showing such a difference which is due to an effect on the planetary electrons.

CHICAGO, ILL.

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THE EQUILIBRIUM BETWEEN CHLORINE AND PLUMBOUS AND PLUMBIC CHLORIDES IN AQUEOUS SOLUTION.

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1. Introduction.

Solutions of lead chloride in strong hydrochloric acid absorb chlorine in much larger quantities than can be accounted for by the solubility of the gas. The solutions exhibit a strong yellow color, and on the addition of ammonium chloride throw down a precipitate of clear yellow octahedral crystals. The composition of these crystals, which can be obtained in a state of great purity, has been found to be represented by the formula $(NH_4)_2PbCl_6$. Cesium and other chlorides produce precipitates of similar composition which in all cases are salts of the hypothetical acid, H_2PbCl_6. By treating the crystals of the ammonium salt with pure sulfuric acid at zero, there has been obtained the tetrachloride of lead, $PbCl_4$. This substance is a heavy yellowish oil, which reacts violently with water.

These facts suggest that the reaction occurring when chlorine is passed into a suspension of lead chloride in hydrochloric acid may be written as follows

$$PbCl_2(s) + Cl_2(g) + 2HCl = H_2PbCl_6; \text{ or}$$

$$PbCl_2(s) + 2Cl^- + Cl_2(g) = PbCl_6^{--}.$$

The purpose of this investigation was to determine the equilibrium conditions of this reaction, with a view also to estimating the plumbous-plumbic reduction potential. Experiments were also made with acid concentrations small enough to permit the precipitation of solid lead dioxide; and the free energy of this compound was calculated from the equilibrium conditions of the reaction

$$PbCl_2(s) + 2H_2O + Cl_2(g) = PbO_2(s) + 4HCl.$$

This research has been carried out with the coöperation of Professor A. A. Noyes and with the aid of the grant made to him by the Carnegie

Institution of Washington. For all this assistance I wish to express my great indebtedness.

2. Preparation of the Equilibrium Mixtures.

The solutions were prepared in a great variety of ways during the preliminary work in an effort to approach equilibrium from both sides. Two of these may be mentioned.

In the first of these preliminary methods glass bombs were filled with lead chloride, hydrochloric acid, and chlorine in such excess that a layer of liquid chlorine was present. After shaking a month at 25°, these bombs were cautiously opened, the excess of chlorine was allowed to escape, and the solutions were then quickly analyzed. The concentration of the complex was shown to be much higher than in solutions prepared at atmospheric pressure. The experiments made by this method established the reversibility of the reaction, even in extreme cases, and showed the influence of chlorine pressure; but it proved not to be susceptible of accurate manipulation.

The other preliminary method tried was the direct production of the lead complex in excess, by allowing lead tetrachloride to act on the acid solution. This method was used with some success, but was abandoned because of the laboriousness of preparing the lead tetrachloride in the pure state.

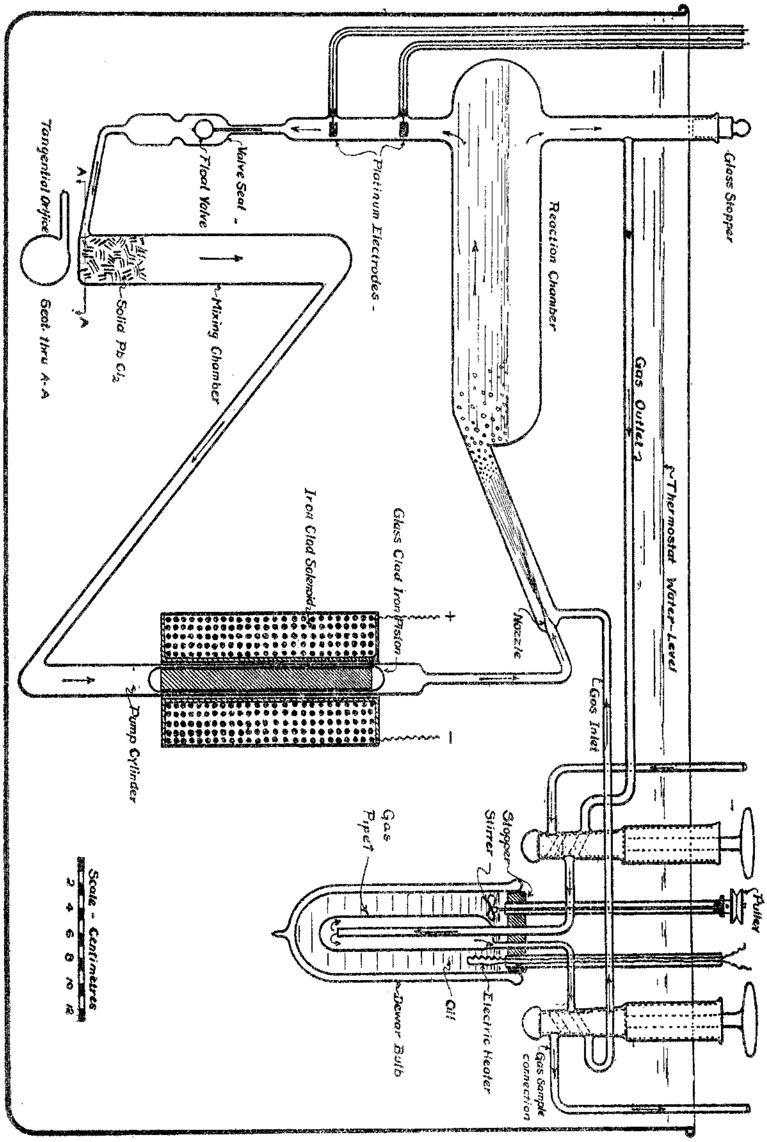
In the method finally adopted the equilibrium (at somewhat different chlorine pressures) was approached from both sides. Solutions of hydrochloric acid in contact with solid lead chloride were treated with chlorine (in the apparatus described below) for periods varying from days to weeks; and samples for analysis were taken. The same solution was then subjected to a lower chlorine pressure for another extended period, and analyses were again made. Even though equilibrium might not be fully reached in either case, it must certainly lie between the values obtained at the higher and lower chlorine pressures.

