordinary air. In the following year, he corrected this value to 2.44 on the evidence then forthcoming for the presence of chlorine oxides in the chlorine he had prepared earlier. The first sample had been prepared by the action of muriatic acid upon hyperoxymuriate of potash, the second by the action of muriatic acid upon manganese (dioxide).

Gay-Lussac and Thénard (7) found the density compared to air to be 2.47. Bunsen (1) first claimed an accuracy of more than three figures. He passed chlorine developed from the reaction between pyrolusite and hydrochloric acid through water and over calcium chloride into a tube of 91.005 cc. capacity. Both ends of this tube were drawn out and one end was connected by means of a vulcanised rubber tube to the chlorine generator and purification system. When the temperature of the tube was constant at

2.1°C., and all the air had been expelled, the rubber tubing was pinched together at the end of the inlet and the finely drawn out tip at the opposite end immersed at once in potassium iodide solution. Complete absorption took place and titration of the liquid emptied into a beaker gave 0.28191 gm. of chlorine contained in a volume occupied by 91.005 cc. of water at a temperature of 4°C. and under a reduced pressure of 0.7457 metres at 2.1°C. On correcting these data by means of the ideal gas law he found the value of the density at 0° and 1 atm. to be 2.4482.

No precise measurements of the density of chlorine gas were made until 1893 but during the intervening years numerous approximate values were determined over a wide temperature range. In 1868, Ludwig (26) carried out determinations over the range 20° to 200°C. making a number of measurements at each of five temperatures but listing only the mean value of each. Ludwig noted that the theoretical density corresponding to Stas' value of the atomic weight of chlorine was 2.45012 and this value was attained only at 200°. He used substantially Bunsen's method with certain small improvements. The pyrolusite used by him was previously digested with water, hydrochloric acid, and sulphuric acid in the order named. The chlorine developed in the usual way was washed through water in a tube 60 cm. x 3 cm. then dried over pure concentrated sulphuric acid in a similar tube. The cell used for the density measurements had a capacity of 340.3 cc. The parts of the apparatus were connected by means of short pieces of glass tubing with flexible interconnections of rubber tubing lined with platinum foil which was shaped to slip inside the glass tubing while the rubber tubing fitted over the outside. No evidence of attack on the rubber by the chlorine was observed. Before making a density determination, the escaping chlorine was tested for complete absorption in potassium iodide.

The results were checked by comparing the titre of an iodine solution prepared by liberation from potassium iodide by a volume of chlorine at known temperature and pressure with the titre of an iodine solution prepared by subliming iodine over pure barium hydroxide in a stream of dried air into weighed tubes, the ends of which were then sealed off and weighed again and the iodine transferred without loss to the potassium iodide solution. The agreement between the two solutions was found to be excellent.

Results:

Temp. °C.	Density (dry air = 1)	No. of Determinations
20°	2.4807	17
50°	2.4783	12

Results - continued

Temp. °C.	Density (dry air = 1)	No. of Determinations
100°	2.4685	5
150°	2.4609	5
200°	2.4502	6

Jahn (10) discussed Ludwig's results and showed that they could be represented by the formula,

$$D = 2.4855 - 0.00017t,$$ as follows:

	Density	
Temp. °C.	By formula	Observed
20	2.4821	2.4807
50	2.4770	2.4783
100	2.4685	2.4685
150	2.4600	2.4609
200	2.4515	2.4502

He considered deviations from the normal value of 2.4501, based on Stas' data, to be caused by molecular aggregation which disappeared only at 200°C. He compared the results with data on bromine and expressed surprise that in the latter element the forces between molecules were broken down at a lower temperature. It was evident then that the attractive forces were not proportional to the masses of the atoms and there must be some force opposing attraction and proportional to the mass of the molecules such, for example, as a centrifugal force arising from rotation.

In the years from 1879 to 1905 there was a mild controversy over the density of chlorine gas at high temperatures. Meyer and Meyer (30) dropped clay ampoules containing samples of platinous chloride into a porcelain tube heated to various high temperatures. The chlorine was volatilised, leaving a solid residue, and the volume of gas liberated at atmospheric pressure measured in the usual manner. The chlorine content was checked by sweeping out the system with carbon dioxide and collecting the iodine in potassium iodide solution where the iodine liberated was titrated with sodium thiosulphate. To prove that the porcelain was not attacked, a weighed piece of it was exposed to a stream of chlorine for one and one-half hours at 1567°, the highest temperature. No change in weight or visible alteration in structure was noted. The weights of the ampoules and the ignited quartz sand used to protect the base of the porcelain vessel from the falling ampoule were also checked for loss, and none was found.

Results:

Temp. °C.	Density found	Density calculated for 2/3 Cl_2
620°	2.42 and 2.46	-
808°	2.21 and 2.19	-
1028°	1.85 and 1.89	-
1242°	1.65 and 1.66	1.63
1392°	1.66 and 1.67	1.63
1567°	1.60 and 1.62	1.63

From the foregoing results the authors concluded that a new theory of the halogens was necessary although they reserved the idea of chlorine at ordinary temperatures being a combination of three atoms, each atomic weight equal to 35.5/3, as well as "die sich unwillkürlich aufdrängende so oft aufgestellte und wieder aufgegebene Muriumtheorie".

Lieben (25) assumed that the work of Meyer and Meyer was correct, that no gas was evolved from porcelain or platinum, but considered the data to be best explainable, not in terms of a smaller unit of chlorine since there was no evidence of such in any known compound, but as due to another law of dilatation valid above 700°C. and different from that followed by such gases as nitrogen, oxygen, sulphur and mercury, previously investigated by Meyer. As an alternative explanation, Lieben proposed the dissociation of chlorine molecules into single atoms. This, if complete, would give a density one-half the normal value whereas if only one-half the molecules decomposed, the density would be two-thirds of the normal value as found by Meyer and Meyer.

Seelheim (35), commenting on the work of Meyer and Meyer, said he found platinous chloride to be volatile in a stream of chlorine gas and also that platinum itself sublimed at bright red heat. Hence he considered that the two-thirds density obtained at high temperature by those authors could be explained by the reaction

$$P_2\ Cl_4 = 2Cl_2 + Pt_2 = 3 \text{ volumes.}$$
$$(2 \text{ vol.} + 1 \text{ vol.})$$

Meyer (29), in replying to Seelheim, said that under the experimental conditions used by him the chlorine was so rapidly evolved there was no chance for volatilisation of the chloride. Further the platinum remained behind as a solid coherent sponge corresponding in weight to the platinum content of the salt. There was no trace of sublimed or crystallized platinum. He also found by repeating certain experiments of Troost and Hautefeuille (40) that only 1% of a sample of platinum was volatilised in a stream of chlorine during one hour at 1570°C., so that in the few seconds required for his own vapor density determinations, not more than 0.01% could possibly have been volatilised in the still atmosphere of chlorine.

Crafts (4) made some modifications in Meyer's apparatus and found an increase in volume of only a few percent instead of fifty percent as found by Meyer.

Langer and Meyer (19) tried to reach the maximum dissociation of chlorine by progressive dilution with air instead of increasing the temperature, as they found that the best porcelain available softened above 1400°C. They prepared chlorine by the action of hydrochloric acid on potassium dichromate and diluted the gas with air in a glass gasometer. A horizontal tube ending in capillaries was brought to the required temperature and filled with a chlorine-air mixture. When temperature equilibrium was obtained, the mixture was swept out with air-free CO_2, the chlorine absorbed in potassium iodide solution and the carbon dioxide in alkali, after which the volume of air was determined in a gas burette. The apparatus was calibrated before and after each determination with air and CO_2. From the known volume of the tube at the temperature of the experiment and at room temperature the gas density was calculated thus; the difference between the volume of pure air at the temperature of the experiment and the volume of air and halogen = the volume of halogen; the weight of halogen was determined by titration of the iodine liberated from the potassium iodide solution. The temperature was that of the room and the pressure that of the barometer less the vapor pressure of the water and the temperature of the experiment did not come into account. Only glass and porcelain were allowed to come into contact with the gas. Special stopcocks requiring no grease were used.

The following values were obtained:

Density of undiluted chlorine at 100°C.	2.50
Density of chlorine diluted with 5 volumes of air at 100°C.	2.51
Density of chlorine diluted with 15 volumes of air at 100°C.	2.46
Density of undiluted chlorine at 900°, mean,	2.44
Density of undiluted chlorine at 1200°, mean,	2.44

All the values agree well with the normal value of 2.45. Langer and Meyer, however, considered that lower density values might well be obtained at higher temperatures and greater dilutions. Against this, however, they cited Crafts (vide supra).

Crafts (5), in summing up the evidence in the preceding, considered that the concept of a progressively increasing coefficient of dilatation for the halogens was unnecessarily complicated, that Berthelot had shown that there was a parallel increase in the heat content of gases which showed the abnormal dilatation, and that the facts were best explained by the assumption of a gradual increase in the internal energy of the molecules leading finally to dissociation at temperatures in the neighbourhood of 1600°.

After this time no further application of volumetric methods was made to determine the thermal dissociation of chlorine except in the experiments of Reinganum (34) who found that there was no evidence of dissociation at 1137° if precautions were taken to prevent chlorine diffusing through the walls of the apparatus.

Toward the end of the above series of investigations the experimental determination of the density of chlorine gas at or near room temperature was carried to a higher degree of precision by the work of Leduc (21) who used an all-glass system with ground joints and stopcocks lubricated with a grease prepared by the action of chlorine upon paraffin and vaseline. The chlorine first used was prepared by the action of hydrochloric acid on potassium dichromate, freed from hydrochloric acid by copper sulphate and dried over pumice soaked in concentrated sulphuric acid. This method was abandoned, however, owing to the difficulty of manipulating the apparatus and liquid chlorine fractionally distilled was used. The mercury in the pump used for the evacuation of the system was protected with a layer of sulphuric acid. The limit of evacuation possible was about 0.2 mm. of mercury. The values of the density of chlorine gas at 0° and 760 cm, varied from 2.4857 to 2.4868 with an estimated precision of better than 1 in 3,000 in the weighted mean value of 2.4865.

In a second paper Leduc (22) considered that his earlier value was 0.005 units too low because analysis had shown the presence of about one part of air in 300 parts of chlorine. He repeated the measurements with chlorine prepared from hydrochloric acid and potassium dichromate, purified from hydrochloric acid over pumice impregnated with copper sulphate, dried over pumice soaked in concentrated sulphuric acid, and stored over sulphuric acid. Despite all precautions the residual air amounted to 12 cc. in 2.28 litres. After all corrections, the nature of which were not mentioned in the paper, had been made, the standard density was considered to be 2.4907 with a round value of 2.491 supposed accurate to one part in 2500. Leduc added that there might be an error due to condensation of gas on the walls of the balloon but that the amount of this error was indeterminable.

The next paper was published by Moissan and du Jassoneix (31). They reviewed the existing literature, methods, and values and made their determinations with two aims in mind (i) the preparation of pure chlorine, and (ii) the measurement of the density in a balloon without a stopcock and enclosing neither air nor moisture.

The apparatus was entirely of glass and the generator was fitted with a rough manometer containing mercury covered with sulphuric acid which acted as a safety valve. Pure concentrated hydrochloric acid was caused to react with natural manganese dioxide which had been previously washed with dilute acid. The hydrochloric acid itself was prepared by the action of pure sulphuric acid on sodium chloride purified by several crystallizations. The chlorine gas was washed in two bubblers containing concentrated sulphuric acid and finally dried over fused calcium chloride, after which it was condensed under slight pressure at -30 to -32°C. in an apparatus of Moissan's invention.

Three series of experiments were carried out. In the first series, the Dumas method was used. Glass balloons with long slender necks were filled with chlorine by displacement of the air, and sealed off at the known temperature of a large bath. Each balloon was weighed against a tare balloon and the chlorine absorbed in sodium hydroxide solution freed from air. There was always a small residual bubble of gas which was taken into account. The balloon was then washed and dried, weighed full of atmospheric air and its volume determined by calibration with distilled water. (The chlorine presumably was determined by precipitation of the total chlorine content with silver nitrate).

Results:

No.	Pressure mm.	Temp. °C.	Density under Standard Conditions (dry air = 1)
1	770	12.5	2.468
2	751	12.5	2.506
3	765	10	2.424
4	763	12.6	2.478
5	762.1	10	2.456

The mean density is 2.4666 and the maximum deviation between any two determinations is 0.082. The authors offered the following criticism.

(a) There was always a residue not absorbable by the solution of alkali.

(b) It was impossible to dry perfectly a gas balloon filled by displacement.

(c) There were uncertainties in the second weighing.

In the second series of experiments the gas was liquefied with a mixture of solid carbon dioxide and acetone and stored in bulbs of 4 cc. capacity containing about 2.5 cc. of liquid chlorine. The sample was put in the density balloon (see following reference) which was then evacuated and the sample broken.

Results:

No.	Pressure, mm.	Temp. °C.	Density, n.t.p.
6	754	0	2.494
7	750	0	2.489

The authors noted that it was difficult to dry chlorine over calcium chloride, a very slow current of gas being required. Accordingly, they collected 20 cc. of liquid chlorine in a glass tube containing fragments of calcium chloride which had been fused in a current of chlorine gas. After this sample had been dehydrated for several weeks, they prepared smaller samples of chlorine as above with the following results:

No	Pressure, mm.	Temp. °C.	Density, n.t.p.
8	761	0	2.433
9	759	0	2.509
10	759	0	2.468
11	753	0	2.335

The errors in the above are also discussed in the following paper. The chief source of error was ascribed to oscillations in the pressure inside the balloon caused by the sudden expansion of the chlorine in passing from liquid to gas.

In the third series, the excess chlorine was caused to flow out through a capillary orifice; hence there was no chilling by sudden expansion and no insuck of air. The balloon was reweighed in this case after rigorous evacuation rather than when filled with air.

Results:

No.	Pressure, mm.	Temp. °C.	Density, n.t.p.
12	762.2	0	2.494
14	756.5	0	2.487
15	758.9	0	2.486
16	756.2	0	2.493

The mean value of these determinations is 2.490 and the maximum deviation between the two extreme values is 0.008. A final source of error was considered to be attributable to the possibility of dissolved air in the liquid chlorine. To remove this uncertainty, liquid chlorine was frozen in liquid air and thoroughly evacuated with a double mercury pump, with the following results:

No.	Pressure, mm.	Temp. °C.	Density, n.t.p.
17	757.7	0	2.488
18	760.6	0	2.492

Here the mean is 2.490, agreeing with the four determinations above, with a maximum of deviation of 0.004.

The second paper by Moissan and du Jassoneix (32) is evidently a more complete discussion of the material of reference (31) with full details of the method of connecting balloons to the evacuation system and the methods of filling with chlorine and of sealing off. The capacity of the balloons was about 600 cc. The weights were verified and were exact. The difference between the 50 gm. weight and the sum of the smaller weights was less than 1 mg. The balance was sensitive to 0.1 mg. A difference of 1 mg. in the weights affected the third decimal by one unit. The barometer and temperature corrections, (the barometer was compared with that used by Leduc), gave a precision in the pressures of between 0.1 and 0.2 mm. A difference of 1 mm. in the pressure influenced the density to three units in the third decimal place. The temperature of the water which filled the neck of the balloon in the calibration of the volume varied some tenths of a degree. The temperature of the mass remained constant. Admitting that 50 cc. of water in the balloon underwent a temperature variation of 0.5°C., a value greater than actual, the corresponding dilatation was only 0.01 cc. The balance used for this purpose was accurate to 0.01 gm. Therefore, the errors in calibration would not attain 0.1 cc. and an error of 1 cc. affected the density to only 4 units in the third decimal place. The mean value, 2.490, was again considered the best value.

The year following the appearance of the work of Moissan and du Jassoneix, Leduc (23) published a note on his work confirming his value of 2.491 ± 0.001 which lay between the best values of Moissan and du Jassoneix. However, none of his determinations, in which the deviation was four times less, fell below 2.490 after all corrections were made, and the mean of his second and best series was 2.4907. Further, as the impurities were probably on the average lighter than chlorine, he considered the arithmetical mean of the results to be a lower limit to the density of the pure gas and he believed the value 2.4918 to be near the true value.

In the same year, Treadwell and Christie (39) noted that the gram molecular volume of chlorine when used in analytical experiments with pure chlorine was too high. As the best values in the literature, especially that of Moissan and du Jassoneix, were for 0°C., and chlorine, having a critical temperature of 140°C., could be expected to show marked deviations from the gas laws at room temperature, they made some careful determinations of the density at 10° and 20°C. The chlorine was prepared in the usual way in an all-glass system by the action of hydrochloric acid on potassium dichromate, and washed and dried in the usual way, with the addition to the train of a heated tube containing asbestos to destroy any chlorine oxides. The chlorine so prepared contained a slight amount of air which was taken care of in the calculations. Bunsen's method of determining the density was used. Two glass cells fitted with stopcocks at each end, of exactly equal volume and of almost exactly equal weight, were used. The volume of each cell was 393.80 cc. and the weight about 78 gm. First, both cells were filled with dry air at the same temperature and pressure and the slight difference in weight noted. Second, one cell was filled with air and the other with chlorine under identical conditions and weighed again. The difference between the two weighings was the weight of the volume of chlorine less the weight of the same volume of air. An air thermostat with good temperature control was used to surround the cells during filling. The chlorine was absorbed by boiled sodium hydroxide solution admitted to the cell and the size of the residual air bubble determined by the volume of sodium hydroxide solution, measured in a gas burette, required to expel it from the cell through the upper tap. The bubble was considered as air and water vapor. If not pure air the error was still small. For example, if it were pure oxygen the error was less than 0.03%.

Results:

No.	Temp. °C.	Pressure, mm.	Density air = 1 (at temp. and press. of meas.)
1	20.3	732.9	2.487
2	20.3	732.2	2.489
3	20.3	728.0	2.488
4	9.9	731.7	2.491
5	10.0	719.0	2.488

As rounded values, the authors take the values 2.488 at 20° and 730 mm., and 2.489 at 10° and 725 mm.

In 1908, Pier (33) in connection with his study of the specific heat of chlorine gas reviewed the literature on gas densities and came to the conclusion that the recorded values from 0° to 300°C. were too high. He considered Moissan's value of 2.490 at 0° and 760 cm. to be the best since several methods and all known precautions were used.

In his own research, Pier used chlorine from a cylinder and determined its purity to be 99.32% by titration of the iodine liberated from potassium iodide by a precisely calibrated volume of the gas and comparison of the calculated content at 760 cm. and 0° with the content calculated from Moissan's value as standard. Subsequent calculations were based on this purity. Over a temperature range the densities at one atmosphere were found to be

Temp. °C.	Density observed
0.00	2.490
50.24	2.4688
100.40	2.4601
150.70	2.4554
184.00	2.4538

Inasmuch as Pier's measurements were all relative to Moissan's value, it is perhaps better not to attach any great weight to his density values although they are probably the best relative values extant in the range 50° to 200°C. Pier also determined mean values of the coefficient   for chlorine in the Gay Lussac relations:

At constant pressure, $v = v_0(1 + \alpha t)$ (i)
At constant volume, $p = p_0(1 + \alpha t)$ (ii)

The value of α in relation (i) varied from 0.003873, between the temperatures 0.00° and 50.24°C., to 0.003760, between the temperatures 150.70° and 184.00°C., while over the temperature intervals from 0.00° to each higher temperature the values varied from 0.003873, between 0.00°

and 50.24°C. to 0.003804 between 0.00° and 184.00°C.

