

indicate a change in the equilibrium constant with the concentration, in the direction found by Saposhnikov, but further experiments will be necessary to decide this question.

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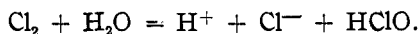
[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 64.]

### THE POTENTIAL OF THE CHLORINE ELECTRODE.

BY GILBERT N. LEWIS AND FRANK F. RUPERT.

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The potential of the chlorine electrode has been studied by numerous observers, but the various determinations are by no means in agreement with one another. Müller,<sup>1</sup> who has made the most recent and the most thorough investigation of this subject, has pointed out the chief cause of the observed discrepancies. Chlorine, in the presence of water, hydrolyzes according to the reaction which was first carefully studied by Jakowkin,



This hydrolysis takes place to a less extent in a solution of any chloride, and especially of hydrochloric acid, than in pure water, but nevertheless it occurs to a sufficient extent to affect the potential of the chlorine electrode, owing to the increase in concentration of chlorine ion. The change in potential due to this hydrolysis was calculated by Müller to be about 1<sup>1</sup>/<sub>2</sub> millivolts in 0.1 normal and 146 millivolts in 0.001 normal hydrochloric acid. The results of Müller for the potential of chlorine at atmospheric pressure against solutions of hydrochloric acid at four different concentrations are given in the following table. The potential in each case is measured against that of a hydrogen electrode in the same solution.

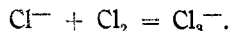
Conc.	Observed e. m. f.	Corrected e. m. f.	Calculated e. m. f.
1	1.366	1.366	...
0.1	1.485	1.486	1.477
0.01	1.546	1.599	1.594
0.001	1.587	1.733	1.712

The first column gives the concentration of the acid in equivalents per liter, the second the observed electromotive force, the third the same after the correction has been made for the increase of chloride ion due to hydrolysis of the chlorine, and the fourth shows the values calculated for the three lower dilutions from that at normal concentration. It is evident that Müller's correction for hydrolysis has to a large extent eliminated the deviations between the calculated and observed values. There remains, however, an uncertainty as to the true value of the poten-

<sup>1</sup> *Z. physik. Chem.*, 40, 158 (1902).

tial of the chlorine electrode amounting apparently to one centivolt or more.

Another possible source of error was mentioned by Müller. It is well known that iodine combines to a large extent with iodide ion to form tri-iodide ion, and it is not improbable that to a certain extent chlorine takes part in a similar reaction, namely,



This reaction would diminish the concentration of the chloride ion in solution and by about the same percentage amount in each concentration. It would not therefore affect the difference between the potentials of chlorine in two different concentrations of hydrochloric acid, but it might nevertheless cause a considerable error in the determination of the absolute potential of the chlorine electrode.

It is obvious that both these sources of uncertainty in the potential of chlorine would to a large extent be avoided if, instead of chlorine gas at atmospheric pressure, chlorine at a relatively small partial pressure were used at the electrode, for the change in chloride ion concentration, due to the reactions above considered, would in both cases be nearly proportional to the partial pressure of the chlorine.

We shall describe in this paper the results of an investigation of the potential of chlorine gas at low pressures. In order to reduce the partial pressure of the chlorine, it was decided to mix it with some inert gas, and it was originally planned to use nitrogen for this purpose. However, in the preliminary experiments, air was used and since it behaved in all respects as a perfectly inert gas, it was used in all the experiments.

The mixture of chlorine and air was stored in a glass carboy of about 45 liters capacity. A glass tube fitting tightly into the neck of the carboy was cemented in by a substance which goes by the trade name of "cementum," composed entirely of inorganic materials. The upper end of this tube was joined to a stopcock. The carboy after partial exhaustion was filled with the desired amount of chlorine, and dry air was then forced in until the pressure inside the carboy exceeded the external pressure by about one-third of an atmosphere. A considerable amount of calcium chloride was always kept in the carboy to act as a drying agent.