The chlorine employed was drawn as needed from a tank of electrolytic liquid chlorine. The lead chloride was purified by recrystallization from water.

3. Apparatus.

As the equilibrium conditions are only slowly attained, it is obvious that the chlorine pressure would not remain constant if the gas escaped against the fluctuating atmospheric pressure. Therefore, the systems worked with were always "closed," that is, they were not subject to atmospheric pressure; and the method employed was to stir together the liquid, solid, and gas, and to circulate the gas through some side bulb or pipet, so that a sample of the gas, as well as of the liquid, could be removed for analysis.

The first apparatus consisted of a horizontal glass tube 3 cm. in diameter with smaller vertical tubes at each end. The tops of these tubes were connected through a 25-cc. bulb joined to the tubes by short capillaries. The whole apparatus was then immersed in a thermostat and rocked slowly to and fro about a horizontal axis perpendicular to the plane of the apparatus, so that the liquid flowed repeatedly past the solid in the tube, and at the same time acted as a piston on the gas, forcing it back and forth through the 25-cc. bulb. In the use of this apparatus, a rather



surprising difficulty was met with. The plan was to seal off the 25-cc. bulb as a gas sample; but it was unexpectedly found that considerable quantities of water collected in the capillaries and in the bulb. This form of apparatus was, therefore, abandoned.

After a great deal of experimenting the aparatus shown in the figure was devised. In this apparatus a "gas-pipet" provided with two 3-way stopcocks was introduced between the "gas inlet" and "gas outlet," it being placed in the thermostat within a "Dewar bulb," which was maintained by electric heating at a temperature one degree higher than the rest of the system to prevent condensation. An essential part of the apparatus is the magnetic pump. This consists of an "iron-clad solenoid" and of a "pump-cylinder," within which is a glass-covered bar of iron serving as the piston. The terminals of the solenoid are connected to the 110-volt circuit through a switch operated at intervals of 10 or 15 seconds by a cam (not shown in the sketch). When the solenoid is activated the piston snaps up into the position shown in the drawing, forcing a stream of solution through the "nozzle." This stream of liquid carries large quantities of gas into the main "reaction chamber;" and this gas then circulates through the "gas outlet" and the "gas-pipet" back into the apparatus at the "gas inlet." At the same time, a stream of liquid flows down past the glass "float-valve" and through the "mixing chamber," where it stirs the solid lead chloride thoroughly. When the solenoid is disconnected from the electric circuit the float valve has already closed, and the piston slowly settles to the bottom of the cylinder, restrained by the slow flow of the liquid up the narrow annular space between the piston and the cylinder. All glass connections, including those with the gas-pipet, were made by fusing the parts together.

The only stopcocks were those on the gas-pipet; these were lubricated with paraffin which had been chlorinated at a little above its melting point until on cooling it became of the consistency of vaseline, after which it reacted only very slightly with the chlorine.

In the upright tube between the "reaction chamber" and the "float-valve" were sealed 2 platinum wires enlarged at the ends into disks. These were platinized and served as electrodes to determine the conductance of the solution.

It is hoped that the general plan of this apparatus will be of use in many other investigations. It is frequently desirable to have thorough stirring in an absolutely closed glass system which cannot be rotated or shaken; and there is probably no other method so simple and energetic as this magnetic pump.

4. Methods of Analysis.

The gas pipet was disconnected from the rest of the apparatus by turning the 3-way cocks; the chlorine contained in it was completely driven out by a slow stream of carbon dioxide gas into potassium iodide solution; and the iodine liberated was titrated with thiosulfate. From the known volume and temperature of the pipet the partial pressure of chlorine was calculated with the aid of the perfect-gas law.