The values of α in relation (ii) for chlorine heated in a constant volume cell varied from 0.003807 over the interval 0° to 100.4°C. to 0.003736 over the interval 100.4° to 184.4°C. with a mean value of 0.003774 over the interval 0° to 184.4°C.

Finally, Pier investigated the Law of Boyle-Mariotte, $pv = K$ at constant temperature, and found the ratio $\frac{pv}{p_o v_o}$ for chlorine at 13.5°C. to vary from 1 to 1.013 when the volume ratio $\frac{v}{v_o}$ varied from 1 to 17.81 and the corresponding pressure ratio $\frac{p}{p_o}$ fell from 1 to 0.0569.

There remains only the very precise density determinations of Jaquerod and Tourpaian (12) by two methods, a hydrostatic method using a float suspended in the gas, and a volumetric method wherein the use of stopcocks or cemented connections was entirely avoided. For precise details of the hydrostatic method, reference should be made to Jaquerod (11). In substance a thin glass float of 0.40300 litres volume and weighing with its suspension about two grams was hung inside a glass vessel by means of a fine platinum wire fastened to one arm of a balance. Chlorine was passed in at the base of the vessel by means of a tube leading from the generating and purifying system and drawn away at the top by a water aspirator except when measurements were being made when the chlorine stream was by-passed and the aspirator stopped while the chlorine came to equilibrium with the atmospheric pressure. All measurements were made at atmospheric pressure at or near 725 mm. and at temperatures between 0° and 30°.

The cubic coefficient of dilatation of glass was taken as 0.0000285.

Chlorine was prepared by three different methods:

(1) By the action of pure hydrochloric acid (20%) on Kahlbaum precipitated manganese dioxide. The rate of evolution of chlorine was regulated very easily by means of a water bath.

(2) By the action of pure hydrochloric acid (38%) dropped on crystals of pure potassium permanganate.

(3) By the decomposition of auric chloride in a glass tube heated electrically to 300° to 350°C.

The first and second methods were used in the density determinations by the hydrostatic method, and the third in the volumetric method. The authors also tried as a fourth method electrolysis of a fused mixture of silver and lead chlorides but abandoned it because traces of moisture were evolved from the carbon electrodes.

For the hydrostatic method the chlorine was liberated and purified in all-glass systems. Hydrochloric acid was removed from the chlorine stream by passage through U-tubes containing glass beads and concentrated copper sulphate solution. The drying agents were concentrated sulphuric acid and phosphorus pentoxide. The chlorine was condensed by means of solid carbon dioxide and alcohol and passed from storage as required through a small washing bottle containing sulphuric acid and thence over phosphorus pentoxide to the hydrostatic apparatus. Many irregularities indicating variations in the composition of the gas were noted and the cause was finally traced to the action of light on the moist chlorine coming from the generator. When the generator and connected apparatus as far as the phosphorus pentoxide tube was coated with a thick layer of black varnish and operations conducted with a minimum of illumination, the variations at once fell within the limits of experimental error. The individual measurements differed not more than one part in ten thousand. The tare weight of the float in vacuo was determined before and after each measurement of chlorine by computation from its weight in pure dry oxygen and, as there was a trace of chloride on the platinum suspension where it came into contact with the atmosphere above the cell containing the float, the second tare weight was taken each time.

Summary of the best results over a period of several months:

A. Chlorine prepared from potassium permanganate and hydrochloric acid: five determinations at pressures ranging from 728.17 mm. to 728.49 mm. and temperatures from 18.61° to 18.75°C. gave for the weight of a litre of chlorine at 725 mm. and 15° values ranging from 2.8963 to 2.8969 gm. with a mean value of 2.8966 gm.

B. Chlorine prepared from manganese dioxide and hydrochloric acid: ten determinations at pressures ranging from 727.46 mm. to 728.25 mm. and at temperatures from 9.19° to 15.04°C. gave for the weight of a litre of chlorine at 725 mm. and 15°C. values ranging from 2.8963 to 2.8971 gm. with a mean value of 2.8968 gm.

The mean value for chlorine from both sources was 2.8967 gm. under the stated conditions of temperature and pressure.

For the volumetric method gold chloride was prepared by the action of purified chlorine at 200°C., over two or three hours, on 30 gm. of gold which had been freshly precipitated, washed, and dried. The calibrated volume and a calibrated tube were connected by means of a calibrated Π-shaped piece of capillary tubing sealed at one constricted end to the unit containing the gold chloride, and at the other end, also constricted, to a mercury pump and a manometer containing mercury protected with a layer of concentrated sulphuric acid. The whole system was thoroughly evacuated and the pump sealed off. Chlorine was evolved, by heating the chloride to 300°C., until the pressure in the system was a few mm. over atmospheric. The tubing leading to the chloride was cut open and the whole calibrated unit isolated by sealing off at the constricted ends of the Π-piece. Finally the chlorine was condensed in the small tube and weighed with all the customary precautions (such as are described in connection with the present research).

Two complete and satisfactory determinations were made in this way, one at 17.61° and the other at the ice point. The former gave 2.8960 gm. for the weight of a litre of chlorine at 15° and 725 mm., and the latter 3.0629 gm. for the weight of a litre of chlorine at 0° and 725 mm. The former of these volumetric determinations was in excellent agreement with the mean of the hydrostatic determinations.

Summary for chlorine at 15° and 725 mm:

By the hydrostatic method 1 litre weighs 2.8967 gm.
By " volumetric " 1 litre " 2.8960 gm.

The weighted mean considering the greater number of determinations by the hydrostatic method is 2.8965.

From the mean of five hydrostatic determinations, under average conditions of 15.03°C. and 725 mm., and five similar determinations, at the same pressure and at 9.43°, the coefficient of dilatation between these temperatures was found to be 0.003830. From the two volumetric determinations the coefficient between 0° and 17.61°C. was found to be 0.003842. The mean value of 0.003836 at normal temperatures and 725 mm. was used in the calculations.

From the above data the mean value for the weight of a litre of chlorine at 725 mm. and 0° was found to be 3.0630 gm. The density at 760 cm. was obtained by means of Leduc's value (24) of <u>A</u> in the equation

$$\frac{pv}{p_o v_o} = 1 + A(p - p_o)$$

whence the weight of a litre of chlorine at 760 mm. and 0°C. was found to be 3.214 gm.

2. Introduction to the Method

The preceding survey of the literature shows that the main interest in the past has been the determination of the density of the gas under normal conditions. The work of Pier (33) and that of Jaquerod and Tourpaian (12) come nearest to the secondary aim of the present work which is to obtain some quantitative measurement of the deviations of chlorine gas from the ideal state. The measurements were undertaken primarily for the collection of the data necessary for calculating the solubility of chlorine in water from the vapour pressure of the aqueous solutions. Nevertheless, the density of chlorine gas is of theoretical interest from the standpoint of the attractive forces existing between molecules.

The ideal gas may be described as one for which the simple equation of state is true:

$$PV = RT$$

It is found, however, that no real gas obeys this law except at very low densities and high temperatures. Corrections must be introduced to account for the effect of attractive forces on the pressure and repulsive forces or finite volume effects on the volume. The best known of such equations is that of Van der Waals (41):

$$(P + \frac{a}{V^2})(V - b) = RT$$

Although Van der Waals' equation is markedly more true to the actual behaviour of gases, it is still far from accuracy even at ordinary temperatures and at pressures as low as one atmosphere.

Two equations of state have been proposed by workers in this laboratory. In 1926 Maass and Mennie (27) developed a modification of Van der Waals' equation in which they expressed deviations from ideality in terms of the interdependence of the Van der Waals' constant "b" and the molecular mean free path. The latter is a function of temperature and can be calculated from the coefficient of viscosity which is itself a function of temperature as shown by Sutherland (37) and others (3), (16), (17). The equation may therefore be expressed in the following form:

$$(P + \frac{a}{V^2})(V - B(1 + \frac{c}{T})) = RT$$

or $PV^2 - RTV + a - RTB(1 + \frac{c}{T}) = 0$ and if $B(1 + \frac{c}{T})$ be put equal to b, the equation may then be written $PV^2 - RTV + a - RTb = 0$, whence $a = RT(V + b) - PV^2$

The value of B may be obtained from the relation

$$B = \frac{8\sqrt{2}\,\pi r^3 N}{1 + \frac{c}{T}}$$

where r is the radius of the molecule, N is Avogadro's number, 6.062 x 10^{23}, and c is Sutherland's constant for the gas.

The value of r may be obtained from tables or may be calculated from Chapman's (2) modification of a formula derived by Jeans (13) where

$$k = \frac{0.499m\,\bar{C}}{2\pi d^2}$$

Here k is the coefficient of viscosity at a given temperature, M is the mass of the molecule, $\bar{C}$ is the average molecular velocity $= \sqrt{\frac{8}{3\pi}}$ x (rt. mean square velocity) and d is the diameter of the molecule.

The value of r may then be substituted in the expression $B = \frac{8\sqrt{2}\pi r^3 N}{1 + \frac{c}{T}}$ and the value of B determined. Next the value of b as a function of temperature may be calculated from the expression $b = B(1 + \frac{c}{T})$ and by substituting the value of b in the expression $a = RT(v + b) - PV^2$, the corresponding values of a may be calculated.

Maass and Mennie also showed that when V was put equal to $\frac{M_o}{M^1} \cdot \frac{RT}{P}$, thus defined as the actual volume occupied by the theoretical molecular weight of the gas at corresponding T and P, and the latter value substituted in the equation $PV^2 - RTV + a - RTb = 0$, the resulting equation could be expressed as a power series of M^1 in terms of P:

$$\frac{M^1}{M_o} = 1 + \left(\frac{a - RTb}{R^2T^2}\right)P + 2\left(\frac{a - RTb}{R^2T^2}\right)^2P^2 + \; - - -$$

This series converges rapidly, especially at high temperatures so that to a first approximation the apparent molecular weight varies linearly with the pressure:

$$\frac{M^1}{M_o} = 1 + AP \qquad \text{where} \quad A = \frac{a - RTb}{R^2T^2}$$

In 1932 Cooper and Maass (3), with very precise data on the density and viscosity of carbon dioxide at their disposal, showed that a more accurate modification of Van der Waals' equation than that of Maass and Mennie could be derived by the substitution of an empirical equation representing the variation of viscosity with temperature for the formal expression of Sutherland which, as is well known, fails at temperatures near the boiling point of a gas.

In deriving this equation, Cooper and Maass point out that the viscosity of an ideal gas is proportional to the square root of the temperature, whereas the viscosity of a real gas changes more rapidly than the square root of the temperature. The equation takes the form of

$$PV^2 + a - RTV - RTb \cdot \frac{f(T_o)}{f(T)} = 0$$

or $f(T)\left(PV^2 + a - RTV\right) - RTb \cdot f(T_0) = 0$

or $V \cdot f(T)\left(PV - RT\right) = RTb \cdot f(T_0) - a \cdot f(T)$

and, if $Rb \cdot f(T_0)$ be put equal to b_0

$V \cdot f(T)(PV - RT) = b_0T - a.f(T)$

For many gases the variation of the viscosity relative to the square root of the temperature may be expressed by means of a straight line. In such a case the function of temperature takes the form $(1 + KT)$ and the preceding general expression may be written

$$PV^2 + a - RTV - \frac{RTb(1 + KT_0)}{1 + KT} = 0$$

which rearranged as before, takes the final form, putting in this case $b_0 = Rb(1 + KT_0)$,

$$V(1 + KT)(PV - RT) = b_0T - a - aKT$$

or, putting $b_0 - aK = \lambda$

$$V(1 + KT)(PV - RT) = \lambda T - a$$

Since the left hand side varies linearly with T, the equation may easily be tested. The value of V may be computed by defining it as

$$V = \frac{M_0}{M^1} \cdot \frac{RT}{P}$$

where the symbols have the same value as for the Maass and Mennie equation. The value of $(1 + KT)$ may be calculated from the viscosity line and $(PV - RT)$ from the above volume data. The value of the whole left hand expression may then be plotted against T, the function $(\lambda T - a)$ evaluated, and the equation used to calculate V for any desired conditions. Or, if desired, all the minor constants may be evaluated by working back from the value of $(\lambda T - a)$ through the relations connecting them to give an equation in P, V, R and T.

This equation may also be written in the form of an isothermal by substitution of the equation $V \simeq \frac{M_o}{M^1} \cdot \frac{RT}{P}$ and takes the form

$$\frac{M^1}{M_o} \simeq 1 + \left(\frac{a - \frac{RTb_o}{1+KT}}{R^2T^2} \right) P + 2\left(\frac{a - \frac{RTb_o}{1+KT}}{R^2T^2} \right)^2 P^2 + - - - -$$

where $b_o = Rb(1 + KT_o)$

3. Experimental Details

In view of the reactive nature of chlorine, the apparatus designed for this work was an all-glass system. It was of the general type first used in this laboratory by Maass and Russell (28) and followed in more particular the design employed by Wright and Maass (44), (45) in determining the solubility of hydrogen sulphide. A full description of the method of making the glass membrane manometers is appended to his work by Wright (45) together with a complete bibliography on the subject of glass manometers in general. Certain modifications in the construction and manipulation of the apparatus were required as outlined in the text below and illustrated in the diagrams.

The apparatus was constructed from soft glass with the exception of the section composed of the calibrated volume, the glass manometer, the oil trap, the section containing the bulbs for the condensation of the samples of chlorine, and the section comprised of two Langmuir diffusion pumps. Graded seals were used in making the pyrex-to-soft glass joints in the first two sections, and DeKhotinsky cement in the latter section.

Figure I shows the purification train. It was

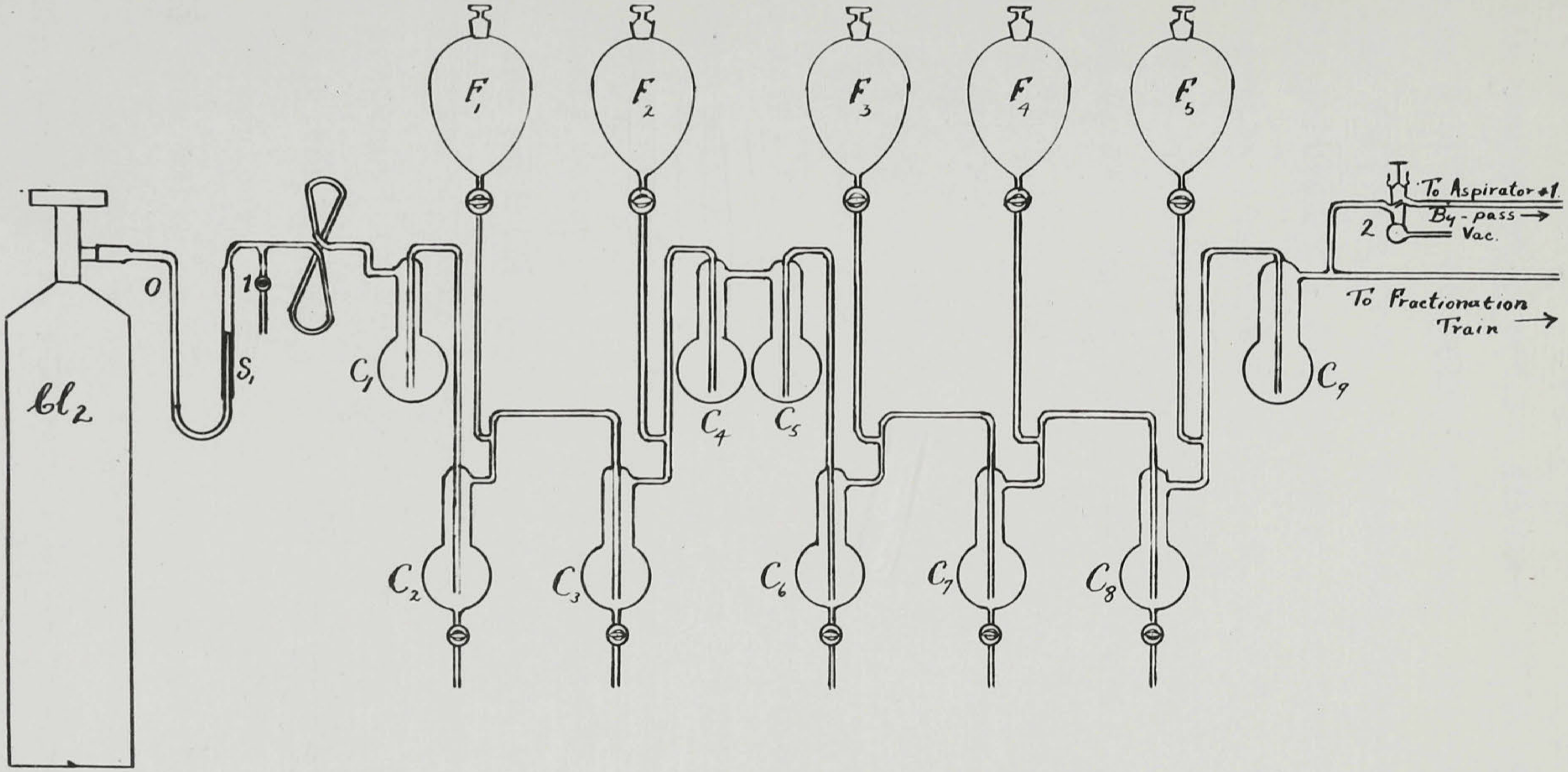

Cl_2
0
1
S_1
C_1
F_1
F_2
F_3
F_4
F_5
C_2
C_3
C_4
C_5
C_6
C_7
C_8
C_9
2
To Aspirator #1.
By-pass →
Vac.
To Fractionation Train →

Figure 1

constructed from 500 cc. separatory funnels and Cloez wash bottles and sealed with sodium silicate at S_1 to the copper outlet tube O of the chlorine cylinder. The cylinder of chlorine was obtained from Canadian Industries Limited. Immediately preceding a distillation, the stopcocks in this train, excepting those beneath F_1, F_2 and C_2, C_3, where ordinary stopcock grease was required, were lubricated with the phosphoric acid mixture described below. Then F_1 and F_2 were filled with potassium permanganate solution and F_3, F_4 and F_5 with concentrated sulphuric acid. With stopcock 1 open, and 2 and 11 slightly open to admit suction from an aspirator, the Cloez wash bottles C_6, C_7, C_8 were filled with sulphuric acid, and then C_2 and C_3 with potassium permanganate solution. Stopcocks 1 and 2 were closed and 3, 6 and 7 opened before the valve on the chlorine cylinder was cautiously opened to flush the system with chlorine. When both the purification and fractionation trains had been completely freed of air, stopcock 6 was closed and the chlorine condensed in the distillation cell D_1 by refrigerating the latter with a mixture of solid carbon dioxide and acetone. When sufficient chlorine had been collected, the valve on the cylinder and stopcock 3 were closed, and stopcocks 1 and 2 opened to prevent the building up of undue pressure in the purification system if the chlorine tank valve were defective. The traps C_1 and C_5 took care of any reverse movement of the liquids caused by pressure of the gas toward the chlorine cylinder. This usually occurred if the valve on the chlorine cylinder had to be closed because the rate of condensation was less than the rate of flow. Traps C_4 and C_9 collected, respectively, potassium permanganate solution and sulphuric acid if these liquids happened to be carried forward by a surge of pressure when the valve of the chlorine cylinder was opened.