The chlorine was prepared in three different ways: first, by the action of concentrated hydrochloric acid on manganese dioxide; second, by forming the solid hydrate of chlorine from gas prepared by the first method, and then decomposing the hydrate; third, by the action of concentrated hydrochloric acid on an excess of potassium permanganate at room temperature.<sup>1</sup> We have no reason to believe that there was any difference

<sup>1</sup> This method has been investigated by Graebe, *Ber.*, 35, 43 (1902), and Lewis and Wedekind, *Z. angew. Chem.*, 22, 580 (1909), and shown to give a gas that is free from the oxides of chlorine.

in the potential of these three varieties of chlorine. In the preliminary measurements differences amounting to several millivolts, which were at first ascribed to impurities in the chlorine, proved later to be due, at least in large part, to an error of an entirely different character. The final series of measurements was made entirely with chlorine prepared by the third method. In every case the chlorine was thoroughly washed and dried before it entered the carboy. All connections between the source of chlorine and the carboy, as well as those between the carboy and the cell in which the potential was measured, were of glass, with the single exception of the cemented joint which we have already mentioned. Early experiments showed that the use of rubber or organic cements led to variable and incorrect results.

After the gas had remained in the carboy sufficient time to insure constancy of composition it was allowed to pass in a slow stream (about 5 cc. per minute) through the apparatus shown in Fig. 1. A is a washing device filled with acid of the same concentration as that used in the electrode chamber. It served to saturate the gas with moisture and also to remove any hydrochloric acid which might have remained in the gas. Passing through this portion of the apparatus the gas entered the electrode chamber at B; thence rising through the hydrochloric acid solution it passed out through the tube C. By means of the three-way cock D it could be then led off through the trap E or could be sent through the tube F to the apparatus for analyzing the gas, which is not shown in the figure.

The electrode chamber and the tube IK contained a solution of hydrochloric acid. The tube K was immersed in a vessel communicating with the standard electrode. Two stopcocks were placed in this tube and at least one of these stopcocks remained closed, the film of liquid remaining between the stopcock and its socket affording sufficient electrical contact. Lest, however, a potential difference establish itself between the two sides of the stopcock, two cocks were placed in series so that either one could be opened during the measurements. The electrode G was half immersed in the hydrochloric acid solution. It consisted of about  $1\frac{1}{2}$  sq. cm. of platinum-iridium foil (15 per cent. iridium) and was welded to a platinum-iridium wire sealed through the glass stopper H. The gas which passed through the cell was analyzed by passing it through a solution of potassium iodide to absorb the chlorine, and titrating the iodine set free against thiosulfate. The residual gas was collected and measured in a buret over water. Analyses of the same mixture were frequently made throughout a period of several days, but no appreciable change of composition was ever observed.

In the first experiments the chlorine potential was measured against the normal electrode, the end of this normal electrode and the tube K

of the cell shown in Fig. 1 being both immersed in an intermediate reservoir containing tenth-normal potassium chloride, when the cell was filled with tenth-normal hydrochloric acid, and twentieth-normal potassium chloride when twentieth-normal hydrochloric acid was used. A number of measurements were made with both these concentrations of acid and with