Samples of the solution for the analyses were withdrawn into a vacuum pipet. This was done by fitting the pipet with an extension tube, which passed through the opening ordinarily closed by the "glass stopper." The extension tube was thrust 7 or 8 cm. below the surface of the liquid so as to get a sample not affected by the change in chlorine pressure at the surface, which might arise from diffusion of air admitted by the removal of the stopper. In most of the experiments 2 samples were analyzed. In one the lead was determined directly as chloride by evaporating the solution in platinum dishes. In the other the oxidizing chlorine was determined by drawing potassium iodide solution into the vacuum pipet and titrating the liberated iodine in the pipet itself, it having been proved by experiments with known solutions that the presence of lead does not affect the titration.

5. Solubility of Chlorine Gas and of Lead Chloride in Hydrochloric Acid Solutions.

In calculating the concentration of the substances involved in the equilibrium, there is needed, in addition to the analytical data, the solubilities of chlorine gas and of solid lead chloride in the various solutions. The solubilities of the chlorine in hydrochloric acid solutions were obtained as will now be described; and in the subsequent computations with the equilibrium mixtures it is assumed that these solubilities are not influenced by the extent to which the hydrochloric acid initially present is converted into chloroplumbic acid.

The solubility of chlorine in hydrochloric acid of various concentrations was determined in the same apparatus and by the same method as that used in the equilibrium experiments. The values at 25° of the distribution-ratio (that is, the ratio of the millimols of Cl_2 per 1000 g. of water to the partial pressure of the chlorine gas in atmospheres) for various concentrations of hydrochloric acid were found to be as given in Table I. The partial pressures are calculated here, and also in the main equilibrium experiments, from the concentration of the chlorine in the gas with the aid of the perfect-gas law.

TABLE I.—SOLUBILITY OF CHLORINE IN HYDROCHLORIC ACID SOLUTIONS.

Millimols of HCl in 1000 g. of water.........	103.7	286.0	802.0
Distribution-ratio.........................	62.3	60.0	61.1

For the solubility of lead chloride in hydrochloric acid solutions the data of von Ende[1] were used, his values having been checked at 3 points

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[1] *Z. anorg. Chem.*, 26, 129 (1901).

by determinations of my own. A plot of his values was made for interpolating at the special concentrations involved in the equilibrium mixtures.

6. The Results of the Equilibrium Measurements.

Fifteen equilibrium mixtures were prepared and analyzed. In the first 8 of these the formation of the complex was independently derived both by determining the total lead content and the content in oxidizing chlorine; in the last 7 the latter was alone determined. In 11 of the experiments the chloride initially present was only hydrochloric acid; while in the 4 other experiments this was partially replaced by sodium chloride, with the object of determining whether the equilibrium was affected by the hydrogen ion concentration when the chloride ion concentration was kept constant.

The data resulting from the analysis of the equilibrium mixtures and the values computed from them are given in Tables II and III, which are for the most part self-explanatory.

The temperature was always 25°. All concentrations, indicated by symbols in parentheses, are expressed in millimols per 1000 g. of water.

The sodium thiosulfate solution used for titrating the chlorine gas sample and the oxidizing chlorine (ΣCl_2) in the solution was 0.09711 *N* in Expts. 1–6, and 0.09763 *N* in Expts. 7–15.

The lead chloride present as such in the equilibrium mixtures was obtained, with the aid of the plot of von Ende's data above referred to, on the basis of the assumption that the solubility in the mixtures is determined solely by the concentration of the uncombined chloride in it; that is, by that quantity of the hydrochloric acid and sodium chloride initially present which has not been converted into chloroplumbate complex. According to whether this complex is assumed to be $PbCl_6^{--}$ or $PbCl_5^-$, this uncombined chloride has different values, which are found by subtracting from the initial (HCl) or (HCl + NaCl) in the one case twice the concentration of the chloroplumbate complex, and in the other case the concentration itself of that complex. And correspondingly 2 values of the lead chloride present as such, represented by $(PbCl_2)_1$ and $(PbCl_2)_2$ in the tables,[1] were derived from the plot. By subtracting these last quantities from the total lead content (ΣPb) as found by the gravimetric analysis, the concentration of the chloroplumbate complex $(\Delta Pb)_1$ or $(\Delta Pb)_2$, was found. This procedure evidently requires for the determination of either quantity a knowledge of the other; but this difficulty was met by first estimating approximately the complex concentration, and then making a series of successive approximations.

The concentration of free chlorine (Cl_2) in the solution was found by

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[1] In general, symbols with the subscript 1 denote quantities computed under the assumption that the complex acid is H_2PbCl_6; those with the subscript 2 under the assumption that the complex acid is $HPbCl_5$.

multiplying the partial pressure p_{Cl} by the value of the distribution ratio given in Table I for a hydrochloric acid concentration equal to the initial total chloride concentration (HCl + NaCl) in the mixture. By subtracting this chlorine concentration from the total oxidizing chlorine content (ΣCl_2) as determined by the titration of samples of the solution, an independent value, denoted[1] by (ΔCl_2), of the chloroplumbate concentration was obtained. A comparison of these values of (ΔCl_2) with those of $(\Delta Pb)_1$, and $(\Delta Pb)_2$ shows the agreement of the 2 analytical methods.