The chlorine in D_1 was now allowed to warm up and distilled under agitation with an electromagnetic stirrer into D_2, Figure 2. The first and last sixths of the liquid were rejected and the middle two-thirds retained. A rough mercury manometer M_1 was intended as a check on the rate of distillation and as a safety valve if the pressure became too great, but it became clogged with the chloride and was sealed off. Distillation was then controlled by keeping the chlorine below the ebullition point, by watching the rate of condensation as indicated by the evolution of carbon dioxide from the refrigerant around the receiver, and by the colour of the gas in the system, the depth of colour being a rough indication of the concentration. Distillation was repeated from D_2 back to D_1 and thence to D_3 for storage. These three distillations in vacuo following the treatment in the purification train with potassium permanganate and

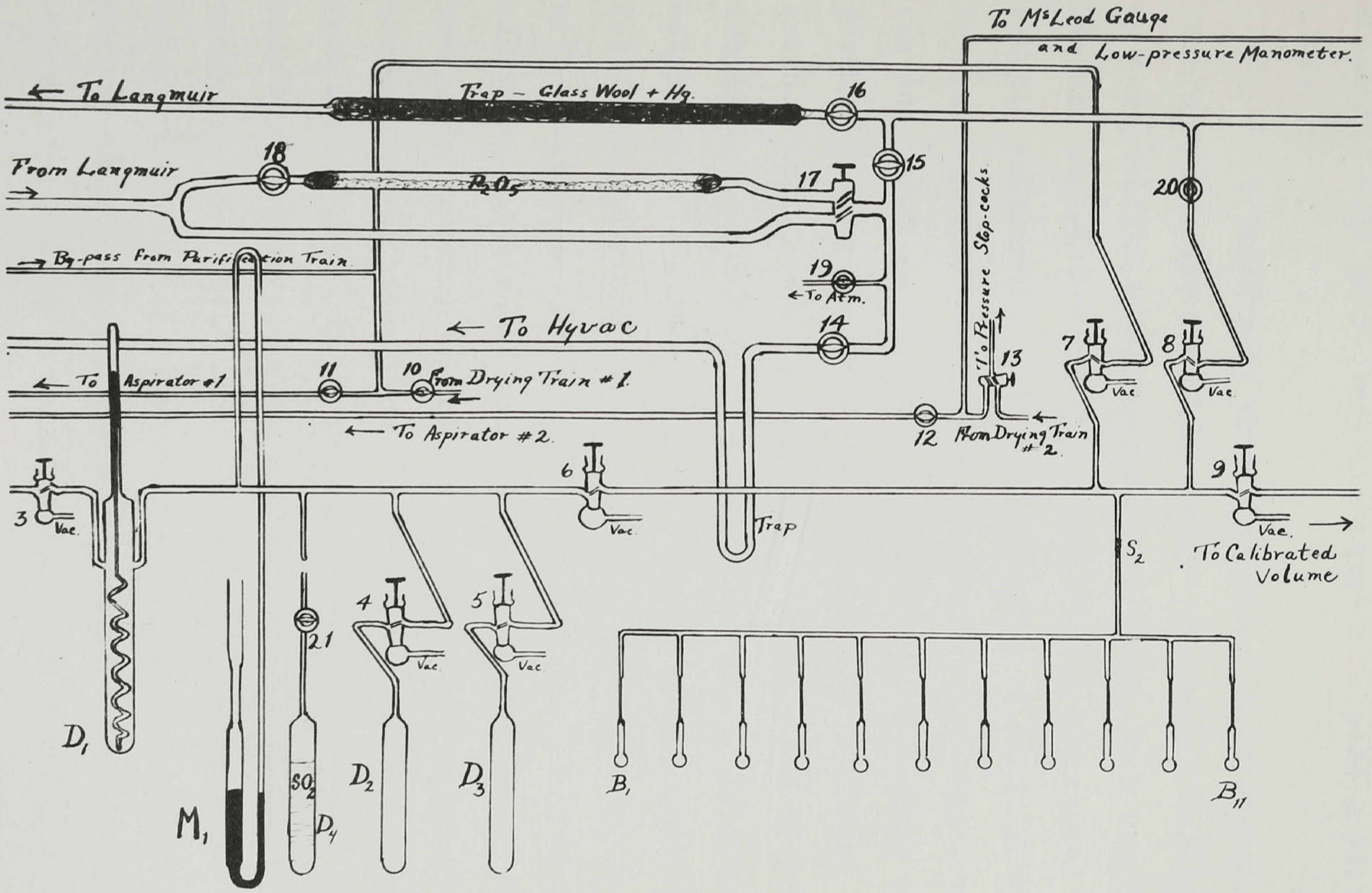

To McLeod Gauge
and Low-pressure Manometer.
← To Langmuir
Trap – Glass Wool + Hg.
16
From Langmuir →
18
P_2O_5
17
15
20
→ By-pass from Purification Train
19
← To Atm.
To Pressure Stop-cocks
← To Hyvac
14
7
8
13
← To Aspirator #1
11
10 From Drying Train #1.
12
From Drying Train #2.
← To Aspirator #2.
Vac.
6
9
3
Trap
S_2
To Calibrated Volume →
4
5
21
D_1
M_1
SO_2
D_4
D_2
D_3
B_1
B_{11}

Figure 2

sulphuric acid gave every assurance of a pure product (20), (42).

A brief note on the lubrication of stopcocks in such a system may be of interest. Ordinary lubricants, such as the paraffin-vaseline-rubber mixtures, were useless because the rubber and other unsaturated substances were readily chlorinated with the formation of solid products. Several types of phosphoric acid lubricants were tried and the one found most satisfactory was made according to the formula of Stephen (36). It consisted of a mixture of ortho-, meta-, pyro- phosphoric acids prepared by partial dehydration at 300°C. of a mixture of 18 gm. of glacial metaphosphoric acid with 35 gm. of 85% orthophosphoric acid. It was found advisable to use mercury-seal stopcocks with vacuum bases, the mercury to keep the lubricant from absorbing moisture at too rapid a rate, the vacuum to prevent a tendency toward channeling of the lubricant when the system was under vacuum and to prevent the stopcocks from being blown out at pressures greater than one atmosphere. Once the stopcocks had been settled snugly in place by vacuum at the base, it was advisable to release the vacuum there except during runs in order to prolong the life of the lubricant. Such a precaution applies to all types of vacuum stopcocks even when lubricated with the best of organic lubricants such as those of the "Apiezon" type and is imperative when inorganic lubricants of low lubricity must be used. A rough manometer in the stopcock vacuum system indicated the degree of vacuum applied.

Incidentally it was found advisable to use one aspirator for the control of the vacuum here and for removing chlorine from the system in general, and a separate aspirator for controlling the vacuum on the pressure stopcocks lubricated with stopcock grease as well as the levelling devices on the low-pressure manometer and the McLeod gauge. Two separate drying trains were also used, each consisting of two Drexel wash bottles containing concentrated sulphuric acid followed by a long glass tube containing phosphorus pentoxide. One drying train supplied air to the manometric system and the vacuum stopcocks lubricated with grease, the other supplied air to the chlorine system and its stopcocks. These precautions might seem redundant but experience with the corrosive nature of even minute traces of chlorine on mercury proved their value. Unless such precautions were taken, the mercury menisci in the manometers rapidly lost their definition and errors were introduced in the pressure measurements.

The most interesting part of the apparatus was the glass manometer G, Figure 3, used in the calibrated volume for the vapour density measurements and in the cell for the measurement of the solubility of chlorine in water.

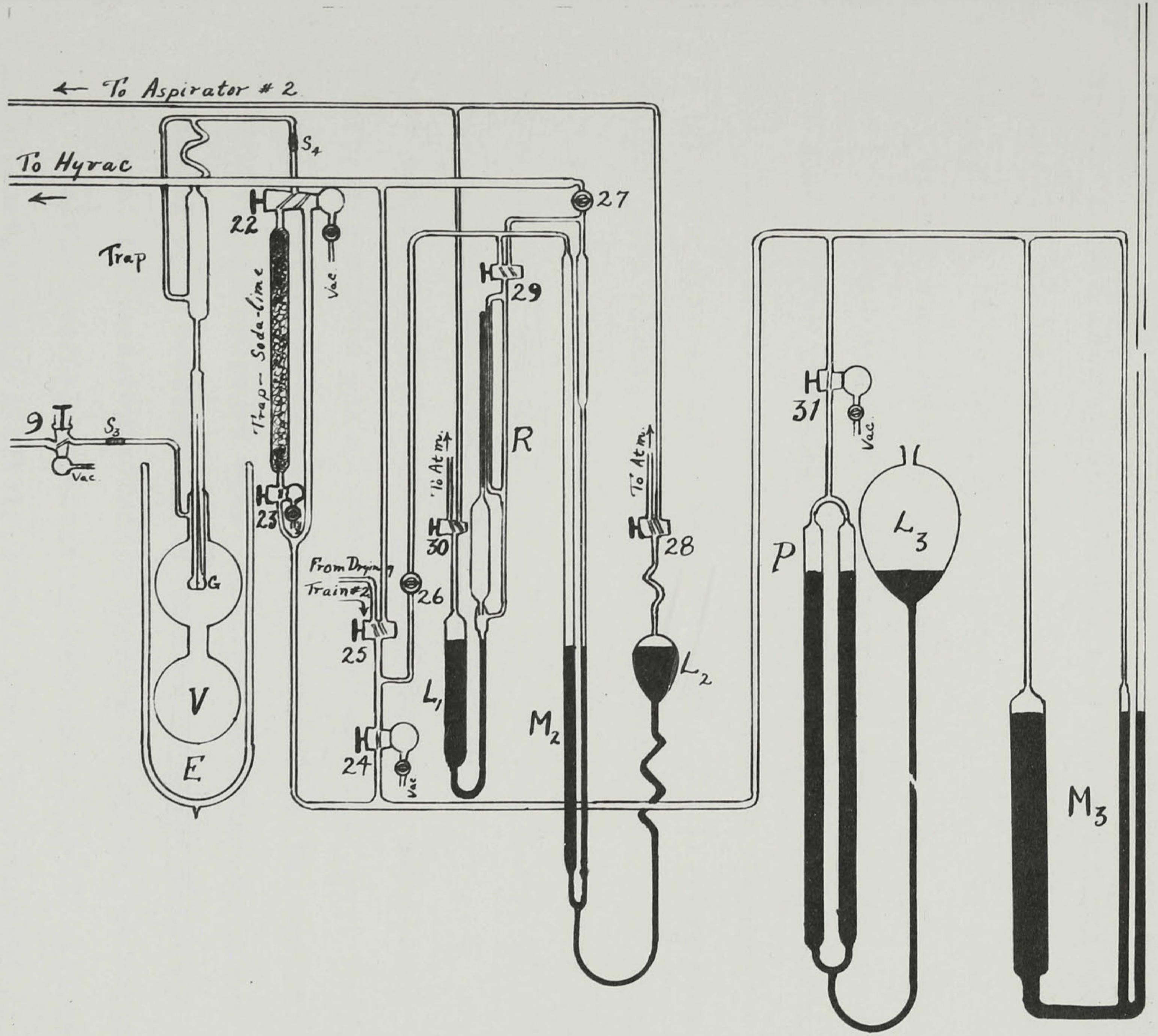

← To Aspirator # 2
To Hyrac
←
S4
27
22
Trap
Vac
29
Trap - Soda-lime
9
S3
Vac
31
Vac
R
To Atm.
To Atm.
23
Hg
30
28
P
L3
G
From Drying Train #2
26
25
L2
L1
V
M2
24
Vac
E
M3

Figure 3

The type described by Wright (45) was used in the present work and the qualities described by him "simplicity, ruggedness, ease of operation, complete immersion of the system in the thermostat, and absence of any change in the properties of the system with temperature" were found by the authors to be true in a general way, but they also found that when a consistent precision of 0.1 mm. was required, the instrument was rather delicate and when, in addition, one side of the pressure balancing system, that in contact with the chlorine, had to be controlled with stopcocks lubricated with an inorganic lubricant, the difficulties of control were almost insurmountable. The obvious suggestion in a pointer-viewing system of the optical projection type is to increase the magnification and in the second part of the work this was done. The results were gratifying in part but it was found that the difficulty of preventing distortion of the glass tubing containing the glass membrane by slight stresses and strains incidental to the operation of the vapour pressure cell, and the fact that the glass manometer must necessarily be calibrated under slightly different and non-reproducible strains prior to the actual run made the overall sensitivity obtainable by the increased magnification only slightly better than that obtained by the most sensitive manometer used in the vapour density measurements. On the other hand, the difficulties of manipulation were definitely decreased. The method of calibrating the glass manometer was to determine the zero position of pointer and index under evacuation of both sides of the diaphragm. Air was then admitted to one side and the pressure and pointer deflection determined. This was done for a number of pressures, and a curve drawn to show the millimetres of mercury corresponding to any given pointer deflection. The pointer sensitivity was 0.5 mm./scale division and the scale could be read to 0.2 of a division. It was first planned to use sulphur dioxide gas as a medium for the calibration of the volume, and the connections to the chlorine system are indicated on Figure 2, but the gas was found to react with the phosphoric acid lubricant used on the stopcocks. Dimethyl ether, the density of which is known to one part in 5,000 (unpublished work of Dr. C. C. Carpenter), was also used instead of sulphur dioxide but it was found to be unsuitable because of a high adsorption in the phosphoric acid lubricant. Tapp (38) also found that phosphorus pentoxide was not suitable for the dehydration of dimethyl ether. Accordingly, the method of calibrating the volume thus in situ was abandoned and the cell calibrated by filling with water and weighing. This method, however, when carried out with a volume of nearly a litre connected to a delicate glass membrane, provided too great a hazard and by a slight compromise the cell was calibrated in situ as follows:

Supplementary distillation and condensation units for sulphur dioxide were set up and the stopcocks in these were lubricated in the ordinary way with stopcock grease. This system was connected to the cell to be calibrated only through the mercury seal stopcock 9 which, for the purpose of calibration, was lubricated also with stopcock grease. At the conclusion of the calibration runs, which were conducted after the same manner as the chlorine vapour density runs except that in view of the non-corrosive nature of sulphur dioxide no precautions were necessary to protect the manometers in the system, stopcock 9 was removed from its barrel, both plug and barrel were cleaned carefully with ether, re-lubricated with the phosphoric acid mixture, and replaced with the usual protective covering of mercury. The sulphur dioxide used in the calibration was passed from the storage cylinder into a distillation train where it received a triple fractionation in vacuo after the same method described for chlorine. Three runs were made as for chlorine and from the weight of the samples condensed out and the pressure-temperature data corresponding to each, the volume of the cell was determined by substituting in the ideal gas law equation, $pv = \frac{W}{M} RT$, the values of p, T, w and the apparent molecular weight for the pressure and temperature of each run obtained from the data of Cooper and Maass (3a). Because of the high accuracy of these data, the volume of the cell was thus determined with suitable precision. In order to further check the calibration of the cell, a volume of about one litre was accurately calibrated with water (9) in the usual gravimetric way and the volume of the cell determined by allowing air at measured pressure to expand from the cell into the one-litre volume which had been previously evacuated. From the equation involving the initial and final pressures and volumes, as described under the calibration of the cell used in the solubility measurements, the volume was found to be in good agreement with that obtained by the sulphur dioxide method above.

When a supply of chlorine had been prepared, the system, on the manometer side through stopcocks 15, 25, 24 and 22, and on the calibrated volume side through 15, 20, 8 and 9, was evacuated with the Hyvac pump and the cell itself and the condensation unit bounded by the stopcocks 6 and 7 more completely evacuated by inserting two Langmuir diffusion pumps in series with the Hyvac, i.e., by closing 15 and opening 16 and 17. Then stopcocks 8 and 9 were closed and 5 and 6 opened and the chlorine allowed to vaporize. Next the cell was carefully filled by opening 9 very slightly and maintaining simultaneously a balanced pressure on the glass membrane by admitting dry air on the upper side through 25. The cell was flushed several times in this manner before commencing a series of runs. To remove the chlorine, the water aspirator was connected through 7 and at the same time the balancing pressure was maintained by again connecting the Hyvac pump to the manometer side.

When the cell finally had been filled with pure chlorine, a well lagged bath containing water was placed around it, and the temperature carefully regulated by hand between 0° and 10° by adding finely crushed ice, between 10° and room temperature by means of a balance between the cooling effect of a copper coil carrying tap water, pre-cooled if necessary, and a 100 watt electric heater in series with a relay operated by a thermoregulator, and between room temperature and 75° by one or more heaters of 500 watt capacity controlled with rheostats and regulated precisely by the thermoregulator system. The regulation by hand was within 0.1°C. and the thermoregulator control within 0.02°C. Temperatures were read on standard thermometers. Circulation in the water bath was maintained by means of a motor driven stirrer which could be stopped when readings of the glass manometer were being taken. These readings constituted corrections to the pressure as read on the mercury manometer M_2 and were read on a scale fixed on the apparatus on which a magnified image was projected by optical means including a mirror on a wall

10 feet distant so that the total length of the beam was 20 feet. Ample time, about one-half hour, was allowed for the equalization of temperature and pressure within the cell and then some three readings of the pressure were taken at intervals of 5 to 10 minutes. The mean was taken as the best value. Meanwhile the chlorine was removed from the condensation unit by means of the water aspirator through a drying train of calcium chloride backed on the cell side by a phosphorus pentoxide tube. The condensation unit was thoroughly flushed by some five to seven washings with air dried over sulphuric acid and phosphorus pentoxide and evacuated as completely as possible with the Hyvac and diffusion pumps. A tube filled with glass wool through which mercury was dispersed helped to protect the diffusion pumps from traces of chlorine. Evacuation was checked with a sensitive McLeod gauge R. One of the small bulbs was then refrigerated with liquid air and the chlorine condensed therein while the pressure above the glass manometer was balanced by a proportional degree of evacuation. When condensation ceased, the bulb was sealed off and the small residual pressure was read on the manometer. This constituted a correction to be subtracted from the chlorine pressure obtained in the cell during the run.

The residual pressures so obtained were corrected for expansion into the connecting tubing by means of the ideal gas law. Any differences in temperature between the cell and the tubing were also taken into account. The volume of the tubing itself was determined by means of the ideal gas law from the drop in pressure when air or chlorine at known temperature, pressure, and volume in the cell was allowed to expand into the tubing. Once the volume of the tubing had been determined in this way for a first run, its value in successive runs in the same series was obtained by subtracting the known volume of the bulbs sealed off.

For pressures above one atmosphere, the pressure stopcock 24 was closed, and air, suitably compressed by means of the levelling bulb L_3 in the cylinders P, was admitted through stopcock 31. The pressures were read on the tall open manometer M_3 to which the barometric pressures were added. Residual pressures were read as before on M_2. The low pressure manometer M_2 was provided with an etched mirror scale on which pressures could be estimated to 0.1 mm. The tall open manometer M_3 had a scale consisting of four boxwood meter sticks which had been checked by Wright (43), and had been found accurate within the readibility of the mercury column, against a wood scale, or within 0.5 mm. Temperatures of both mercury columns were read from thermometers spaced at intervals of from 30 to 50 cm. along their lengths, and each mean temperature so obtained was used in conjunction with the correction for a glass scale as given in Landolt-Börnstein (18) in reducing the pressures to centimetres of mercury at 0°C.