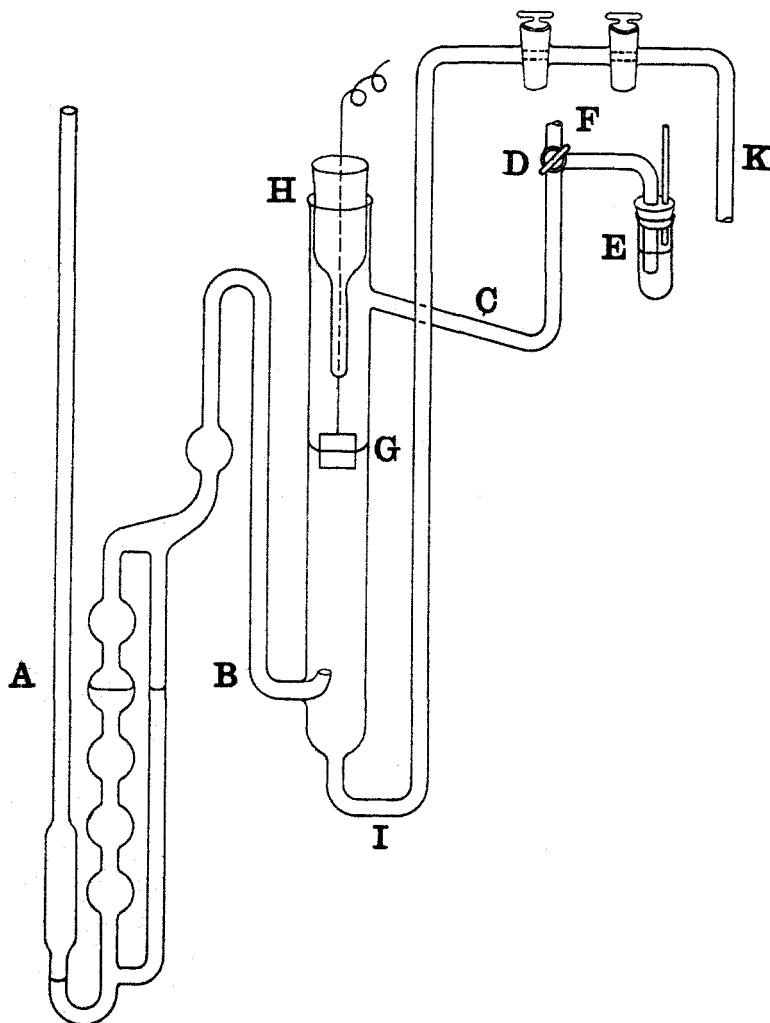


Fig. 1.

different pressures of chlorine gas ranging from 0.12–0.03 atmosphere. A single filling of the gas reservoir with chlorine served for a number of experiments, successive dilutions of the chlorine being made by partly exhausting the reservoir and refilling it with dry air under pressure.

Altogether in these first experiments eleven measurements were made with tenth-normal, and ten with twentieth-normal hydrochloric acid. From the observed electromotive forces the potential of chlorine at atmospheric pressure against a normal solution of chloride ion was calculated. In this calculation the potential of the normal electrode was taken as zero and a correction was made for the potentials between the liquids. This calculation need not be discussed further here, because it will be treated in detail in connection with the final series of measurements. The value thus obtained for the potential of the chlorine electrode was 1.082 volts for the tenth-normal solution, with an average deviation of 0.001 volt, and 1.083 for the twentieth-normal solution with an average deviation of 0.003. These results were all obtained with chlorine prepared in part by the first and in part by the second of the methods described above. A later series of 13 measurements in tenth-normal hydrochloric acid, with chlorine prepared by the third method, at pressures ranging from 0.20–0.05 atmosphere, gave the value 1.082 with an average deviation of 0.002 volt. These results were sufficient to indicate a substantial agreement between the measurements in tenth- and twentieth-normal hydrochloric acid and to fix the absolute potential of the chlorine electrode within a few millivolts.

It seemed, however, desirable to investigate a little more closely the cause of the observed deviations between the individual measurements, especially as these differences did not appear to be due to any lack of constancy in the chlorine electrode itself. In the experiments of Müller the potentials only became constant to within one or two millivolts after the lapse of many hours, while in our experiments a much higher constancy was obtained in from one to two hours. In one experiment the platinum-iridium foil which served as electrode was removed from the cell and highly charged with chlorine by electrolysis. When replaced in the cell the electromotive force returned within an hour and a half to within a few tenths of a millivolt of its former value, thus indicating that the potential is very nearly if not quite independent of the previous treatment of the electrode.

The source of error was finally traced to changes in the liquid potentials. A standard electrode was made with mercury and calomel in a tenth-normal solution of hydrochloric acid and the potential of this electrode against the normal electrode was measured with tenth-normal potassium chloride as an intermediate electrolyte. The electromotive force of this combination was found to change on standing, due doubtless to the inter-diffusion of the electrolytes. On renewing the liquids in the connecting tubes of the electrode cells, and in the intermediate vessel, the original value was obtained. These experiments indicated that the deviations of the previous measurements of the chlorine potential among

themselves might be largely or altogether due to changes in the liquid potentials, and that the best values from previous experiments were not, as we had supposed, those obtained after long standing, but the somewhat lower values reached after a comparatively short time.

In order to eliminate liquid potentials entirely we continued the series of measurements with chlorine prepared by the third method and with 0.1 *N* hydrochloric acid, the earlier results of which we have summarized above. Now, however, the measurements were made against the calomel electrode in 0.1 *N* hydrochloric acid instead of the normal electrode. The results of this change were extremely satisfactory. It was evident immediately that values much more constant and reproducible than those previously obtained could now be expected. The first experiment after this change was made with chlorine at a partial pressure of 0.049 atmosphere. The following table gives the several measurements of the electromotive force at the times (from the beginning of the experiment) given in the first column.

TABLE I.