The concentration of the chloride ion constituent in the solution, represented for the 2 cases of complex formation in the tables by $(Cl^-)_1$ and $(Cl^-)_2$ is found by the expressions:[2]

$$(Cl^-)_1{}' = (HCl + NaCl) - 2(\Delta Pb)_1 + 2(PbCl_2)_1{}',$$

or $$(Cl^-)_1{}'' = (HCl + NaCl) - 2(\Delta Cl_2) + 2(PbCl_2)_1{}''.$$

$$(Cl^-)_2{}' = (HCl + NaCl) - (\Delta Pb)_2 + 2(PbCl_2)_2{}',$$

or $$(Cl^-)_2{}'' = (HCl + NaCl) - (\Delta Cl_2) + 2(PbCl_2)_2{}''.$$

Equilibrium constants were calculated under the 2 assumptions that the chloroplumbate complex has the formula $PbCl_6^{--}$ and that it has the formula $PbCl_5^-$; and that, correspondingly, the equilibrium involved is that of the first or second of the following reactions:

$$PbCl_2(s) + Cl_2(g) + 2Cl^- = PbCl_6^{--}.$$

$$PbCl_2(s) + Cl_2(g) + Cl^- = PbCl_5^-.$$

The corresponding mass-action expressions are:

$$\frac{(PbCl_6^{--})}{(Cl^-)^2(p_{Cl})} = K_1; \text{ and } \frac{(PbCl_5^-)}{(Cl^-)(p_{Cl})} = K_2$$

In calculating the values of the equilibrium constants by these equations, the concentrations were expressed in mols (instead of millimols), and the ionization of all the substances was assumed to be complete. This assumption probably does not lead to results very far from the truth, owing to the partial compensation of the incomplete ionization of the hydrochloric acid by that of the $HPbCl_5$ or H_2PbCl_6.

7. Discussion of the Equilibrium Results.

An examination of the equilibrium constants given in Tables II and III shows that the check determinations on the same mixture by the same analytical method are in general in good agreement, the average devia-

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[1] These symbols (ΔPb) and (ΔCl_2) used for the chloroplumbate complex are increments in the sense that they represent the increase in lead content or oxidizing chlorine content that results from formation of the complex.

[2] In general, symbols to which single "accents" are appended, denote quantities calculated from the determination of the lead content; those to which double "accents" are attached denote quantities calculated from the determination of the oxidizing chlorine content.

TABLE II.—THE RESULTS OF THE EQUILIBRIUM MEASUREMENTS.

Equilibrium Mixture. No.	1.	2.	3.	4.	5.	6.	7.	8.
Initial concentration of acid (HCl)	103.7	103.7	103.7	103.7	286.0	286.0	286.0	286.0
Cc. $Na_2S_2O_3$ for Cl_2 in 62.01 cc. of gas	47.36	44.69	48.30	37.01	46.46	40.96	47.40	38.02
Partial pressure of Cl_2 in atmospheres (p_{Cl})	0.905	0.854	0.924	0.708	0.888	0.783	0.906	0.727
Grams of sample for lead determination	49.21	55.57	47.59	51.46	47.27	38.16	58.87	65.44
Grams of $PbCl_2$ found in this sample	0.3210	0.3592	0.3104	0.3094	0.3441	0.2607	0.4352	0.4228
Total lead content (ΣPb)	23.71	23.49	23.71	21.83	26.78	25.14	27.29	23.73
$(PbCl_2)'_1$ from solubility plot, assuming H_2PbCl_6	17.31	17.26	17.31	16.90	8.36	8.32	8.40	8.28
$(\Delta Pb)_1$ equal to $(\Sigma Pb) - (PbCl_2)'_1$	6.40	6.23	6.40	4.93	18.42	16.82	18.89	15.45
$(PbCl_2)_2'$ from solubility plot, assuming $HPbCl_5$	16.44	16.40	16.44	16.28	7.94	7.90	7.98	7.86
$(\Delta Pb)_2$ equal to $(\Sigma Pb) - (PbCl_2)_2'$	7.27	7.09	7.27	5.55	18.84	17.24	19.31	15.87
$(Cl^-)_1'$ equal to $(HCl) - 2(\Delta Pb)_1 + 2(PbCl_2)_1'$	125.5	125.7	125.5	127.6	265.9	269.0	265.0	271.7
$(Cl^-)_2'$ equal to $(HCl) - (\Delta Pb)_2 + 2(PbCl_2)_2'$	129.3	129.4	129.3	130.7	284.1	284.6	282.7	293.8
Grams of sample for oxidizing chlorine	32.95	28.69	37.57	25.16	19.83	27.03	21.08	23.36
Cc. $Na_2S_2O_3$ solution used for this sample	42.53	33.54	48.34	25.02	29.20	35.02	31.49	28.30
Oxidizing chlorine content (ΣCl_2)	63.1	57.5	63.0	48.9	72.0	63.3	73.1	59.2
(Cl_2) from p_{Cl} by distribution ratio	56.4	53.2	57.2	44.2	53.3	47.0	54.4	43.6
(ΔCl_2) equal to $(\Sigma Cl_2) - (Cl_2)$	6.7	4.3	5.8	4.7	18.7	16.3	18.7	15.6
$(PbCl_2)_1''$ from solubility plot, assuming H_2PbCl_6	17.4	16.8	17.2	16.9	8.4	8.3	8.4	8.3
$(PbCl_2)_2''$ from solubility plot, assuming $HPbCl_5$	16.4	16.2	16.3	16.2	8.4	8.3	8.4	8.3
$(Cl^-)_1''$ equal to $(HCl) - 2(\Delta Cl_2) + 2(PbCl_2)_1''$	125.1	128.6	126.4	128.0	265.4	270.0	265.4	271.4
$(Cl^-)_2''$ equal to $(HCl) - (\Delta Cl_2) + 2(PbCl_2)_2''$	129.8	131.8	130.5	131.4	284.1	286.3	284.1	287.0
K_1' equal to $1000(\Delta Pb)_1 \div [((Cl^-)_1')^2 p_{Cl}]$	0.449	0.462	0.440	0.428	0.293	0.297	0.297	0.288
K_1' mean	**0.445**		(A.D., 0.005)		**0.294**		(A.D., 0.002)	
K_1'' equal to $1000(\Delta Cl_2) \div [((Cl^-)_1'')^2 p_{Cl}]$	0.473	0.304	0.393	0.405	0.299	0.285	0.293	0.291
K_1'' mean	**0.394**		(A.D., 0.022)		**0.292**		(A.D., 0.002)	
K_2' equal to $(\Delta Pb)_2 \div [(Cl^-)_2' p_{Cl}]$	0.0621	0.0641	0.0608	0.0600	0.0747	0.0774	0.0754	0.0743
K_2' mean	**0.0617**		(A.D., 0.0007)		**0.0754**		(A.D., 0.0005)	
K_2'' equal to $(\Delta Cl_2) \div [(Cl^-)_2'' p_{Cl}]$	0.0570	0.0382	0.0481	0.0505	0.0703	0.0728	0.0725	0.0746
K_2'' mean	**0.0485**		(A.D., 0.0047)		**0.0726**		(A.D., 0.0005)	