Pressures were reduced to isothermal values by means of the relation

$$\frac{P_{\text{isotherm}}}{T_{\text{isotherm}}} = \frac{P_{\text{thermostat}}}{T_{\text{thermostat}}}$$

a relation which is perfectly valid over one or two degrees.

Each bulb having been filled and sealed off was allowed to come up to room temperature, washed in dry ether, allowed to come to equilibrium with the atmosphere in the balance case, and weighed to the nearest tenth of a milligram. It was then cooled in liquid air and the tip broken off over a sheet of black glazed paper so that any fragments of glass might not escape notice. The chlorine in the bulb was then allowed to evaporate in a tube connected through a 2-way stopcock to a water aspirator. When the chlorine had evaporated and the bulb warmed to room temperature, it was flushed four or five times with air dried over sulphuric acid and phosphorus pentoxide and admitted to the tube through the other arm of the two-way stopcock, then removed to the balance case to be weighed with the tip and any fragments of glass collected from the glazed paper. Inasmuch as the bulbs were carefully made with capillary tips there were few fragments.

When the empty bulb had come to equilibrium with the atmosphere, it was weighed with the usual precision. Finally the correction for the volume of air displaced by the bulb was made by adding to the weight of the chlorine, as determined by the difference between the two weighings described above, the weight of air contained in the bulb during the second weighing. This was determined by filling the bulb with water, weighing it a third time, and determining the volume of the bulb from the weight of water contained. Finally, the weight of the air contained in the bulb at the second weighing was calculated from tables of the density of dry air at the temperature and barometric pressure noted at the time of the second weighing.

4. Experimental Results

The experimental results are tabulated in Tables I to IV. In these tables the reduced pressures given are corrected as shown in the specimen calculation for the residual pressure in the cell after condensation of the sample. The values of M^1, the apparent molecular weight, have been calculated from the corresponding data by means of the equation:

$$M^1 = \frac{wRT}{PV}$$

where w is the weight of the gas in gm.

R is the gas constant, 0.082046 l.-atm.

T is the temperature in °K

P is the pressure in atm., and

V is the volume of the cell in litres.

The molecular weights so obtained were plotted on a large scale as in Fig. 4 and curves drawn through the points to the theoretical molecular weight of 70.91. From these curves values of the apparent molecular weight at each temperature were picked off at pressures of from 20 to 160 cm. These are given in Table V.

Specimen Calculation:

Temperature	15.00°C. or 288.18°K
Initial Pressure, reduced to 0°C.	112.22 cm.
Residual Pressure, corrected for expansion	.21 cm.
Change in Pressure, as listed in Tables I to IV	112.01 cm.
Volume of Cell	540.9 cm.
Weight, Bulb + Cl_2	5.3866 gm.
Weight, Bulb	2.9559 gm.
Weight, Cl_2	2.4316 gm.
Weight, Bulb + H_2O + wire suspension	7.42 gm.
Weight, Bulb + wire suspension	3.61 gm.
Weight, H_2O	3.81 gm.
Weight, air in Bulb, 0.00119 x 3.8	0.0045 gm.
Weight, Cl_2 Total	2.4361 gm.

$$\text{Molecular Weight, } M^1 = \frac{2.4361 \times 0.082046 \times 288.18}{\frac{112.01}{76.00} \times 0.5409} \;..\; 72.25$$

Table I

Molecular Weights at 15°C.

T.°C.	P cm.	W gm.	V. l.	M^1
15.00	26.19	0.5611	0.5409	71.17
15.00	27.45	0.5888	0.5409	71.26
15.00	49.04	1.0546	0.5409	71.44
15.00	49.73	1.0711	0.5409	71.55
15.00	75.04	1.6216	0.5409	71.79
15.00	75.21	1.6244	0.5409	71.75
15.00	112.01	2.4361	0.5409	72.25
15.00	129.32	2.8216	0.5409	72.48
15.00	157.62	3.4594	0.5409	72.91
15.00	160.27	3.5199	0.5409	72.96

Table II

Molecular Weights at 35°C.

T °C.	P cm.	W gm.	V. l.	M^1
35.00	23.61	0.4727	0.5409	71.14
35.00	29.22	0.5864	0.5409	71.31
35.00	45.83	0.9218	0.5409	71.45
35.00	47.06	0.9469	0.5409	71.48
35.00	49.29	0.9912	0.5409	71.44
35.00	74.85	1.5105	0.5409	71.69
35.00	75.09	1.5168	0.5409	71.76
35.00	120.46	2.4461	0.5409	72.14
35.00	123.39	2.5133	0.5409	72.36
35.00	158.53	3.2385	0.5409	72.57
35.00	159.32	3.2533	0.5409	72.54

Table III

Molecular Weights at 50°C.

T °C.	P cm.	W gm.	V. l.	M^1
50.00	20.49	0.3915	0.5409	71.17
50.00	23.82	0.4550	0.5409	71.16
50.00	24.05	0.4578	0.5409	70.92
50.00	49.58	0.9500	0.5409	71.38
50.00	49.86	0.9553	0.5409	71.38
50.00	74.70	1.4356	0.5409	71.59
50.00	75.19	1.4464	0.5409	71.64
50.00	121.98	2.3594	0.5409	72.06
50.00	128.65	2.4879	0.5409	72.05
50.00	153.44	2.9808	0.5409	72.37

Table IV

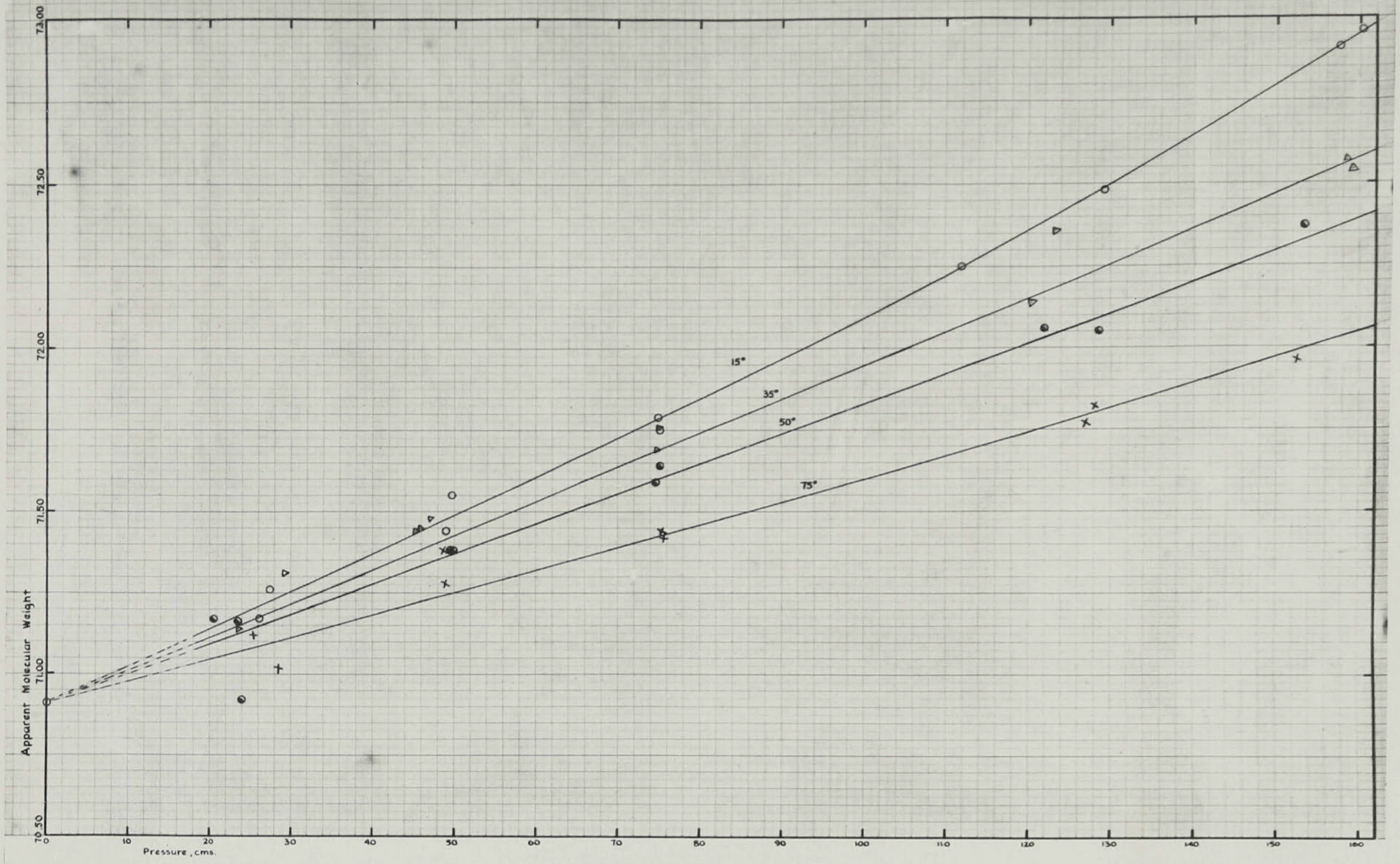
Molecular Weights at 75° C.

T °C.	P cm.	W gm.	V. l.	M^1
75.00	25.41	0.4502	0.5409	71.11
75.00	25.46	0.4505	0.5409	71.02
75.00	48.72	0.8665	0.5409	71.38
75.00	48.95	0.8693	0.5409	71.28
75.00	75.40	1.3420	0.5409	71.44
75.00	75.59	1.3451	0.5409	71.42
75.00	126.92	2.2696	0.5409	71.77
75.00	128.01	2.2905	0.5409	71.82
75.00	152.50	2.7341	0.5409	71.96

Table V

Variation of Molecular Weight with Temperature and Pressure

Pressure	15°	35°	50°	75°
20 cm.	71.14	71.11	71.09	71.04
40 cm.	71.37	71.32	71.28	71.18
60 cm.	71.61	71.53	71.46	71.32
80 cm.	71.84	71.74	71.64	71.46
100 cm.	72.09	71.95	71.83	71.60
120 cm.	72.36	72.15	72.01	71.74
140 cm.	72.65	72.36	72.20	71.89
160 cm.	72.95	72.57	72.39	72.05



Apparent Molecular Weight
73.00
72.50
72.00
71.50
71.00
70.50
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
Pressure, cms.
15°
35°
50°
75°

Figure 4

5. Discussion of the Results

There are few precise data in the literature with which to compare the results. However, Jaquerod and Tourpaian (12) give 2.8965 grams as the mean value, by their two methods of a litre of chlorine gas and 15° and 725 mm. By the use of Leduc's value of A (24) as used by these authors to reduce their pressures to the standard atmosphere, the apparent molecular weight of chlorine gas at 15° and 760 cm. is found to be 71.85. The present work gives the value 71.80, the deviation being less than 1 part in 1400. Inasmuch, however, as calculation of the apparent molecular weights at 0° and 760° from the data of Leduc (22), (23) and Jaquerod and Tourpaian, the latter being the accepted value (8), give respectively 72.19 and 72.03, it is probable that Leduc's value of A is too high. Accordingly a better comparison is afforded by comparing the present data with that of Jaquerod and Tourpaian at observed pressures rather than at reduced values.

Calculation from their observed density at 15° and 725 mm. gives an apparent molecular weight of 71.79. Under the same conditions the present work gives 71.75. If the results obtained by Jaquerod and Tourpaian for the volumetric method only are considered, the apparent molecular weight is 71.78 at 15° and 725 mm. Consequently the probable precision of the present data under the conditions of comparison is about 1 part in 2000.

A second test of this data may be made by calculating the apparent molecular weights by means of an equation of state. The Cooper and Maass (3) equation was tried first. The viscosity data for chlorine are not particularly concordant but the function f(T) can be evaluated with reasonable accuracy. The function (PV-RT), on the other hand, is known only to 1 part in 200 to 300 when the molecular volume V is known to 1 part in 25,000. Consequently, slight variations in the value of V, which in turn depends on the calculated value of the molecular weight, and the latter in turn upon the measured densities, can affect the values of the left hand side of the expression to such an extent that the calculations of $(\lambda T - a)$ become uncertain. In the present instance, where a precision of 1 part in 2000 is the limit claimed, the mean precision in V could not be more than 1 in $\frac{250}{12.5}$ or 5% and this does not permit of a precise determination of $(\lambda T - a)$.

Accordingly, the simpler equation of Maass and Mennie (27) was used to evaluate the data. First the value of B in equation was found by substituting in the expression

$$B \approx \frac{8\sqrt{2}\,\pi r^3 N}{1 + \frac{c}{T}}$$

the values given by Jeans (14), (15) for r and c:

$$B = \frac{8\sqrt{2}\,\pi\,(2.70 \times 10^{-8})^3 \times 6.062 \times 10^{23}}{1000\left(1 + \frac{199}{273.2}\right)}$$

$$= 0.2454$$

The variation of b with temperatures was then calculated by means of the equation $b = B(1 + \frac{c}{T})$ and the following values obtained.

Table VI

Values of b in the Maass and Mennie equation:

Temp. °C.	15.0	35.0	50.0	75.0
$b = B(1 + \frac{c}{T})$	0.4150	0.4039	0.3966	0.3857

To evaluate a, corresponding molecular volumes and temperatures at a pressure of one atmosphere were substituted in the equation $a = RT(V + b) - PV^2$. For subsequent calculations the mean value of $a = 17.22$ for the temperature range covered was taken. By substituting this value of a and the above values of b in the Maass and Mennie equation for the molecular weight isotherm, values of the apparent molecular weight were calculated at each temperature and at pressures of one and two atmospheres using the expanded series as far as the term in P^2.

In Table VII the values calculated in this manner are compared with the experimental results. The maximum deviation is less than 1 part in 1,400.

Table VII

Comparison of calculated and observed molecular weights

Temp. °C.	Molecular Weights			
	Calculated	Observed	Calculated	Observed
15	71.85	71.80	72.83	72.83
35	71.68	71.70	72.48	72.49
50	71.56	71.61	72.27	72.31
75	71.43	71.43	71.99	71.99

Examination of the molecular weight vs. pressure isotherms show that the data are not as precise as could be desired. The somewhat better agreement between points at the higher pressures shows that the measurement of the pressure is the source of most of the error, and this can be traced to the additivity of small errors consequent upon the use of the glass manometer. Wright (43) found that the glass manometer was not capable of the precision which he desired in his measurements of the density of hydrogen sulphide. Owing to the fact that dry hydrogen sulphide does not react to any appreciable extent with mercury, he was able to make his density measurements without the interposition of the glass manometer. In the present work, the use of the glass manometer could not be avoided. To obtain the desired degree of accuracy in future experiments, the following changes are recommended: (1) the use of a cathetometer for reading the small differences in the manometer levels when calibrating the pointer displacement per mm. of mercury; (2) the use of a rigid metal support fitted with collars and adjustable screws by means of which the glass manometer may be fastened perfectly rigid so that no torsional or bending stresses may affect the zero reading of the instrument; (3) the glass manometer, cell and optical projection system should be mounted on a solid support independent of supports for bath, stirrers, etc. In other words, all the customary precautions used in mounting delicate optical apparatus should be taken.

With such precautions it should be possible, especially if the measurements can be carried to three or four atmospheres by the use of a non-reactive organic lubricant such as "Apiezon N" on the stopcocks, to obtain the desired degree of precision in the density measurements, and to determine more closely the degree of correlation between the experimentally determined densities and the equations of state which have been proposed.

PART II.

THE SOLUBILITY OF CHLORINE IN WATER.

1. Survey of Literature.

The solubility of chlorine in water has been the object of systematic study for nearly one hundred years. In 1839 Gay-Lussac (15) published in his memoirs on cohesion, the value of 3.04 volumes of chlorine per volume of water as the maximum solubility. In 1843, Pelouze (37) published approximate values over a temperature range as follows:-

Temperature °C.	Vols. water.	Vols. of chlorine at n.t.p. dissolved
0	100	175 - 180
9	100	270 - 275
10	100	270 - 275
12	100	250 - 260
14	100	250 - 260
14	100	245 - 250
30	100	200 - 210

Temperature	Vols.water.	Vols. of chlorine at n.t.p. dissolved.
40	100	155 - 160
50	100	115 - 120
70	100	60 - 65

The concentration of halogen was determined by titration of the solution with normal arsenious solution as proposed by Gay-Lussac. Pelouze noted that the maximum solubility was at 9° - 10°, the same temperature at which the hydrate ceased to form or disappeared completely, and that above or below this temperature the solubility became progressively less. He also noted that when the hydrate began to form the depth of color in the solution diminished, i.e., the solution had been supersaturated. Pelouze also noted that when water saturated with chlorine was agitated with air, it lost almost at once its content of chlorine, a phenomenon which seemed remarkable to him since nitrogen and oxygen were so insoluble in water. Hence to obtain complete saturation, the water in which chlorine was being dissolved should be agitated because if any air remained in the flask there would be displacement of a certain amount of chlorine and analyses would be inaccurate.

Gay-Lussac (16) cited Pelouze's values as above and added his own values as taken from his note book of 1839. The two sets of data are not very concordant as may be seen by comparison with the following:

Temperature. °C.	Vols. of chlorine at 760 and 0° per vol. of water.
0	1.43
3	1.52
6.5	2.08
7	2.17
8	3.04
10	3.00
17	2.37
35	1.61
50	1.19
70	0.71
100	0.15

In 1855 Schönfeld (47) published solubility determinations for temperatures above 10° since the hydrate was formed below 10°. He prepared chlorine from hydrochloric acid and potassium dichromate and washed the gas through distilled water. The samples were obtained by means of a siphon tube and gas outlet which could be closed, thereby forcing the solution out through the siphon into a measuring vessel.

The chlorine content was determined by titrating the iodine with standard sodium thiosulphate. Schönfeld's results are as follows:-

Temp. °C.	Bunsen Solubility coefficient.
11.0	2.5674
18.8	2.2075
23.7	1.9572
30.4	1.7308
37.2	1.5027
41.5	1.3073.

In the same journal and in the same year Roscoe (43) published an extensive review of the properties of chlorine solutions which was also published in another journal in the following year.(44). Roscoe prefaced his paper with brief references to Henry's (1803) and Dalton's (1807) Law: the amounts of gas dissolved by a liquid vary as the pressure under which absorption takes place. He noted that the law had been regarded as an ungrounded hypothesis until Bunsen(7) showed it to have foundation in a true law. Much of Bunsen's work was carried out with gases of slight solubility but Schönfeld and Carius had shown the applicability of the law to gases of great solubility.

Roscoe confined his work to the absorption relations between chlorine and water at temperatures approaching that at which the hydrate was formed. He prepared chlorine by the electrolysis of hydrochloric acid, washed the gas through water and dried it over fused calcium chloride. The density was determined at room temperature and barometric pressure by titrating by Bunsen's volumetric method the iodine liberated from potassium iodide solution by a known volume of the gas.