Hours.	E. M. F.
1	1.0500
2 <sup>3</sup> / <sub>4</sub>	1.0507
3	1.0508
3 <sup>1</sup> / <sub>2</sub>	1.0508

New hydrochloric acid was now placed in the electrode vessel and the measurements were continued with the same chlorine mixture, with the following results:

TABLE II.

Hours.	E. M. F.
<sup>3</sup> / <sub>4</sub>	1.0507
1 <sup>1</sup> / <sub>2</sub>	1.0509
2	1.0509
6 <sup>1</sup> / <sub>2</sub>	1.0509
18	1.0506
19 <sup>1</sup> / <sub>2</sub>	1.0507
20 <sup>1</sup> / <sub>2</sub>	1.0507
22	1.0507
24	1.0508

Similar experiments were made with successive dilutions of the chlorine gas with equally satisfactory results. These results are given in Table III, in which the first column shows the percentage of chlorine by volume in the gaseous mixture; the second the atmospheric pressure, *P*, in millimeters; the third the partial pressure, *p*, of the chlorine in atmospheres; the fourth column gives the observed electromotive force *E*<sub>1</sub>; the fifth the electromotive force *E*<sub>2</sub>, calculated for chlorine at atmospheric pressure by the equation  $E_2 = E_1 - \frac{RT}{2F} \ln p$ .

TABLE III.

% Cl <sub>2</sub> .	P.	$\phi$ .	E <sub>1</sub> .	E <sub>2</sub> .
4.88	763	0.0490	1.0508	1.0895
4.88	767	0.0492	1.0509	1.0896
4.88	770	0.0495	1.0510	1.0896
2.47	[760]	0.0247	1.0421	1.0896
2.47	767	0.0249	1.0424	1.0898
2.47	746	0.0243	1.0419	1.0896
1.258	748	0.0124	1.0330	1.0894
1.258	754	0.0125	1.0330	1.0893
0.619	772	0.00629	1.0242	1.0892
0.619	775	0.00631	1.0243	1.0893
0.293	772	0.00298	1.0154	1.0900
0.293	760	0.00293	1.0150	1.0899
0.293	760	0.00293	1.0150	1.0899

Average, 1.0896

This series of results is eminently satisfactory. The average deviation of the figures in the last column from the mean is less than 0.0002 volt. Moreover, there is no apparent trend in the values as we proceed from the higher to the lower chlorine pressures. Indeed the small differences which exist between the values for different partial pressures of chlorine are doubtless due to inaccuracies in the analysis of the gas mixture. The agreement of the independent values obtained with the same gas mixture shows that our chlorine electrode is reproducible within about 0.0001 volt.

If our theory as to the cause of the early discrepancies in our work be true, we should expect the electromotive forces previously obtained to be concordant with those of Table III in those cases in which the boundaries between the electrolytes were known to have been freshly established. Four such cases were found in our note-book, belonging to the series of which the experiments in Table III form the conclusion. These four experiments are given in Table IV, where the columns have the same significance as in Table III, except that from the observed electromotive force is subtracted the measured potential between the normal electrode and the calomel electrode in tenth-normal hydrochloric acid, thus making these values comparable with those in Table III.

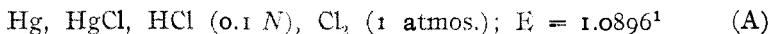
TABLE IV.

% Cl <sub>2</sub> .	P.	$\phi$ .	E <sub>1</sub> .	E <sub>2</sub> .
19.75	758	0.197	1.0941	1.0907
9.85	[760]	0.0985	1.0837	1.0892
4.88	[760]	0.0488	1.0747	1.0892
4.88	[760]	0.0488	1.0752	1.0896

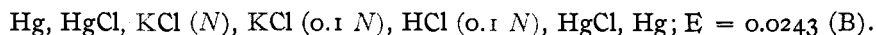
Average, 1.0897

The agreement is sufficient. We may conclude therefore that the poten-

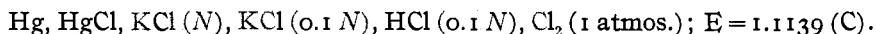
tial of the chlorine electrode, within the limits of experimental error, changes with the partial pressure of the chlorine by the theoretical amount, when the chlorine pressure varies between 0.20 and 0.003 atm. Starting with the value given in Table III for the electromotive force of the cell,



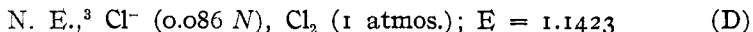
we may proceed in two entirely different ways to calculate the normal electrode potential of chlorine. We determined as the electromotive force of the combination,



Combining this with the above cell, we have



The potential between normal and tenth-normal potassium chloride will be neglected. That of HCl (0.1 *N*), KCl (0.1 *N*), is 0.0284.<sup>2</sup> We thus find for the above combination exclusive of liquid potentials; that is, for the combination,



if we take the degree of dissociation of tenth-normal HCl as 0.86, equal to that of KCl, for which assumption we have abundant evidence.