Table III.—Results of the Equilibrium Measurements.

Equilibrium Mixture. No.	9.	10.	11.	12.	13.	14.	15.
Initial concentration acid (HCl)	802	802	802	286	286	103.7	103.7
Initial concentration of chloride (HCl + NaCl)	802	802	802	802	802	286.0	286.0
Cc. $Na_2S_2O_3$ solution for Cl_2 in 62.01 cc. of gas	40.85	48.81	41.86	46.19	42.61	49.42	43.30
Partial pressure of Cl_2 in atmospheres (p_{Cl})	0.786	0.824	0.806	0.889	0.821	0.952	0.84
Grams of sample for oxidizing chlorine	16.84	23.36	20.54	25.13	17.14	51.99	40.97
Cc. $Na_2S_2O_3$ solution used for this sample	37.78	55.67	48.03	51.16	36.44	77.60	53.95
Oxidizing chlorine content (ΣCl_2)	111.7	118.8	117.0	102.5	106.7	73.5	64.8
(Cl_2) from (p_{Cl}) by distribution ratio	48.8	51.2	50.0	55.2	51.0	57.1	50.0
(ΔCl_2) equal to (ΣCl_2) —(Cl_2)	62.9	67.6	67.0	47.3	55.7	16.4	14.9
$(PbCl_2)_1$ from solubility plot, assuming H_2PbCl_6	4.9	4.9	4.9	4.8	4.8	8.3	8.3
$(PbCl_2)_2$ from solubility plot, assuming $HPbCl_5$	4.8	4.8	4.8	4.7	4.7	7.9	7.9
$(Cl^-)_1$ equal to $(HCl + NaCl) - 2(\Delta Cl_2) + 2(PbCl_2)_1$	686	677	678	717	701	270	273
$(Cl^-)_2$ equal to $(HCl + NaCl) - (\Delta Cl_2) + 2(PbCl_2)_2$	750	745	745	764	755	285	287
K_1 equal to $1000\,(\Delta Cl_2) \div [(Cl^-)_1^2\, p_{Cl}]$	0.170	0.178	0.180	0.103	0.114	0.236	0.238
K_1 mean	0.176	(A.D., 0.002)		0.108		0.237	
K_2 equal to $1000\,(\Delta Cl_2) \div [(Cl^-)_2\, p_{Cl}]$	0.107	0.109	0.112	0.070	0.090	0.060	0.061
K_2 mean	0.109	(A.D., 0.001)		0.080		0.061	

tion of the mean (the A. D. values[1]) exceeding about 1% in only 3 out of the 14 sets of values. Moreover, those based on the determination of the total oxidizing chlorine agree with those based on that of the total lead content in the case of the solutions of medium concentration (HCl = 286.0), but not in the case of the most dilute solution (HCl = 103.7) for which the values based on the chlorine determinations are obviously affected by fairly large errors.