The absence of free oxygen was evident from the fact that the volume of hydrogen liberated by the electrolysis was equal to the volume of the chlorine. Furthermore, the absence of chlorine oxycompounds in the gas was demonstrated by the fact that the determination of total chlorine by iodine liberated from potassium iodide by a volume of the gas was equal to the determination of total chlorine as chloride. Hence Roscoe considered that as the absorption coefficients of hydrogen and chlorine were already known, a single determination of the solubility of the mixed gases from electrolysis should indicate whether or not chlorine obeyed the absorption law. The value so found by Roscoe was 20% too high for chlorine and he attempted to find the reason for the abnormal absorption.

First any minute concentration of chlorine oxides in the gas could not have produced it. But chlorine might react toward water as toward bases and form hydrochloric acid and an oxide of chlorine. Such compounds would not have been in the gas mixture because they would have been absorbed. A partial decomposition of water by chlorine into hydrochloric and hypochlorous acids would most satisfactorily account for the irregularities. However, if such a decomposition took place the determination of total chlorine by the amount absorbed under known volume, temperature and pressure, and by total chloride from the resulting solution would give the same results. Now if a gas such as carbon dioxide which obeys Henry's Law were passed into the solution, chlorine should be replaced according to the relative absorption coefficients.

If hydrochloric acid and a volatile oxide of chlorine were present together with free chlorine, the chlorine and oxide of chlorine would be driven out in amounts different from that of hydrochloric acid which, dissolved in a large excess of water, is not volatile. Thus the volumetric and silver nitrate methods would give unlike results because the original relation by which hydrochloric and hypochlorous acids were present in proportions capable of forming chlorine and water would no longer exist. The experiment showed after three hours aspiration with a stream of carbon dioxide that chlorine water prepared and kept in the dark gave exactly the same results volumetrically and by silver nitrate, so Roscoe considered that the supposition of a decomposition of water by chlorine was unfounded. To check the method he aspirated a mixture of chlorine oxides with carbon dioxide and found them to be volatile. He also tried adding hydrochloric acid to the aqueous solution of chlorine and found a diminished absorption of chlorine. One assumption remained: at temperatures near that at which the hydrate formed, the atoms of chlorine might exert an attraction on those of the other gas and thereby lessen the accuracy of the law of absorption. Roscoe calculated the amounts of chlorine which did not obey the law of absorption from the solubility of mixtures of chlorine with carbon dioxide and with hydrogen and found that with hydrogen, the amount of chlorine not obeying the law diminished from the temperature of hydrate formation, while with carbon dioxide the amount not obeying the law was approximately constant. He was unable, however, to come to any conclusions regarding the nature of the effect.

Redetermination of the solubility of chlorine in water was made by Goodwin (17) in 1882. He used a similar method to that of Schönfeld (47) in preparing his samples and as he determined the solubility in water below 10° the siphon tube was lightly plugged with asbestos to retain the hydrate. Samples were measured in a 10cc. specific gravity flask which was stoppered, washed, immersed in potassium iodide solution and the liberated iodine titrated with standard thiosulphate. The saturator was surrounded by a water bath. The temperatures were read on a thermometer graduated in tenths and were read in a bath which was allowed to gradually warm to room temperature. Above room temperature the readings were taken in a bath cooling from two or three degrees above the desired temperature. The thermostating was thus of a primitive type but at the least the conditions were described.

Goodwin obtained the following results for the Bunsen coefficient of solubility:

Series I: Thermometer not readily readable below 12° because that part of the stem was within the saturator.

p - 761.9mm.

Temp. °C.	
4	1.8717
5	1.9080
7.5	2.1079
8.9	2.4350
9.6	2.6077
10.3	2.7104
10.8	2.9438
11.5	2.9894
14.3	2.5350
23.5	2.1534
32.5	1.7354
39.0	1.4083
45.0	1.1636
50.0	1.0812

Series II. Special thermometer.

p = 750mm.

Temp. °C.	
6.9	2.2931
8.4	2.5469
9.3	2.7135
10.2	2.9012
13.3	2.9344

15.2	2.6133
20.9	2.3143

Series III. Special thermometer. p = 756.2

Temp. °C.		(Schönfeld)
10.1	2.8741	2.59
11.2	2.7267	2.53
11.3	2.7001	2.54
13.7	2.5079	2.42
21.7	2.0422	2.21
32.1	1.5766	1.67
32.2	1.6111	1.66
36.7	1.3802	1.48

When graphed these data show a variation too great for experimental error. Series I was begun in the presence of a small amount of chlorine hydrate. In Series II the water was semi-solid before the determinations were begun. Series III was begun at 10° without formation of the hydrate. The curves show that the solubility was greater in proportion to the amount of hydrate formed. (This indicates supersaturation of the liquid by the melting hydrate). Goodwin thought that the curve before decomposition of the hydrate was best represented by II and that if the hydrate on decomposing formed hydrochloric acid or hypochlorous acid the solubility would be increased. In this connection the solution was tested after titration and found to be neutral until after the hydrate had decomposed, then distinctly acid.

Goodwin considered that Schönfeld's data gave too low a maximum solubility and that an initial rapid fall as seen in data III was more probable than a gradual descent. He assumed that chlorine hydrate was formed at 10° but remained in solution. Decomposition between 10 and 15° would then produce the sudden descent in the curve. Below 10° the hydrate crystallized out. Goodwin explained the ascending portion of the curve in the presence of the hydrate as due to the increasing solubility of the hydrate following the general law of the solubility of a solid in water while the descending portion of the curve represented the solubility of a gas in water which decreased with temperature.

The best determinations of the solubility of chlorine in water made hitherto are evidently those of Winkler (53). Unfortunately the original paper was not available to the authors so that details of the method cannot be discussed. His values taken from Landolt-Börnstein (29) are as follows:

Temp. °C.	Absorption coefficient, B	Solubility in Gms Cl_2 /100 gms H_2O
10	3.148	0.9972
11	3.047	.9654
12	2.950	.9346
13	2.856	.9050
14	2.767	.8768
15	2.680	.8495
16	2.597	.8232
17	2.517	.7979
18	2.440	.7738
19	2.368	.7510
20	2.299	.7293
21	2.238	.7100
22	2.180	.6918
23	2.123	.6739
24	2.070	.6572
25	2.019	.6413
26	1.970	.6259
27	1.923	.6112
28	1.880	.5975
29	1.839	.5847
30	1.799	.5723
35	1.602	.5104
40	1.438	.4590
45	1.322	.4228
50	1.225	.3925
60	1.023	.3295
70	0.862	.2793
80	0.683	.2227
90	0.39	.127
100	0.00	.000

Isambert (25) was the first to measure the dissociation pressure of chlorine hydrate. The hydrate itself was mentioned as early as 1811 by Davy (10) who noted that a solution of oxymuriatic gas in water froze more readily than pure water. Isambert referred to Faraday's use of the hydrate to produce liquid chlorine (12) and noted that while the hydrate disappeared in the open air at about 8° it could persist to summer temperature in a closed tube. As the products of dissociation were liquid water and a gas, it was necessary to agitate the liquid a great number of times at any given temperature in order to obtain a constant pressure. Equilibrium was attained more rapidly in raising the temperature than in lowering it. In measuring the dissociation pressures Isambert used mercury as the manometric liquid, protecting it with a layer of sulphuric acid. The hydrate was introduced into a flask cemented to a manometer tube, the flask was sealed off and the hydrate heated to expel air, with the manometer tube dipping into sulphuric acid. As the flask cooled mercury was allowed to rise in to manometer tube. For higher pressures, a tall manometer tube was used, and with a little sulphuric acid in the manometer the hydrate was heated as above to expel air after which mercury was poured into the manometer tube. Isambert did not resort to elaborate temperature control. In his own words:

"Pour le plus grand nombre de cas je me suis contenté de prendre les mesures des tensions aux températures que l'eau prenait soit par le refroidissement nocturne, soit dans la journée par l'élévation de température du laboratoire."

He noted also that the vapor pressure of the hydrate was constant at a given temperature, as shown by two apparati of different sizes containing very different quantities of water and hydrate which gave the same value of 1400mm. at 14.5°, and 947 and 952mm. at 11°. He accordingly placed the hydrate of chlorine among the substances exhibiting the dissociation which had been studied by Sainte-Claire Deville.

Isambert's results follow:

Temperature °C.	Pressure of hydrate mm.
0.0	230
3.3	375
3.6	400
5.0	481
5.7	530
5.9	545
6.6	571
7.2	595
7.6	644
8.0	671
8.8	722
9.1	776
9.5	793
10.1	832
11.0	950
11.5	1015
11.7	1032
12.9	1245
14.5	1400

Under the above conditions the hydrate was always present. Even in a closed tube at 24° the hydrate persisted and as soon as the temperature was lowered part reformed under a pressure of about four atmospheres. In an open vessel below 9°, according to Isambert only the hydrate formed and dissolved; above 9° there was a solution of the gas in water. Moreover a current of air passed into the solution below 9° little by little removed all the chlorine as though it were dissolved and not in combination.

He added that the dissociation curve resembled that of the ammoniacal chlorides, e.g., $3\ NH_3 \cdot Ag\ Cl$ (now $2\ NH_3 \cdot Ag\ Cl$) except that the pressures increase a little more rapidly with temperature.

In 1884 Roozeboom published the first of a series (40) (41) (42) of more precise investigations on the behavior of chlorine solutions in the presence of the hydrate as well as on the constitution of the hydrate itself. It will be convenient here to discuss only his measurements of the dissociation pressure of the hydrate, and later to review briefly the work on the constitution of the hydrate, since the establishment of its formula has recently been called into question by Liebhafsky (31) who assumes a variable hydration of the halogens to explain the anomalous temperature coefficient associated with aqueous halogen solutions.

Roozeboom prepared the hydrate in situ by passing the chlorine into a cell which was afterward connected to a manometer by means of a rubber tube. The mercury was protected by a 2cm. layer of aqueous sea salt. His values were a little lower than those of Isambert and he suspected that in Isambert's apparatus there had been a slight decomposition of the water with liberation of oxygen which would have increased the pressure. In the open air the hydrate decomposed at 9.6° instead of at 9° as found by Isambert, and in a closed tube the critical temperature of decomposition was 28.7°C. The hydrate formed in any solution in which chlorine was present in greater concentration than it could dissolve under a pressure equal to the dissociation pressurw for the temperature in question. Roozeboom satisfied himself on that point by analysing a solution saturated at 6° under a pressure of 48cm. It contained 0.707% of chlorine in agreement with the value below for the concentration of the solution accompanying the hydrate.

Dissociation pressure of chlorine hydrate:

Temp. °C.	Pressure mm.Hg.
0	249
2	320
4	398
6	496
8	620
9	701
10	797
12	992
14	1240
16	1522

Concentration of chlorine in solutions which can accompany the hydrate:

Temp. °C.	V.P. of solution, mm. Hg.	Chlorine in solution %
0	249	0.505
3	355	0.611
6	496	0.709
9	701	0.900
12.5	10.5	1.10
20	10.5	1.82
28.5	10.5	3.50

The percentage of chlorine increased with the temperature. Inasmuch as when the temperature of a vessel containing solid hydrate solution and gas decreased, the quantity of hydrate decreased at the expense of the dissolved chlorine as well as the free gas, the maintenance of the solid hydrate was dependent both upon the free gas and the quantity of solution introduced with it. Pelouze and Gay-Lussac had found that a solution of chlorine saturated under a pressure of one atmosphere showed a maximum of solubility between 9° and 10°. Their explanation was that the hydrate dissolved as such and that the solubility increased with temperature while above 9°-10° it was a case of solubility of a gas. Roozeboom pointed out however that the existence of the solid hydrate in their solution was the cause that the solutions far from being saturated under a pressure of 760mm. were saturated under a pressure varying from 250 to 760mm between 0° and 9° so that the concentration of dissolved gas increased with the temperature.

But above 9.6° the hydrate could not exist under a pressure of 760mm. and there was obtained as a current of chlorine was passed in a really saturated solution the concentration of which decreased with temperature in the usual way. Hence the maximum solubility was at 9.6° because the solution accompanying the crystals was at the same time saturated under a pressure of 760mm. The maximum was not evident in the case of a solution saturated below 9.6° without the formation of the hydrate. The following table gives the composition of solutions which are saturated at a pressure of 760mm. at the temperatures indicated.

Temp. °C.		Chlorine content.%
12		0.87
9		0.95
6		1.07
3	x	1.23
0	x	1.44

x Extrapolated values.

The freezing point of a solution of chlorine in equilibrium with the hydrate was found by Roozeboom to be -0.24°. Le Chatelier (9) a little earlier had given 1° for this eutectic point. Roozeboom also found that the liquid could be undercooled to -3°C. but not to between -4° and -7°

as found by Le Chatelier. At the moment of freezing the temperatures rose above -1°C and after equilibrium was established between the eutectic mixture and the gas phase a higher pressure was found than when the hydrate was in the presence of the undercooled solution. The data concerning this range are:

Temp. °C.	V.P. of solution,mm.	V.P. of ice,mm.
0.0	252	---
-0.24	244	244
-1	233	234
-2	200	223
-3	183	213
-4	-	203
-6	-	185
-8	-	169
-10	-	156

In 1884, almost coincident with Roozeboom's investigations, Le Chatelier (9) obtained the following values for the vapour pressure of chlorine hydrate in liquid water and in ice.

In liquid water:

Temp. °C.	U.P.mm.
9	746
8	700
3	420
1	340
0	320
-1	290
-2	230
-3	210
-4	205
-5	146
-6	153

In solid water.

Temp. °C.	U.p.mm.
-1	290
-3.5	262
-7	230
-14	175

The values are somewhat higher than those of Roozeboom.

The Constitution of Chlorine Hydrate.

As has been previously mentioned in the reference to Roozeboom's work, the constitution of chlorine hydrate is still a matter of interest in connection with a modern theory of halogen solutions. The first attempt to determine its constitution was made by Faraday (12) in 1823. He produced the crystals by putting a little water in a bottle of chlorine gas and found that they formed better in the dark than in the light. He also noticed that the crystals sublimed in the bottle at or below freezing, presumably in an atmosphere of chlorine.

The crystals were prepared for analysis by pressing between sections of bibulous paper at 32°F. with minimum exposure to the air. They were weighed in water at 32°F, then weak ammonia was added in excess and after 24 hours the solution was heated slightly, neutralized with nitric acid and the chloride precipitated with silver nitrate and weighed. Taking his maximum value for the chlorine content Faraday attributed to the hydrate the formula $Cl_2 .10H_2O$ although he suspected the ratio of chlorine to water might be larger.

Pelouze (37), 1843, had shown that when hydrochloric acid was dropped into hypochlorous acid at 2 or 3° chlorine was displaced and combined with the water to form the hydrate rapidly. Göpner (19), 1875, discussed the reputed formation of a hydrate HCl. HClo. $9H_2O$ in this manner but showed that the Wölter's (54) test with mercury did not give conclusive evidence of the presence of hypochlorous acid since either chlorine or hypochlorous acid tended to form $HgCl_2$ which with excess mercury formed HgCl.

Schiff (45) gave a general discussion of the theory that chlorine hydrate contained hypochlorous acid. His main argument against the formula HOCl. HCl. $9H_2O$ was that a hypochlorous acid solution of the concentration occurring in a hydrate of that formula was decomposed rapidly in the light whereas chlorine hydrate was quite stable under the same conditions.

The remaining literature deals with the ratio of chlorine to water and continues from Faraday's work. In 1883, Maumené (33) claimed the existence of variable hydration depending upon the concentration (or pressure) of chlorine. The freshly prepared hydrate contained 12 molecules of water per molecule of chlorine, whereas the hydrate prepared in a closed 'u' tube in the presence of excess chlorine contained only four molecules of water. He also claimed that the tetra hydrate could be dissolved in a little aqueous solution while still in the closed U-tube to form a hydrate with the formula

$Cl_2 7H_2O$.

Roozeboom (41) in connection with the experiments, described above, criticised Faraday's method of drying the hydrate and prepared his own samples by centrifuging the hydrate prepared by slow precipitation from solution under the pressure of the partly decomposed hydrate. Analysis of these crystals gave the formula $Cl_2 8H_2O$. Roozeboom considered the change of $Cl_2 10H_2O$ to $Cl_2 8H_2O + 2H_2O$ to be impossible since both fresh and aged crystals had the same dissociation temperature and pressure.

In 1901 de Forcrand (14) by calculation from thermal data found the hydrate formula to be $Cl_2 7H_2O$. He criticised Villard's (51) assumption of the formula $Cl_2 6H_2O$ on the ground that it was difficult to think that Roozeboom could have had left two to three molecules of uncombined water in his crystals.

Recently Bouzat (5) applied the method of de Forcrand and calculated from their dissociation curves the formulas of several gas hydrates which were found to conform to the general formula $M6H_2O$. They are characterized by instability and a low heat of formation. In the same year Bouzat and Azinières (6) applied the method of Villard (51) (52) which had been noted experimentally by Ditte (11). The hydrate was formed in the presence of a large excess of chlorine in a sealed tube. After twenty-four hours the excess chlorine was allowed to evaporate at 0° through a capillary opening. The weighed tube was then immersed in potassium iodide and the free iodine was titrated, a correction being made for the chlorine gas above the hydrate. In a second series the chlorine was allowed to evaporate over a period of six hours through an outlet immersed in sulphuric acid. The true value of n in $Cl_2 \cdot nH_2O$ was believed to lie between the values found by the corrected and uncorrected methods and the formula $Cl_2 6H_2O$ was assigned.

The latest determinations of the formula of the hydrate were carried out by Anwar-Ullah (2). Several methods were used. In the first, water weighed in a thin glass bulb was broken in an atmosphere of chlorine connected to a gas burette. The method failed owing to the slow absorption of the gas caused by the formation over the water of a thin crust of hydrate which was almost impervious to the gas. Ditte (11) had noticed the same phenomena even in the presence of liquid chlorine. The second method was essentially that of Bouzat and Azinières but after storage of from 4½ to 9 months Anwar-Ullah obtained a mean value of 6.12 for n compared to the value of 6.45 obtained by Bouzat and Azinières.

The higher values of n were attributed to the presence of uncombined water resulting from the extreme slowness of the reaction.

In his third series of experiments Anwar-Ullah took crystals of the hydrate which had been formed at 0° in aqueous solutions and dried them on a sintered glass filter at 0°C in an atmosphere of chlorine. The dry crystals were transferred on a cooled glass spatula to weighed ammonia or potassium iodide solutions and analysed. The mean value of n from eight determinations was 6.015 showing that the same hydrate was formed from aqueous solutions as was formed in the presence of excess chlorine under pressure.

General discussion of the constitution of Chlorine water.

Various opinions regarding the constitution of chlorine water have been expressed in the foregoing discussion. Hypochlorous acid was discovered by Balard (3) in 1833. Pelouze (37) in 1843 had shown that chlorine hydrate could be produced by dropping hydrochloric acid into hypochlorous acid at 2 to 3°C. Schönbein (46) in 1847 showed the presence of an oxidizing agent in chlorine water which had been exposed to light by its precipitation of the dioxide from solutions of manganese salts. Millon (34) in 1849 found that even fresh chlorine water showed an oxidizing action on manganese chloride and he considered that the chlorine was replacing the hydrogen in water and that if the phenomenon had certain limits it was because the hydrochloric acid formed at the same time, destroyed in its turn the hypochlorous acid and regenerated the chlorine.