We may now make an entirely different calculation of the electromotive force of this same combination (D) from combination (A) which does not involve any liquid potentials. Since the concentration of chloride ion is the same in 0.1 *N* HCl as in 0.1 *N* KCl, the potential of the chlorine electrode against a 0.1 *N* KCl calomel electrode would be the same as that against the 0.1 *N* HCl calomel electrode except for liquid potentials, but the difference between the potential of the calomel electrode in *N* and 0.1 *N* KCl is 0.0528.<sup>4</sup> We have, then, only to add this value to the electromotive force of combination (A) to obtain once more that of combination (D), namely 1.1424. The agreement is excellent.

Finally we have only to reduce the results to normal concentration of chloride ion. From the Nerust equation we have

<sup>1</sup> The positive sign of *E* indicates the tendency of the current to pass from left to right.

<sup>2</sup> This value is obtained from the modified form of the Planck equation given by Lewis and Sargent, *THIS JOURNAL*, 31, 363 (1909). The equivalent conductivity of HCl (0.1 *N*) is taken as 389.9 (Lewis and Sargent), that of KCl (0.1 *N*) as 128.8 (Kohlrausch). The original equation of Planck leads to a very different value (0.0266) for this liquid potential.

<sup>3</sup> Normal electrode.

<sup>4</sup> This value is obtained from the measurements of Sauer, *Z. physik. Chem.*, 47, 146 (1904) at 18°, and the known temperature coefficients of the normal and decinormal electrodes.



$\text{Cl}_2$  (1 atm.),  $\text{Cl}^-$  (0.086 *N*),  $\text{Cl}^-$  (*N*),  $\text{Cl}_2$  (1 atm.);  $E = -0.0629$   
and adding this to combination (D) we find

$$\text{N. E.}, \text{Cl}^- (\text{N}), \text{Cl}_2 (1 \text{ atm.}); E = 1.0795$$

or

$$\text{Cl}_2 (1 \text{ atm.}), \text{Cl}^- (\text{N}), \text{N. E.}; E = -1.0795.$$

Wilsmore<sup>1</sup> gives as the potential of the chlorine electrode against the normal electrode  $-1.134$ . Müller,<sup>2</sup> in his summary, gives a value which reduces to  $-1.0702$  against the normal electrode. This value, however, was based on his measurements with normal hydrochloric acid. Between a hydrogen and a chlorine electrode both in 0.1 *N* hydrochloric acid, he obtained the electromotive force  $-1.4849$ . Assuming the hydrochloric acid to be 86 per cent. dissociated, this corresponds to a normal chlorine potential of  $-1.0761$ , and if we make Müller's correction for the hydrolysis of chlorine this value is raised to  $-1.0775$ , a value which differs by only 2 millivolts from our own.

#### Summary.

In order to eliminate complications due to hydrolysis of chlorine the potential of chlorine was measured at low partial pressures ranging from 0.2–0.003 atmosphere. Dry air used as a diluent behaved as a completely inert gas.

After the elimination of liquid potentials the potential of chlorine at low partial pressure was found to be constant and reproducible to about 0.0001 volt.

The values of the potential of chlorine at atmospheric pressure calculated from the potential at several low pressures agree among themselves with an average deviation from the mean of less than 0.0002 volt.

The electrode potential of chlorine at atmospheric pressure in chlorine ion at normal concentration was calculated from the observed electromotive forces by two independent methods. The results of these two methods were in excellent agreement, and the electrode potential of chlorine against the normal electrode is  $-1.0795$ , a value which is probably correct within two- or three-tenths of a millivolt.

This value differs widely from those given previously by Wilsmore and by Müller, but agrees within two millivolts with the value obtained by recalculation from the experiments of Müller in tenth-normal hydrochloric acid.

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<sup>1</sup> *Z. physik. Chem.*, 35, 291 (1900).

<sup>2</sup> *Loc. cit.*