It may also be pointed out that, while the partial pressure of the chlorine gas was not varied within wide limits, yet within the limits involved the concentration of the complex formed is proportional to the partial pressure. This is seen best by comparing Expts. 3 and 4 and Expts. 7 and 8, in which the chlorine pressure differs in the ratio about 9:7, while the corresponding equilibrium constants differ by only 1 to 3%.

The further conclusions to be drawn appear much more clearly from a consideration of the summary of best values derived from the means in the preceding tables and presented in Table IV.

TABLE IV.—BEST VALUES OF THE EQUILIBRIUM CONSTANTS.

HCl in mols	0.104	0.104	0.286	0.286	0.802
HCl + NaCl in mols	0.104	0.286	0.286	0.802	0.802
$K_1 = (PbCl_6^{--})/p_{Cl}(Cl^-)^2$	0.44	0.24	0.29	0.11	0.18
$K_2 = (PbCl_5^-)/p_{Cl}(Cl^-)$	0.062	0.061	0.074	0.080	0.109

An examination of the values in Table IV leads to the following conclusions.

The values of K_1 (corresponding to the complex $PbCl_6^{--}$) increase somewhat each time the acid concentration is increased, while the total chloride is kept constant; but they decrease very rapidly each time the total chloride concentration is increased, while the acid concentration is kept constant; thus between the acid concentrations 0.104 and 0.802 N the value of K_1 varies 2.5 fold. This fact makes it clear that the plumbic lead is not present mainly in the form of the complex acid $H_2^+PbCl_6^{--}$.

The values of K_2 (corresponding to the complex $PbCl_5^-$), on the other hand, remain remarkably constant each time the total chloride concentration is increased while the hydrogen ion concentration is kept constant. This fact indicates that $H^+PbCl_5^-$ is the complex acid which is mainly present in these moderately dilute solutions. The values of K_2 do however, increase not inconsiderably (20–40%) each time the acid concentration is increased while the total chloride concentration is kept constant. This shows that hydrogen ion has an effect of secondary magnitude on the equilibrium—an effect arising perhaps from a more rapid decrease in the ionization of the complex acid $HPbCl_5$ than in that

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[1] These are calculated by the expression $\Sigma\delta/(n\sqrt{n})$, where $\Sigma\delta$ is the sum of the deviations of the separate values from the mean value, and n is the number of these separate values.

of hydrochloric acid, with increasing concentration. The fact that the effect of increasing the hydrogen ion concentration is to increase the proportion of complex in the solution, and not to decrease it, shows that there is no considerable hydrolysis of the complex into such products as $HPbCl_4(OH)$. The fact that the solid salts that have been separated are salts of the acid H_2PbCl_6, and not of $HPbCl_5$, is doubtless because the former acid is produced, in accordance with the mass-action law, in considerable proportion in hydrochloric acid solutions of larger concentrations than those involved in these measurements.

For the equilibrium constant $(PbCl_5^-)/(Cl^-)p_{Cl}$ of the complex ion $PbCl_5^-$ the mean of the values obtained with the 4 more dilute acid solutions may be adopted, namely the value **0.070**; the concentrations being expressed in mols per 1000 g. of water, the partial pressure of the chlorine being given in atmospheres, and the ionizations of the hydrochloric acid and $HPbCl_5$ being assumed equal. If greater accuracy is desired, the equilibrium constant may be expressed as a function of the concentration c_H of the hydrogen ion constituent, namely by the equation $K_2 = 0.055 + 0.07\ c_H$; and 0.055 may be regarded as the value for complete ionization of the hydrochloric and the chloroplumbic acids.

8. Computation of the Plumbous-Plumbic Reduction Potential.

From the mean value (0.070) of the equilibrium constant derived in the last section we may calculate by the familiar thermodynamic expression $-\Delta F = R\ T \log K$ the free energy decrease attending the reaction

$$PbCl_2(s) + Cl_2(1\ \text{atm.}) + Cl^-(1\ M) = PbCl_5^-(1\ M).$$

By proper substitutions the equation becomes $-\Delta F = 8.31 \times 298.1 \times 2.303 \log_{10} 0.070$, and the free energy decrease is thus found to be -6590 joules.