Roscoe in 1856, (43) (44) had recognized that a partial decomposition of chlorine water into hydrochloric and hypochlorous acids would most satisfactorily account for the abnormal absorption of chlorine in water. He searched for a change in chlorine water which had been aspirated with carbon dioxide, believing that the relation between hypochlorous acid and hydrochloric acid would be changed by the displacement of the more volatile hypochlorous acid, but found the ratio was unchanged. He noted also that the addition of hydrochloric acid diminished the solubility of chlorine.

In 1893 Wölters (54) described the use of mercury as a qualitative test for distinguishing between chlorine and hypochlorous acid. Free chlorine formed mercurous chloride whereas hypochlorous acid formed $HgOCl$ which passed over into a yellowish mixture of $HgCl_2$ and H_gO.

Göpner (19) has criticised the supposed formation of

HCl. HOCl .9H20 as did also Schiff (45) although the formula agreed with the old murium theory of an acid hydrate $MuO_2.H_2O$ which also corresponded with the fact that chlorine united with bases (to form hypochlorites). Schiff also mentioned a statement by Milbau to the effect that a small quantity of hypochlorous acid could coexist with hydrochloric acid. He also thought that the hydrate might form in the presence of hypochlorous acid and noticed that the hydrate had less smell of chlorine than the chlorine solution, although that might be due to a change of tension in the hydrate form. Further the pale color of the fresh hydrate was against a high concentration of chlorine but was deeper than would be expected of $HOCl.HCl.9H_2O$. As evidence against the decomposition he stated that oxidation of mercurous chloride resulted from excess chlorine as well as from hypochlorous acid, that Faraday had shown the hydrate to react with organic substances like chlorine, and that there was no corrosive action by the hydrate on the skin as should be expected from the reputed hypochlorous acid content. Finally, the formation of the hydrate from hydrochloric acid and hypochlorous acid was no proof that the transformation to chlorine and water had not taken place prior to the formation of the hydrate.

Berthelot (4) in reporting a study on the heat of solutions of chlorine in water mentioned the fact that strong chlorine solutions had a more irritating odor than pure chlorine gas and that the color was that characteristic of oxygen compounds of chlorine. The results from the heat of solution of chlorine in water were very discordant, the highest values being two or even more times the lowest. He concluded that the variations were due to a chemical reaction causing the decomposition of water and a variable proportion of oxygen compounds of chlorine. These were produced in the light and in the dark and they suggested the existence of two isomeric states of chlorine but this was refuted by the thermal measurements. He considered the variations to be caused by the presence of traces of foreign compounds capable of starting the reaction in the samples in which decomposition had been more rapid.

Pickering (38) noted that when chlorine water was heated in an open evaporating basin there was a progressive loss of chlorine and an aqueous solution of hydrochloric acid remained after all the active chlorine had been expelled. Goodwin (17) noted that the solubility of chlorine would be increased if the hydrate on decomposing formed hydrochloric or hypochlorous acid. He tested the solution after titration and found that it was neutral until after the hydrate decomposed then definitely acid. He determined the solubility of chlorine in concentrations of hydrochloric acid varying from 10 to 25% and found a large increase in solubility, increasing with the acid concentration.

The classic investigation of the hydrolysis of chlorine solutions is acknowledged with unanimous consent to be that of Jakowkin (26) who examined the problem by means of distribution coefficient and conductivity measurements. By both methods he found that in the dark the reaction $Cl_2 + H_2O = HOCl + HCl$ goes to an equilibrium. He prepared a concentrated solution of chlorine in carbon tetrachloride, diluted it to the required degree with carbon tetrachloride, shook measured quantities of the solution and water together, and assuming that HCl and HOCl were insoluble in carbon tetrachloride determined the distribution of chlorine between the carbon tetrachloride and the water by analytical methods. The distribution of chlorine between the gas phase and carbon tetrachloride was found to be independent of the concentration and as chlorine was known to exist in the gas phase as Cl_2 it must also exist in the same molecular state in carbon tetrachloride. The distribution coefficient of chlorine between carbon tetrachloride and water was taken to be the mean distribution coefficient of chlorine between carbon tetrachloride and 0.1 normal hydrochloric acid on the assumption that that concentration of acid repressed the hydrolysis completely.

Thus if A = total free chlorine in 0.1 normal HCl

and C = chlorine in CCl_4

$\frac{C}{A}$ = K, the distribution coefficient, by definition.

Then in aqueous solutions of chlorine where the solubility is greater than normal owing to the hydrolysis of part of the chlorine, if

A = total chlorine in the water

C = chlorine in the CCl_4

c = unhydrolysed chlorine in the water = $\frac{C}{k}$

$$\frac{A - c}{A} = \alpha$$, the degree of hydrolysis.

Thus assuming the validity of the above assumptions both the degree of hydrolysis and the equal concentrations of HCl and HOCl were determinable.

The table below lists the results of distribution coefficient measurements in pure water. It is evident that the chlorine in the more dilute solutions was greatly hydrolysed. The last column gives the value of K, the concentration constant of the hydrolysis equilibrium where

$$K = \frac{[H^+]\ [Cl^-]\ [HOCl]}{[Cl_2]} = \frac{A^3\ \alpha^3 .10^{-9}}{A\ (1-\alpha).\ 10^{-3}} = \frac{A^2\ \alpha^3 .10^{-6}}{1-\alpha}$$

where A and α have the significance given.

K shows a remarkable constancy. Jellinek (27) commenting on this pointed out that properly each molecular species should be multiplied by its activity coefficient. This coefficient for H^+ and Cl^- was about 0.91 for the first experiment in the table and about 0.95 for the last. (27a) K in the former case should be multiplied by $(0.91)^2 = 0.83$ and in the latter by $(0.95)^2 = 0.90$. This destroyed the constancy. It appeared therefore to Jellinek as though the missing activity coefficients of H^+ and Cl^- were compensated with reference to K by the omission of the activity coefficients of HOCl and Cl_2 which were perhaps not quite equal to unity.

Jakowkin's results for the hydrolysis of chlorine in pure water at 0°C from measurements of the distribution coefficient:

A Total Cl in H_2O Mols. $10^3/l.$	C Cl_2 in CCl_4 Mols. $10^3/l.$	c Unhydrolyzed Cl_2 in H_2O $= C/20.$ Mols. $10^3/l.$	α degree of hydrolysis $\frac{A-c}{A}$	$K.10^4$ mol./l.
17.87	148.7	7.435	0.584	1.53
12.49	78.37	3,919	0.686	1.60
8.618	38.44	1.922	0.777	1.56
6.017	17.47	0.8735-	0.855	1.56
5.034	11.34	0.5670	0.887	1.58
3.713	5.243	0.2621	0.029	1.57
			Mean	

Jakowkin also determined the equilibrium constant by means of conductivity measurements. Since hydrochloric acid conducts well whereas the chlorine and hypochlorous acid conduct scarcely at all, a comparison of the conductivity of chlorine water with the known conductivities of hydrochloric acid should give the degree of hydrolysis. Jakowkin divided the specific conductivity of chlorine water by the molarity of the total chlorine and assumed this to be the molar conductivity of chlorine water. Division of this value by the molar conductivity of hydrochloric acid at infinite dilution, or as is nearly identical, by the molar conductivity of chlorine water at infinite dilution gave then the degree of hydrolysis. Jellinek pointed out that the molar conductivity of HCl should be divided by its equilibrium concentration but since the hydrochloric acid concentrations were rather dilute the distinction was not important. From a series of measurements of this type where the degree of hydrolysis by conductivity measurements was used to determine the proportion of unhydrolysed chlorine in aqueous solutions of 0^{o}, the distribution coefficient $K = \frac{c}{C}$, where c represented the concentration of unhydrolysed chlorine and C as before the concentration of chlorine in carbon tetrachloride, was found by Jakowkin to be more constant than where the hydrolysis was repressed by the addition of hydrochloric acid. Further, the hydrolysis constant K at 0° determined from conductivity measurements was found to be 1.58 in excellent agreement with the value 1.57 obtained from the distribution coefficient data.

Jakowkin also determined by distribution measurements the degree of hydrolys of chlorine in aqueous solutions at five temperatures between 6° and 60° and found the constant to increase with temperature. A corresponding increase in the degree of hydrolysis was shown by conductivity measurements at 25° compared to those obtained at 0°.

The progressive repression of the hydrolysis by hydrochloric acid was shown by distribution measurements for chlorine between carbon tetrachloride and 0.00625N, 0.0125N and 0.025N HCl. The shape of the curves obtained indicated that the hydrolysis was completely repressed in the above-mentioned 0.1 NHCl. Similar measurements were made in several concentrations of nitric acid. Here as might be expected, in the absence of the chloride ion, the hydrolysis was repressed to a lesser degree. Iakowkin also investigated the effect of other acids and some metal chlorides. The influence of a chloride ion was similar to that of an hydrogen ion.

In 1901 de Forcrand (13) in calculating the heat of formation of chlorine hydrate from dissociation curves, observed that traces of hydrochloric acid were always formed, which would have the effect of increasing the pressure and decreasing a little the calculated heat of formation. As the quantity to add would always be very small and variable with the conditions of the experiment, he thought best to neglect it.

Richardson (39) in 1903 published the results of extensive experiments on the distillation of chlorine water. In reviewing Pickering's (38) work he enquired whether or not the formation of hydrochloric acid in the residue was accompanied by the separation of hydrochlorous or other volatile oxyacid or whether active chlorine escaped only in the free state.

The results showed that when chlorine water was distilled even below the boiling point, a partial decomposition took place, hypochlorous acid and free chlorine passed over while hydrochloric acid remained behind. The quantity of hypochlorous acid in the distillate was less than the hydrochloric acid in the residue. When the chlorine water was distilled at the boiling point, in the presence of a stream of chlorine gas, no decomposition took place, the quantity of hypochlorous acid in the distillate being equal to the quantity of hydrochloric acid in the residue. Distillation with complete reflux in the presence of a stream of chlorine gas showed that there was no decomposition when separation of the two acids was prevented. Mixing of the distillate and residue from distillation in a current of chlorine produced a solution having all the properties of chlorine water, showing that the reaction was reversible.

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl$$

It was also found that the hydrolysis was proportional to the dilution. At maximum dilution all the chlorine reacted to form HCl and HOCl. No free chlorine escaped in the distillate. Progressive distillation and sampling in a stream of chlorine gas showed decreasing yields of hypochlorous acid. This showed that the increasing concentration of HCl in the residue by separation through distillation and through loss of water by evaporation was repressing the degree of hydrolysis. Further tests with added hydrochloric acid and distillation in a stream of chlorine gas gave diminishing yields until one part of concentrated hydrochloric acid to eight parts of chlorine water prevented entirely the separation of hypochlorous acid. Finally distillation in vacuo at room temperature showed that hypochlorous acid was still separated under such conditions.

Since 1903, only a few scattered studies have been made upon chlorine solutions. Most of the investigations have dealt with the more easily handled bromine and iodine solutions and the data on chlorine appended for comparison have been taken from Jakowkin's work sometimes with recalculations in terms of the units favoured by each particular investigator. For example, Lewis and Randall (30) gave the value 4.84×10^{-4} compared to Jakowkin's value 4.64×10^{-4}.

Passing mention has been made of the solubility of chlorine in some aqueous salt solutions. As later workers in this laboratory will continue the study into such fields it will be convenient only to mention that among monovalent ions the highly hydrated lithium and hydrogen ions increase the solubility of chlorine whereas the lesser hydrated ions such as sodium and potassium decrease the solubility (17), (18), (36). Goodwin (17)(18) found that the presence of chlorides in general lowered the temperatures of maximum solubility and the temperature at which the hydrate appeared. Sherrill and Izard (48) determined the solubility of chlorine at 25° and one atmosphere in H_2SO_4, HCl, B_aCl_2, KCl and N_aCl and computed the concentration of an assumed trichloride ion. The recent work of Liebhafsky (31) to which reference has already been made shows that the equilibrium measurements of Jakowkin (26) on chlorine solutions are in line with other evidence from kinetic measurements which shows that the chlorine, bromine and iodine exhibit anomalous temperature coefficients. As an explanation of the facts, Liebhafsky assumes that the temperature region where anomalies occur is the region in which the degree of hydrolysis is changing, where two halogen species exist at comparable concentrations and in rapid equilibrium with each other. Further experimental data are necessary to confirm the theory.

Two papers have been published very recently by Shilov (49)(50) and co-workers on the rate of the reaction.

$$Cl_2 + H_2O = HOCl + H^+ + Cl^-$$

as measured by the conductivity of chlorine solutions and of chlorine solutions in the presence of phenol which reacts with the hypochlorous acid. The results of the two methods agreed very well. Even at 0° the hydrolysis proceeded very rapidly. When a concentrated solution of chlorine was diluted the conductivity reached its final values in two minutes but measurements in the first minute gave values somewhat below the final value showing that the rate was rapid but finite.

It is evident then that the exact nature of the chlorine hydrolysis is at present in a state of flux. Further data are urgently needed and it is hoped that the present study of the vapour pressure of the aqueous solutions, the first to be conducted over a range of pressures as well as temperatures and in vacuo will find a place in the ultimate analysis of the phenomena connected with the hydrolysis of the halogens,

2. Introduction to Method

The methods hitherto used for determining the solubility of chlorine in water have been based upon the gravimetric and volumetric analysis of the chlorine content of an aqueous solution saturated at the given temperature by means of a stream of chlorine gas entering beneath the surface of the water. Such methods are open to objection. The amount of dissolved air in the water is uncertain. Pelouze (37) and Richardson (39) noted the displacing effect of air on dissolved chlorine. Moreover the water must either be saturated at a pressure slightly greater than atmospheric or if the chlorine stream is stopped when the sample is taken evaporation of chlorine from the surface of the solution reduces the true solubility by some uncertain quantity.

The method applied to this investigation has been used by others in this laboratory for the determination of the aqueous solubility of such gases as sulphur dioxide (32) (8) (35) (20), carbon dioxide (35) ammonia (35) and hydrogen sulphide (55).

The results which they have obtained demonstrate the simplicity and convenience of vapour pressure measurements for the measurement of solubility. The following section describes the apparatus and its manipulation which follows closely that of Wright (55) except for the changes necessary for introducing the chlorine into the cell.

3. Experimental Details

The apparatus consisted essentially of two sections, the cell for the solution, A, and the glass manometer, G, connected by means of a flexible U-tube.

The glass manometer first used in this work was similar to that described by Wright (55) in that the thin glass bulb was blown on the lower end of a piece of 12 mm. pyrex tubing and the pointer was attached to the inner surface of the bulb which was afterwards surrounded by an outer envelope connected to the solution cell proper. The unit constructed in this way functioned well at the higher concentrations of chlorine but the dead space was too large for accuracy at the lower concentrations.

A slightly different type of glass manometer was built and this type is illustrated in Figure 5. As can be seen from the diagram the mounting of the pointer on the outside of the bulb reduced the dead space to a minimum. The value of this improvement is shown in the discussion where the importance of measurements in the region of low chlorine concentration is clearly evident.

The cell A was equipped with a magnetic stirrer S operated by the solenoid C, and had an arm B through which water could be introduced. The glass manometer was continued

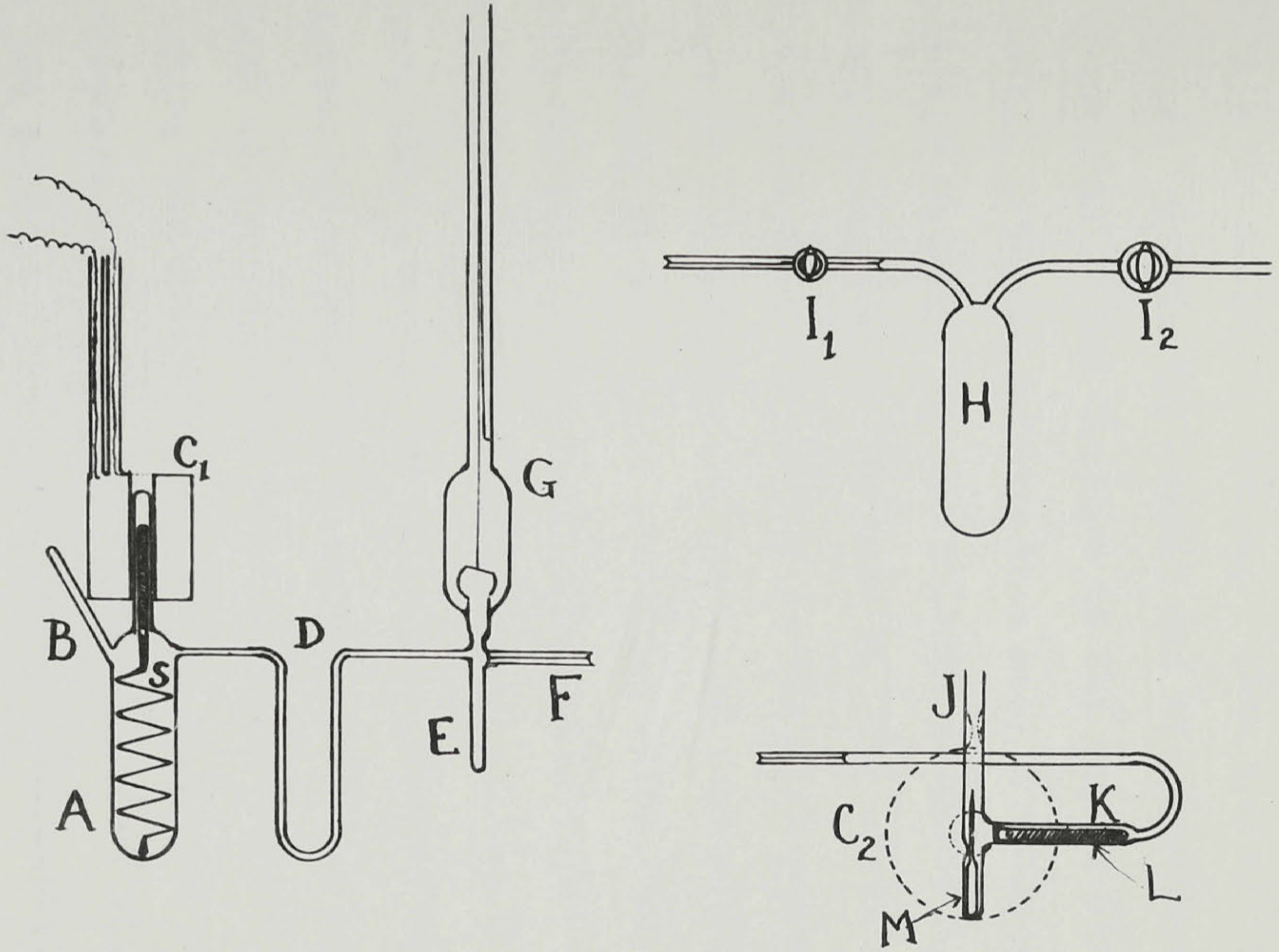


Figure 5

downward into a small cell E into which chlorine was condensed in the manner later outlined. The small spur F was made of capillary tubing. When the above unit had been assembled, tested for leaks, and the manometer calibrated as described in the section on the vapour density of chlorine, a volume calibration cell H equipped with a capillary stopcock I_1 and a large stopcock I_2 was sealed at its capillary end to the spur F. The other end of the calibration cell was sealed to the high-vacuum system. The volume of the calibration cell had been accurately determined by filling it with cold distilled water, immersing it in a precisely controlled thermostat maintained at a temperature measured on a standard thermometer of 25.4°C. for several hours, then closing the stopcocks, drying the tips, and weighing at a temperature several degrees lower. The tare weight of the cell was determined in the usual way by weighing the empty unit with the stopcocks open to the atmosphere and subtracting the weight of the air contained in the cell at the temperature and barometric pressure of weighing. The volume of the cell was then determined from the known density of water at the calibration temperature, 25.4°C.