The above reaction results when 2 faradays (2 F or 193,000 coulombs) of electricity are passed from left to right through the cell,

$$PbCl_2(s),\ PbCl_5^-(1\ M) + Cl^-(1\ M)\ ||\ Cl^-(1\ M),\ Cl_2(1\ \text{atm.}).$$

The electromotive force of this cell is, therefore, $-6590/193000$, or -0.034 volt. The value corresponding to the equilibrium constant 0.055 for complete ionization is -0.037 volt. Adding to the value -0.034 the specific electrode potential of chlorine, that is, the electromotive force (-1.356 volts) of the cell[1]

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[1] This value is derived as follows. From a critical consideration of the measurements of Wolff (*Z. Elektrochem.*, 20, 19 (1914)), and of Lewis and Rupert (THIS JOURNAL, 33, 306 (1911)), made by J. B. Dickson in this laboratory, 1.086 volts has been obtained as the best value of the electromotive force at 25° of the cell $Hg + Hg_2Cl_2$ (s), HCl (xM), $Cl_2(1\ \text{atm.})$. Noyes and Ellis (THIS JOURNAL, 39, 2541 (1917), found 0.270 volt for the cell $H_2(1\ \text{atm.}),\ H^+\ (1\ M)\ ||\ Cl^-(1\ M), Hg_2Cl_2\ (s) + Hg$. Taking the sum of these 2 quantities and changing its sign, we get -1.356 volts as the specific electrode-potential of chlorine.

$$Cl_2(1\ \text{atm.}),\ Cl^-(1\ M)\ ||\ H^+(1\ M),\ H_2(1\ \text{atm.}),$$

we obtain —1.390 volts for the electromotive force of the cell

$$PbCl_2(s),\ PbCl_5^-(1\ M) + Cl^-(1\ M)\ ||\ H^+(1\ M),\ H_2(1\ \text{atm.}).$$

This is the specific electrode potential or reduction potential of the combination constituting the left-hand part of this cell.

The corresponding reduction potential of the combination Pb^{++} $(1\ M) + Cl^-(1\ M) + PbCl_5^-(1\ M)$ may be found by noting that the solubility-product[1] of plumbous chloride, $(Pb^{++}) \times (Cl^-)^2 = 0.0000418$, is the value of (Pb^{++}) in a solution 1-molal in Cl^-, and that the reduction potential is increased by the amount $(R\ T/2\ F) \log (1/Pb^{++})$ when the plumbous ion concentration is increased from (Pb^{++}) to 1-molal. The value of this expression when $(Pb^{++}) = 4.18 \times 10^{-5}$ is + 0.130 volt, and the specific reduction potential of the $Pb^{++} + PbCl_5^- + Cl^-$ combination is, therefore, —1.260 volts.

9. Determination of the Equilibrium in the Presence of Lead Dioxide.

At somewhat lower concentrations of acid than those involved in the preceding equilibrium measurements the hydrolysis of the chloroplumbic acid goes so far that lead dioxide is precipitated according to the equation:

$$HPbCl_5 + 2H_2O = 5HCl + PbO_2(s)$$

The corresponding reaction starting with solid lead chloride is:

$$PbCl_2(s) + 2H_2O + Cl_2(g) = Pb_2O(s) + 4HCl$$

The reaction was first studied in the apparatus used for the previous measurements. The resistance of the solution, measured between the pair of platinized electrodes sealed into the apparatus as shown in the figure, served as an index of equilibrium. This test is very sensitive, inasmuch as 4 hydrochloric acid molecules are formed for each molecule of plumbous chloride that reacts.

The reaction was found to take place much more slowly than in the preceding measurements; and, since in this case an error in the measurement of the partial pressure of the chlorine produces little error in the result, a simpler apparatus was devised which made it possible to carry on several experiments at the same time. This apparatus consisted of 4 tubes, 3 cm. in diameter and 25 cm. long, lying side by side in a horizontal position. The tubes were half filled with liquid; and chlorine gas was passed in series through the spaces above the liquid, escaping finally at atmospheric pressure. The whole arrangement was given a reciprocating motion in a horizontal plane by means of a motor and eccentric. Connection with the chlorine source was maintained through a flexible system of spiral glass tubes, entirely free from rubber joints.

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[1] Taking the molal solubility as 0.0389 (Noyes, *Z. physik. Chem.*, 9, 623 (1892)) and the ionization as 0.562 as derived from the conductance ratio (Hunt, THIS JOURNAL, 33, 802 (1911); see also THIS JOURNAL, 39, 1543 (1917).

Two of these tubes were filled with lead chloride and distilled water, and two with 0.2 *N* hydrochloric acid, solid lead chloride, and solid lead dioxide. The dioxide used in one experiment was prepared by precipitating it electrolytically on a platinum anode; that used in another experiment was made by diluting a chloroplumbic acid solution with water. Chlorine was passed through; and at intervals of several days the resistances of a certain conductivity cell of pipet form filled successively with the several solutions was determined. The results are tabulated in Table V.

TABLE V.—RESISTANCE OF THE EQUILIBRIUM MIXTURES WITH LEAD CHLORIDE AND DIOXIDE.

Initial State.	4 days.	7 days.	11 days.	17 days.
$PbCl_2(s) + H_2O$	365	332	310	298
$PbCl_2(s) + H_2O$	334	320	310	300
$PbCl_2(s) + PbO_2$(electrolytic) + 0.2 *N*.HCl	294	294	295	295
$PbCl_2(s) + PbO_2$(precipitated) + 0.2 *N*.HCl	235	269	272	273

From the results in Table V the mean resistance of the final equilibrium mixture is found to be 292 ± 5 ohms. This value, which is the resistance in ohms of the pipet cell filled with the equilibrium mixture, was compared with the resistances of the same cell filled with known hydrochloric acid solutions saturated with lead chloride. By this comparison the concentration of the acid ($HCl + HPbCl_5$) in the equilibrium mixture was found to be 0.099 molal. This method of comparison is reliable since previous measurements had shown that there is only a small change in resistance when a hydrochloric acid solution saturated with lead chloride is saturated with chlorine gas.