The calibration of the vapour pressure cell unit was carried out as follows: The vapour pressure cell and the calibration cell were interconnected and filled with air at atmospheric pressure as read on the low pressure manometer M_2. Then the stopcock I_1 was closed and the calibration cell thoroughly evacuated by means of the Hyvac and Langmuir diffusion pumps. Finally, the stopcock I_2 was closed and the air in the vapour pressure cell allowed to expand into the evacuated cell and the resulting pressure read on the manometer in the usual way. During the sequence of operations, the two cells were thermostated so that the relation for an ideal gas,

$$p_1v_1 = p_2v_2$$

held true. In this case, the relation could be written:

$$p_1v_1 = p_2(v_1 + v_2)$$

where p_1 and p_2 are respectively the initial and final pressures and v_1 and v_2, respectively, the volume of the vapour pressure cell and the volume of the calibration cell. The latter equation can be written in the form:

$$v_1 = \frac{p_2}{p_1 - p_2} \cdot v_2$$

and was so used in the determination of the volume of the various cells used.

From 3 to 5 runs were used in the above manner, after which the calibration cell was cut away from the vapour pressure cell and a small cell designed for the introduction of chlorine samples under vacuum was sealed to the same spur F. This cell, hereafter called a "breaker-unit", consisted of a vertical tube J with a horizontal arm K containing a glass-enclosed iron core L such as is commonly attached to a glass stirrer for operation by means of a solenoid. Both ends of the enclosing glass tube were thickened for protection against breakage on impact, and the end adjacent to the tube J was flattened to give greater chance of direct impact on the stem of the phial. For moving the "hammer" a powerful electro-magnet was provided with a field concentrated in a soft iron core. The horizontal arm was continued into a slender tube which formed a U in the same plane and terminated in a piece of capillary tubing used for sealing to the spur F.

The next step was to introduce a phial of chlorine M into tube J. The phial was cooled in a mixture of dry ice and acetone and a hook formed at the solid end of the stem. A file scratch was made on the hollow stem at such a height as to be between the floor of the horizontal arm and the saddle indented in the side of the tube J opposite. The phial was then allowed to warm to room temperature when it was immersed in water at 40°C. At this temperature the vapour pressure of chlorine is about 11 atmospheres (23) or nearly 4 atmospheres above that corresponding to the room temperature of about 23°C., giving a reasonable margin of safety in the subsequent operations. After the test, the phial was weighed and then by means of a wire loop attached to the hook the phial was lowered into position in the tube J with the file mark facing the magnetic hammer (and opposite the saddle) and the top of the tube sealed to the high vacuum line. A constriction was made at the top of J for convenience in sealing off without undue liberation of gas. To prevent excess heat reaching the phial during the latter operation, the lower part of J was immersed in dry ice-acetone mixture. Finally the cell was tested for leaks in the chlorine-holding system.

The filling of the cell was accomplished by opening the system to the atmosphere, blowing open the tip of the filling arm B, and weighing in distilled water from a weight pipette. The tip was then sealed keeping the volume as close to the original magnitude as possible. Then the water was purified from dissolved gases by careful freezing from below followed by thorough evacuation with the Hyvac and diffusion pumps, the process being repeated three or four times after which the chlorine-water system was sealed off at the constriction provided above the chlorine sample.

Mixing of the water and the chlorine was brought about by breaking the chlorine phial, condensing the chlorine in the base E of the manometer cell with liquid air, sealing off the "breaker-unit" at F, and allowing the water and chlorine to mix. Great care was necessary in this operation and the following precautions were observed: First, the vapour pressure of the chlorine was reduced by surrounding the tube J with liquid air for half an hour. Owing to the high vacuum and small contact surface in the cell this length of time was necessary for all but the smallest samples of chlorine to cool to a safe temperature for the breaking of the phial. The liquid air was then placed around E and the phial broken by causing the magnetic hammer to impact upon its stem. The intensity of the impact was regulated by the distance to which the hammer was withdrawn from the stem, and the placing of the solenoid C_2 relative to the stem when the switch was thrown for the impact. Usually, an angle of 90° or a little more, between the axis of the horizontal tube K and the axis of the core of the solenoid, was sufficient to break the stem of the phial. On no account was the axis of the core of the solenoid placed in a line with the axis of the tube K, since the resulting impact of the hammer would have shattered the wall of the tube J. No further control on the evaporation and condensation was necessary than to raise gradually the level of the liquid air surrounding the tube E to complete the condensation by exposing fresh glass surface. The heat of evaporation of the chlorine was sufficient at all times to maintain the latter at a low temperature and prevent "bumping" in the phial. When condensation was completed the unit containing the empty phial was sealed off from the vapour pressure unit and set aside for the subsequent weighing of the phial and fragments. The chlorine was cautiously allowed to melt and warmed to the temperature of a dry ice-acetone mixture. Then the water in the cell A was allowed to melt but as the pressure of the chlorine was of the order of 6 cm. compared to 2 cm. for the water, no condensation of water took place in the glass manometer space. The most convenient method of mixing the chlorine and water was to maintain the water cell at 0°C. with ice, carefully distill the chlorine over into the water where it dissolved to form the hydrate with a vapour pressure of about 25 cm.

For a solubility run the cell was surrounded with a well-lagged bath filled with water, and equipped with electric heaters, a stirrer, a cooling coil, a standard thermometer graduated in tenths, and a mercury thermo-regulator. As for the density measurements from 0° to 10°C., the temperature was regulated by hand with additions of crushed ice and, as the temperature was read by means of a small telescope, the regulation was well within 0.1°C. Between 10°C.. and room temperature, a balance was secured between the cooling coil fed by tap water, pre-cooled in an ice bath where necessary, and the heater system controlled by the thermo-regulator in series with a relay system which controlled a small heater of 100 watts capacity. For temperatures above room temperature to 75°C. the main regulation was supplied by one or more 500 watt heaters controlled by rheostats and maintained within the required limits by the relay-regulator system. The latter permitted temperature control within 0.02°C.

The absence of any photochemical decomposition (1) under the experimental conditions was proved by the reproducibility of the total pressures for widely differing concentrations of chlorine. Care was taken to avoid direct illumination from the 400-watt lamp used in the optical system for viewing the pointer displacement of the glass manometer, and the lamps used for reading thermometers were switched on only when necessary. The cell itself was protected by deep immersion in the heavily lagged thermostat.

Each sample of chlorine and water was carried over the temperature range from 0° to an upper limit which varied from 40°C., for the highest concentrations, to 70 - 80°C. for the lower concentrations. The upper temperature limit was, of course, determined by the pressure limit of the apparatus which was about four atmospheres.

Pressures and temperatures were recorded as in Part I, together with the weights of the chlorine and water. At concentrations and temperatures where the hydrate was formed, Isambert's (25) note regarding the slow rate at which equilibrium was attained was amply confirmed. With a small stirrer consisting of a glass spiral, about 3/8 of an inch in diameter by 2 inches long, from six to ten hours were required.

This stirrer was, therefore, replaced by a glass spiral 4 inches long and 1 inch in diameter, only slightly smaller than that of the cell itself. With a stirrer of this size and very vigorous agitation, equilibrium between hydrate, solution and vapour phase was attained in two hours.

4. Experimental Results

The total pressures recorded in the preceding section were reduced to centimetres of mercury at 0° by applying the usual corrections (28).

From the total pressures, the known vapour pressures of water (23a) and the known amounts of chlorine and water in the cell, together with its internal volume, the concentration of the solution at each temperature was calculated, as outlined below, where the symbols and the quantities which they represent are as follows:

D = density of water (22)
d = density of liquid chlorine (21)
m_1 = total weight of chlorine in the cell
m_2 = weight of chlorine in solution
M^1 = apparent molecular weight of chlorine
M_o = theoretical molecular weight of chlorine
M_1 = theoretical molecular weight of water
P_1 = total observed pressure in atm.
P_2 = vapour pressure of water in atm. (23a)
R = gas constant in litre atm.
T = temperature in ^{o}K.
V_1 = volume of cell in litres
V_2 = volume of water in litres

V_3 = volume of vapour phase in litres

W = weight of water in the cell

w = weight of water in the vapour phase

As a first approximation, the volume of the vapour phase is equal to the volume of the cell assumed to be constant less the volume of the water:

$$V_3' = V_1 - V_2 = V_1 - \frac{W}{D}$$

There is a correction to this volume of the vapour phase due to the increase in the volume of the liquid phase by the amount of chlorine dissolved in the water. As a first approximation the weight of chlorine in the solution, calculated by means of the ideal gas law applied to the chlorine in the vapour phase, is

$$m_2' = m_1 - \frac{V_3' M^1}{RT} (P_1 - P_2)$$

and its volume is $\frac{m_2'}{d}$.

Therefore, assuming that the volumes of liquid water and liquid chlorine are additive, the volume of the gas phase to a second approximation is:

$$V_3'' = V_3' - \frac{m_2'}{d}$$

The weight of chlorine dissolved is then to a second approximation,

$$m''_2 = m_1 - \frac{V''_3 M^1}{RT} (P_1 - P_2)$$

Further approximations are unnecessary since the changes are within the experimental error. A small correction, w, was applied at the highest temperatures for the weight of water in the gas phase. This correction entering by subtraction from the total weight of the water is obtained by means of the ideal gas law:

$$w = \frac{P_2 V''_3 M_1}{RT}$$

With the above equations and the data obtained experimentally, and from the references indicated, the solubilities were calculable in any desired units and could be plotted against either partial pressures of chlorine or concentrations in the gas phase.

From plots of solubility vs. temperature, and concentration in the gas phase vs. temperature for each run, corresponding data at a series of temperatures were picked off and a plot of solubility vs. concentration in the gas phase gave the isothermal solubilities of Figure 6.

The essential data obtained from the eight successful runs are contained in Tables VIII to XV. From these tables the solubility of chlorine at each temperature and partial pressure may be calculated in any desired units. The solubilities are here calculated in mol ratios from which mol fractions may be readily obtained.

The cross-sectional data for the isothermals of Figure 6 are listed in Tables XVI to XVIII.

In Table XIX the best existing data, that of Winkler (53), for solutions saturated under a total pressure of one atm. is compared with data selected from the present work. The discrepancies indicate supersaturation or saturation under slightly greater pressures than atmospheric in the earlier data at the lower temperatures with probable loss of chlorine at the higher temperatures.

TABLE VIII

V. P. Run No.4

Vol. of cell = 146.5 cc.

Wt. of chlorine = 1.3160 gm.

Wt. of water = 38.12 gm.

Temp. °C.	p.p.of Chlorine cm.	Vol.of V phase cc.	Weight of chlorine in solution gms.	Mols Chlorine dissolved per mol of water X 10^3
15.00	140.93	107.8	0.7014	4.655
25.00	189.73	107.8	0.5118	3.426
35.05	213.37	107.8	0.4405	2.938
45.11	233.91	107.7	0.3875	2.585
55.10	251.72	107.5	0.3495	2.332
65.10	267.27	107.3	0.3238	2.161

- -

TABLE IX

V. P. Run No. 5

Vol. of cell = 152.6 cc.

Wt. of chlorine = 1.7109 gm.

Wt. of water = 38.56 gm.

Temp. °C.	p.p. of Chlorine cm.	Vol. vapour phase cc.	Weight of chlorine in solution gms.	Mols Chlorine dissolved per mol of water X 10³
5.00	43.77	113.0	1.5068	9.940
10.00	79.10	113.1	1.3466	8.886
20.00	223.20	113.5	0.6890	4.547
30.00	254.88	113.5	0.5829	3.843
40.10	281.43	113.3	0.5079	3.350
30.00	255.11	113.5	0.5809	3.832
20.00	223.40	113.4	0.6889	4.542
16.97	212.65	113.5	0.7294	4.807

- -

TABLE X

V. P. Run No.6

Vol. of cell	152.6 cc.
Wt. of Chlorine	0.9808 gm.
Wt. of water	39.77 gm.

Temp. °C.	p.p. of Chlorine cm.	Vol. vapour phase cc.	Weight of chlorine in solution gms.	Mols Chlorine dissolved per mol of water X 10^3
15.00	112.87	112.5	0.4695	3.002
40.10	155.69	112.3	0.3320	2.123
15.00	113.11	112.5	0.4689	2.999
50.10	167.73	112.2	0.3081	1.971
15.00	113.10	112.5	0.4680	2.999
28.00	138.14	112.4	0.3814	2.439
60.10	178.22	111.9	0.2864	1.831
15.00	113.38	112.5	0.4673	2.988

TABLE XI

V. P. Run No. 7

Vol. of cell = 77.3 cc.

Wt. of Chlorine = 0.2812 gm.

Wt. of water = 42.32 gm.

Temp. °C.	p.p. of Chlorine cm.	Vol. vapour phase cc.	Weight of chlorine in solution gms.	Mols Chlorine dissolved per mol of water X 10^3
5.00	30.89	34.8	0.2370	1.423
15.00	42.16	34.7	0.2230	1.340
25.00	53.78	34.7	0.2094	1.258
35.05	65.02	34.6	0.1973	1.185
45.10	75.53	34.5	0.1871	1.125
15.00	42.18	34.7	0.2230	1.340
55.10	85.22	34.3	0.1788	1.074
15.00	42.23	34.7	0.2229	1.339
65.10	93.86	34.0	0.1726	1.037
15.00	42.23	34.7	0.2229	1.339
75.05	101.34	33.8	0.1682	1.011
15.00	42.30	34.7	0.2228	1.338

TABLE XII

V. P. Run No.8

Vol. of cell = 77.3 cc.

Wt. of Chlorine = 0.4321 gm.

Wt. of water = 41.34 gm.

Temp. °C.	p.p.of Chlorine cm.	Vol. vapour phase cc.	Weight of chlorine in solution gms.	Mols Chlorine dissolved per mol of water X 10^3
10.00	61.18	35.7	0.3434	2.112
20.10	81.47	35.7	0.3177	1.953
30.00	101.15	35.6	0.2948	1.813
40.10	119.97	35.4	0.2753	1.694
50.10	137.16	35.2	0.2592	1.594
60.10	152.60	35.0	0.2465	1.516
70.10	166.04	34.8	0.2371	1.458
80.00	177.83	34.5	0.2311	1.421
10.00	61.34	35.7	0.3432	2.110

- -

TABLE XIII

V. P. Run No.9

Vol. of cell = 77.3 cc.

Wt. of Chlorine = 0.1109 gms.

Wt. of water = 41.75 gms.

Temp. °C.	p.p. of Chlorine cm.	Vol. vapour phase cc.	Weight of chlorine in solution gms.	Mols Chlorine dissolved per mol of water X 10^3
2.00	8.58	35.4	0.0983	0.598
8.50	10.52	35.4	0.0958	0.583
15.00	12.43	35.4	0.0935	0.569
25.00	15.37	35.3	0.0901	0.549
35.05	18.17	35.2	0.0872	0.531
45.10	20.63	35.0	0.0850	0.518
55.10	22.89	34.8	0.0832	0.507
65.10	24.84	34.6	0.0819	0.499
75.05	26.41	34.4	0.0811	0.494
25.00	15.48	35.3	0.0900	0.548

- -

TABLE XIV

V. P. Run No.10

Vol. of cell = 77.3 cc.

Wt. of Chlorine = 0.4415 gm.

Wt. of water = 41.94 gm

Temp. °C.	p.p. of Chlorine cm.	Vol. vapour phase cc.	Weight of chlorine in solution gms.	Mols Chlorine dissolved per mol of water X 10^3
1.00	27.13	35.1	0.4018	2.435
2.00	30.55	35.1	0.3969	2.405
4.00	38.82	35.1	0.3851	2.333
6.50	52.34	35.1	0.3660	2.218
9.00	60.36	35.2	0.3549	2.215
16.00	74.60	35.1	0.3373	2.044
35.05	113.67	34.9	0.2925	1.772
55.10	149.70	34.5	0.2591	1.570
17.00	76.68	35.1	0.3347	2.028

TABLE XV

V. P. Run No.11

Vol. of cell = 77.3 cc

Wt. of Chlorine = 0.8318 gm.

Wt. of water = 41.85 gm

Temp. °C.	p.p.of Chlorine cm.	Vol. vapour phase cc.	Weight in chlorine in solution gms.	Mols Chlorine dissolved per mol of water X 10^3
8.00	62.63	34.9	0.7424	4.510
10.00	79.02	34.9	0.7194	4.370
12.00	99.80	34.9	0.6903	4.193
14.00	125.56	34.9	0.6542	3.973
16.00	154.20	35.0	0.6136	3.727
20.00	171.88	35.0	0.5916	3.594
30.00	215.68	34.9	0.5398	3.280
40.10	257.50	34.7	0.4956	3.010
45.10	277.33	34.6	0.4759	2.891
50.10	296.15	34.6	0.4756	2.779
25.00	193.98	34.9	0.5654	3.433

Table XVI

Data for Figure 6

5°		10°		15°	
C'	C	C'	C	C'	C
0.0054	0.591	0.0062	0.580	0.0069	0.568
0.0179	1.422	0.0208	1.380	0.0237	1.337
		0.0351	2.117	0.0402	2.028
		0.0357	2.132	0.0408	2.055
				0.0642	2.984

Table XVII

Data for Figure 6

20°		30°		40°	
C'	C	C'	C	C'	C
0.0076	0.558	0.0090	0.538	0.0100	0.523
0.0265	1.296	0.0318	1.219	0.0364	1.154
0.0452	1.991	0.0544	1.811	0.0624	1.692
0.0460	1.980	0.0558	1.836	0.0642	1.709
0.0690	2.748	0.0764	2.370	0.0814	2.121
0.0970	3.708	0.1102	3.156	0.1183	2.744
0.0997	3.583	0.1183	3.273	0.1366	3.004
1.271	4.530	0.1402	3.848	0.1496	3.347

Table XVIII

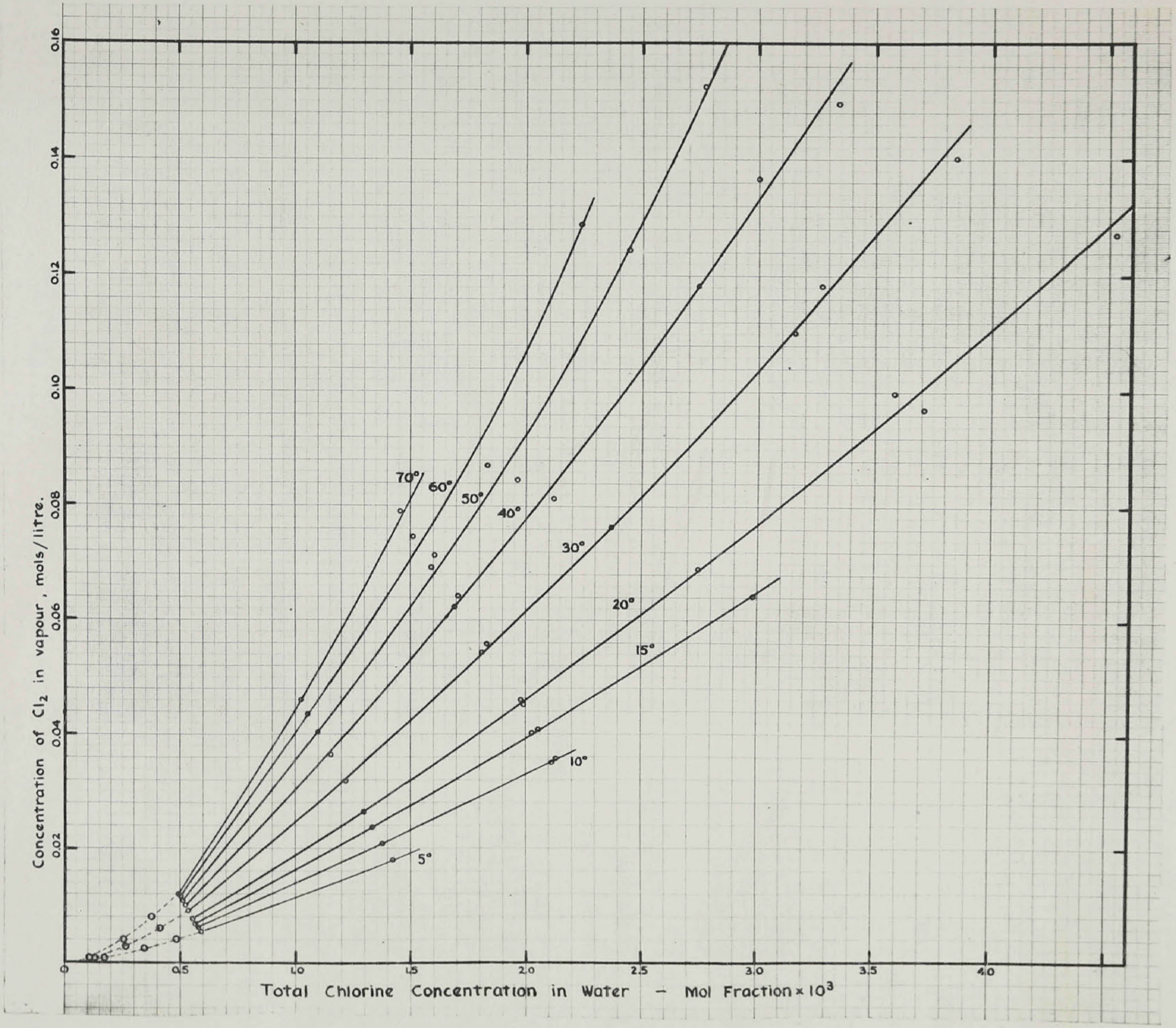
Data for Figure 6

50°		60°		70°	
C'	C	C'	C	C'	C
0.0109	0.512	0.0116	0.502	0.0120	0.495
0.0404	1.098	0.0436	1.054	0.0461	1.024
0.0692	1.593	0.0746	1.514	0.0790	1.458
0.0713	1.608	0.0871	1.832		
0.0847	1.963	0.1288	2.236		
0.1244	2.442				
0.1525	2.771				

Table XIX

Solubility of Chlorine in Water

Temp. °C	Soly. mols Cl_2/mol H_2O x 10^3 Present Work	Winkler
15	2.132	2.190
20	1.855	1.878
30	1.457	1.470
40	1.200	1.185
50	1.050	0.993
60	0.930	0.837
70	0.858	0.704



Concentration of Cl_2 in vapour, mols/litre.
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
Total Chlorine Concentration in Water – Mol Fraction × 10^3
70°
60°
50°
40°
30°
20°
15°
10°
5°

Figure 6

5. Discussion of Results

The hydrolysis of chlorine may be represented by the equation,

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl$$

at equilibrium according to the Law of Mass Action

$$\frac{[Cl_2]\ [H_2O]}{[HCl]\ [HOCl]} = K \qquad (1)$$

where the brackets refer to concentrations in solution since the concentration of the water is nearly constant, and

$$[HCl] = [HOCl]$$

$$[Cl_2] = \frac{K}{k'} [HCl]^2 = K' [HCl]^2$$

hence
$$[HCl] = \sqrt{\frac{[Cl_2]}{K'}} \qquad (2)$$

Also the concentration of chlorine in the water as represented by the abscissae on the graph is the sum of the free chlorine in the water together with its hydrolysis products, i.e.,

$$C = [Cl_2] + [HCl] + [HOCl]$$

$$= [Cl_2] + 2 [HCl]$$

$$= [Cl_2] + 2 \sqrt{\frac{[Cl_2]}{K'}} \qquad (2)$$

In Figure 6 the isothermals, giving the relation between the concentration of chlorine in the vapour and in the solution, exhibit a slight concavity towards the vapour in each of the curves. Furthermore an apparent extrapolation towards the lower axis would at first sight appear to indicate that they would all converge in the neighbourhood of 0.025 mol % of chlorine in the solution. This, of course, is theoretically impossible as they must pass through the origin. It was not feasible to make measurements, experimentally, at low concentrations. There is, however, a logical explanation for the form and direction of the curves based on the hydrolysis of chlorine. This hydrolysis is most effective at very low concentration as the following formulation of equilibria will show.

The HCl at such low concentrations constitutes no measurable vapour pressure to the total vapour pressure (35) so that no correction is necessary in the calculation of the concentration of the chlorine in the gas phase.

Now $[Cl_2] = HC'$ (3) where H is ~~the~~ Henry's constant and ~~thus~~ C' the concentration of the chlorine in the gas phase (2). Therefore, substituting in equation (2)

$$C = HC' + 2\sqrt{\frac{HC'}{K'}} \qquad (4).$$

By putting $H = \alpha$ and $2\sqrt{\frac{H}{K'}} = \beta$ equation (4) takes the simple form

$$C = \alpha C' + \beta \sqrt{C'} \qquad (5)$$

By taking two points on each of the isothermals, α and β can be calculated for each of them. The values are given in Table 20. The test of the validity of the above reasoning is then given by calculating intermediate points on the isothermals and especially by calculating the points at low concentrations to see if the curves take a reasonable form as the concentration approaches zero.

In Figure 6 this has been done for the two extremes and the middle isothermal. The points are represented by circles through which the corresponding curves are continued as dotted lines. There is good agreement in the region where measurements have been made and the extrapolated isothermals show that on the basis of the hydrolysis the sharp inflection toward the origin is accounted for.

Intermediate values of C', the concentration of chlorine in the vapour phase at a mid-point on each isothermal are also listed in Table XX, together with the values of the concentration of chlorine in the solution calculated for these points by means of equation (5). The observed values of C are tabulated for comparison.

Table XX

Temp. °C.	α	β	C'	C_{calc}.	$C_{obs.}$
5	42.9	4.95	0.0120	1.057	1.040
10	35.7	4.59	0.0204	1.384	1.350
15	29.5	4.27	0.0372	1.923	1.910
20	23.3	4.17	0.0672	2.649	2.700
30	15.9	4.10	0.0752	2.325	2.340
40	12.1	3.80	0.0788	2.017	2.020
50	8.05	3.95	0.0840	1.821	1.870
60	5.96	4.09	0.0680	1.473	1.460
70	5.39	3.73	0.0456	1.039	1.020

SUMMARY

A historical survey has been made of the density determinations of chlorine and the density of chlorine gas has been determined over the temperature range 15°C. to 75°C. and for pressures from 25 to 160 cm. The data are consistent to within 0.1% with the values predicted by the Maass and Mennie equation of state. The accuracy is not sufficiently great to permit correlation with the Cooper and Maass equation. The deviations are to be ascribed chiefly to the cumulative effect of small errors on the measurement of the pressure but the tabulated viscosities of chlorine are somewhat uncertain and may be a source of a deviation of the predicted values from the experimental data.

The density data have been applied to the determination of the solubility of chlorine in water over the range 10°C. to 75°C. and 10 cm. to 300 cm. pressure. The conclusions of Jakowkin (26) regarding the reversible hydrolysis of chlorine in aqueous solution in the dark are confirmed qualitatively. More exact knowledge of the equilibrium depend upon the determination of conductivities. The plan for this research project had included the conductivities but owing to the difficulties in the manipulation of chlorine it was not possible to complete the whole project. Accordingly some of the theoretical conclusions as indicated in the text must be considered as tentative and as indicative of the road to be followed in further research upon the properties of chlorine solutions.

Nevertheless an hypothesis based on the hydrolysis of chlorine has been shown to be in agreement on a quantitative basis with the experimental data as represented by the partial vapour pressure isothermals of chlorine.

BIBLIOGRAPHY

GENERAL INTRODUCTION

(1) Campbell,W.B. and Maass,O. Can. J.Research, 2: 42 .1930

(2) Cooper,De Le B.and Maass,O. Can. J.Research, 2:388. 1930
Cooper,De Le B.and Maass,O. Can. J.Research, 4:283. 1931

(3) Cooper,De Le B.and Maass,O. Can. J.Research, 4:495. 1931

(4) Gishler,P.E.and Maass,O. Can. J.Research,B,13:308.1935

(5) Gishler,P.E. and Maass,O. Can. J.Research,B.13;370.1935

(6) Gishler,P.E. and Maass,O. Can.J.Research,B.14:301,1936

(7) Gurd,G.W. , Gishler,P.E. and Maass,O. Can.J.Research,B.13:209,1935

(8) Heritage,C.C., Chem. & Met.Eng. 44:9 1937

(9) Maass,C. Unpublished Thesis,McGill University

(10) Maass,C. and Maass,O. J. Am.Chem.Soc. 50: 1352 1928

(11) Mellor,J.W. A Comprehensive Treatise on Inorganic and Theoretical Chemistry; Vol.II. PP.258,262 London, 1922

(12) Morgan, O.M. and Maass O. Can.J.Research, 5: 162. 1931

(13) Quinn, E.L. and Jones,C.L. Carbon Dioxide. A.C.S.Monograph. No.72.

(14) Review of Pulp and Paper Industry. Chem. & Met. Eng. 44:66. 1937.

(15) Stewart, W.W. and Maass,O. Can.J.Research,6:453,1932.

(16) Stewart,W.W. and Maass,O. Can.J.Research,11:530,1934.

PART I

1. Bunsen,R. Liebig's Ann. 86: 265 1853

2. Chapman,S. Phil Trans. A. 216: 279 1915

3. Cooper,D.Le B. & Maass,O. Can. J. Research. 6: 596 1932

3a. Cooper,D. Le B. & Maass,O. Can.J.Research, 4: 495 1931

4. Crafts,J.M. Comp.rend. 90: 183 1880

5. Crafts,J.M. Comp.rend. 98:1259 1884

6. Davy,H. Phil.Trans. 100: 245 1810
Phil.Trans. 101: 30 1811

7. Gay-Lussac,J.L. & Thénard,L.J.
Recherches physico-chimiques
Paris. 2: 128 1811

8. International Critical Tables, 3: 3

9. " " ", 3: 24

10. Jahn,H. Ber. 15:1242 1882

11. Jaquerod,A. Archives des Sciences
phys. et nat. de Genève,
(VI) 31: 20 1911

12. Jaquerod,A. and Tourpaian M.
J.Chem.phys. 11. 3 1913

13. Jeans,J.H. The dynamical theory of
gases. 4th edition. p. 276
Cambridge University Press, 1925

14. Jeans,J.H. The dynamical theory of gases,
4th edition. p. 288.
Cambridge University Press. 1925

15. Jeans, J.H. The dynamical theory of gases.
4th edition. p. 331 1925

16. Jones, J.E. Proc. Roy. Soc. 106A:441 1924

17. Keyes, F. Chem. Rev. 6: 210 1929

18. Landolt and Börnstein, Physikalisch-Chemische
Tabellen, 5th ed.
Hauptwerk I, p. 68

19. Langer, C. and Meyer, V. Ber. 15: 2769 1882

20. Lassar-Cohn. Arbeitsmethoden, 1923, p. 253

21. Leduc, A. Comp. rend. 116: 968 1893

22. Leduc, A. " " 125: 571 1897

23. Leduc, A. " " 140: 642 1905

24. Leduc, A. " " 148: 407 1909

25. Lieben, A. " " 89: 353 1879

26. Ludwig, E. Ber. 1: 232 1868

27. Maass, O, & Mennie J.H. Proc. Roy. Soc.
London. A. 110: 198 1926

28. Maass, O, & Russell, J. J. Am. Chem. Soc. 40: 1561 1918

29. Meyer, V. Ber. 12: 202 1879

30. Meyer, V. & C. Ber 12: 1426 1879

31. Moissan, H. & du Jassoneix, A.B.
Comp. Rend. 137: 1198 1903

32. Moissan, H. & du Jassoneix, A.B.
Ann. Chim. Phys. (8) 1: 145 1904

33. Pier, M. Z. phys. Chem. 62: 385 1908

34. Reinganum, M. Z. phys. 6: 514 1905

35. Seelheim, F. Ber. 12: 2066 1879

36. Stephen, H.N. J. Am. Chem. Soc. 52: 635 1930

37. Sutherland W. Phil.Mag. 36: 507 1893

38. Tapp J.S. Private Communication

39. Treadwell, F.P. and Christie, W.A.K.
Z. Anorg. Chem.. 47: 446 1905

40. Troost, L. and Hautefeuille P.
Comp. rend. 84: 947 1877

41. Van de Waals Die Kontinuitat des
gasformigen und
flussigen zustandes,
Leipzig 1881

42. Wasmuht, R. Chem.Fabrik. (1929) 145-7, 158-9.

43. Wright, R.H. Thesis, McGill University, 1931

44. Wright, R.H. & Maass, O.
Can.J.Research 5: 442 1931

45. Wright, R.H. & Maass, O.
Can.J.Research 6: 94 1932

PART II

1. Allmand, A.J. Cunliffe, P.Q. and Maddison, R.E.W.
J.Chem.Soc. T 127: 822 1925

2. Anwar-Ullah, S. Jour, Chem.Soc. 1172: 1932

3. Balard, A.J. Ann. Chim. Phys. (2) 57: 225, 1834

4. Berthelot, M. Ann.Chim.Phys.(5) 5: 318 1875

5. Bouzat, A. Comp.Rend. 176: 253 1923

6. Bouzat, A. and Azinières L.,Comp.rend. 177: 1444 1923

7. Bunsen, R. Liebig's Annalen, 93: 1 1855

8. Campbell, W.B. and Maass O. Can.J.Research
2: 42 1930

9. Le Chatelier, H. Comp.rend. 99: 1074 1884

10. Davy, H. Phil.Trans. 101: 30 1811

11. Ditte, A. Comp.rend. 95: 1283 1882

12. Faraday, M. Quart.J.Science, 15: 71 1823

13. de Forcrand, R. Comp.rend. 133: 1304 1901

14. de Forcrand, R. " " 134: 991 1901

15. Gay-Lussac, J.L. Ann.Chim.Phys (2) 70: 426 1839

16. Gay-Lussac, J.L. Ann.Chim.Phys. (3) 7: 113 1843

17. Goodwin, W.L. Trans.Roy.Soc. of Edinburgh 30: 597 1882

18. Goodwin, W.L. Ber. 15: 3039 1882

19. Göpner, C. Ber. 8: 287 1875

20. Gurd, G.W., Gishler, P.E. and Maass O. Can.J.Research, B, 13: 209 1935

21. International Critical Tables 3: 20

22. International Critical Tables 3: 24

23. International Critical Tables 3: 202

23(a). International Critical Tables 3: 210

24. International Critical Tables 3: 256

25. Isambert, F. Comp.rend. 86: 481 1878

26. Jakowkin, A.A. Z. phys. Chem. 29: 613 1899

27. Jellinek, K. Lehrbuch der physikalischen Chemie. Vol. lV. P. 256 1933

27(a). Jellinek, K. Lehrbuch der physikalischen Chemie. Vol. lII. P. 576

28. Landolt - Börnstein Physikalisch-Chemische Tabellen, 5th Ed. Hauptwerk I:68 1923

29. Landolt - Börnstein Physikalisch-Chemische Tabellen, 5th Ed. Hauptwerk 1:763 1923

30. Lewis and Randall. Thermodynamics, P. 507. 1st Ed. 1923

31. Liebhafsky, H.A. Chem. Reviews. 17: 89 1935

32. Maass, C. and Maass, O. J.Am.Chem.Soc. 50: 1352 1928

33. Maumené, G . Bull. Soc. Chim. (2) 39: 397 1883

34. Millon, N.A.E. Comp.rend. 28: 42 1849

35. Morgan, O. and Maass, O. Can.J.Research, 5: 162 1931

36. Oliveri - Mandalà. Gazz.chim. ital. 50; II: 89 1920

37. Pelouze, J. Ann.Chim.phys.(3) 7: 176 1843

38. Pickering, S.U. J.Chem.Soc. 37: 139 1880

39. Richardson, A. J.Chem.Soc. 83: 380 1903

40. Roozeboom, H.W.B. Rec.Trav. Chim.Pays-Bas, 3: 54-66 1884

41. Roozeboom, H.W.B. Rec.Trav.Chim.Pays-Bas, 4: 69 1885

42. Roozeboom, H.W.B. Z. phys. Chem., 2: 452 1888

43. Roscoe, H.E. Leibig's Ann. 95: 357 1855

44. Roscoe, H.E. J.Chem.Soc. 8: 15 1856

45. Schiff, H. Ber. 8: 419 1875

46. Schönbein, C.F. Pogg.Ann. 72: 450 1847

47. Schönfeld, F. Liebig's Ann. 95: 8 1855

48. Sherrill, M. and Izard, E.
J.Am.Chem.Soc. 53: 1667 1931.

49. Shilov, E.A. and Kupenskaya, G.V.
Comp.rend. Acad.Sci.
(U.S.S.R.) 2: 222 1934

50. Shilov, E.A. and Solodushenkov, S.M.
Comp.rend. Acad.Sci.
(U.S.S.R.) 3: 15 1936

51. Villard, P. Ann. Chim. Phys.(7) 11: 289 1897

52. Villard, P. J. Phys. Chem. (3) 5: 453. 1896

53. Winkler, L.W. Math. Természettudományi Ertesito
25: 86 1907

54. Wölters, W. J. prakt. chem. (2) 7: 468 1873

55. Wright, R.H. and Maass, O.
Can.J.Research 6: 94 1932

Claims for Original Research

The vapour density of chlorine has been measured over a larger pressure and temperature range than had been previously done. While the results are in agreement with the best determinations made at atmospheric pressure between 0° and 20°C., the data at higher pressures and outside of this range of temperature may be regarded as new. Within the range of experimental error the data were shown to be consistent with an equation of state previously tested in this laboratory.

The density data were essential for the evaluation of the solubility of chlorine in water which was measured over a pressure range up to four atmospheres and a temperature range from 0° to 70°C. Here again the only reliable data available were at a total pressure of one atmosphere and while there was fair agreement, whatever discrepancy there was could be accounted for by the errors inherent in the experimental technique used by previous observers.

The solubility data have been analysed from the point of view of a hydrolysis of chlorine in aqueous solution and have been shown to be in agreement with the equations based on this concept.

Throughout the investigation new experimental technique was developed to insure accuracy in the measurement of a system, in which one of the components, in this case chlorine, presented unusual difficulties because of its chemical reactivity.