10. Computation of the Free Energy of Lead Dioxide.

From the value (0.099 molal) of the acid concentration in the equilibrium mixture and from the equilibrium constant K_2 (0.062) at this concentration, we may compute the fraction x of the total acid that is in the form of the complex acid by means of the equation

$$K_2 = \frac{(PbCl_5^-)}{(Cl^-)p_{Cl}} = \frac{0.099x}{(0.099 - 0.099x + 0.034^a)\ 0.97} = 0.062.$$

[a] This term is equal to $2(PbCl_2)$, that is, twice the concentration of lead chloride present as such in the solution as read off the solubility plot.

The value of x is thus found to be 0.076, and that of the chloride ion constituent in the solution (as given by the parenthesis in the preceding expression) to be 0.125 molal.

The equilibrium constant K of the reaction

$$PbCl_2(s) + Cl_2(g) + 2\ H_2O = PbO_2(s) + 4\ H^+Cl^-$$

is, therefore, given by the expression

$$K = \frac{(H^+)^4(Cl^-)^4}{p_{Cl}} = \frac{(0.099)^4\ (0.125)^4}{0.97} = 2.4 \times 10^{-8}.$$

For the corresponding free energy decrease, when the concentrations of H^+ and of Cl^- are one molal and the partial pressure of Cl_2 is one atmosphere, we have

$$-\Delta F = R\ T \log K = 8.31 \times 298.1 \times 2.303 \log_{10} 2.4 \times 10^{-8} = -43{,}500 \text{ joules.}$$

This reaction takes place when 2 faradays are passed from left to right through the cell

$$\left.\begin{matrix}PbCl_2(s)\\ PbO_2(s)\end{matrix}\right\} Cl^-(1\ M) + H^+(1\ M)\ ||\ Cl^-(1\ M),\ Cl_2(1\ \text{atm.}).$$

The electromotive force of this cell is, therefore, —43,500/193,000 or —0.225 volt.

Adding to this the specific electrode potential of the chlorine electrode we get —1.581 volts as the specific electrode potential of the $PbCl_2$, PbO_2 half-cell referred to the molal hydrogen electrode.

Adding to this the quantity (+0.130 volt) computed in the last section for changing the Pb^{++} concentration to one molal from that prevailing in a solution one molal in chloride ion saturated with plumbous chloride, we get —1.451 volts as the specific electrode potential of $Pb^{++} + PbO_2(s) + H^+$.

Adding this to the specific electrode potential (+0.132)[1] of Pb(s), Pb^{++} we get —1.319 volt as the electromotive force of the double cell

$$Pb(s),\ Pb^{++}(1\ M)\ ||\ H^+(1\ M),\ H_2;\ Pb^{++}(1\ M) + H^+(1\ M),\ PbO_2(s)\ ||\ H^+(1\ M),\ H_2.$$

In this double cell when 2 faradays pass from left to right the following reaction takes place

$$Pb(s) + 2\ H_2O = PbO_2(s) + 2\ H_2(1\ \text{atm.}).$$

The free energy decrease attending this reaction is, therefore, 193,000 × (—1,319) or —254,600 joules.

This same reaction evidently takes place when 4 faradays are passed through the cell

$$Pb(s) + PbO_2(s) + H^+(1\ M),\ H^+(1\ M),\ H_2(1\ \text{atm.}).$$

The electromotive force of this cell, or the specific electrode potential of the combination Pb(s), $PbO_2(s) + H^+$ is, therefore, —254,600/386,000 or —0.660 volt.

Finally, by adding to the free-energy equation just derived,

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[1] Noyes and Toabe (This Journal, 39, 1544 (1917)) found 0.132 for this potential; while Lewis and Brighton (This Journal, 39, 1909 (1917)) found 0.1295. The first of these values is here employed, since it was derived from cells involving lead chloride, using the same ionization value, namely that corresponding to the conductance ratio.

$$Pb(s) + 2H_2O = PbO_2(s) + 2H_2(1\ atm.) - 254{,}600\ joules,$$

the following one computed by Lewis and Randall,[1]

$$2H_2(1\ atm.) + O_2(1\ atm.) = 2H_2O + 473{,}600\ joules,$$

we get for the free energy of formation of lead dioxide

$$Pb(s) + O_2(1\ atm.) = PbO_2(s) + 219{,}000\ joules.$$

11. Summary.

In this article has been described an investigation of the equilibrium between solid plumbous chloride and chlorine in hydrochloric acid solutions, including the case where the acid is so dilute that lead dioxide separates as a solid phase. The apparatus required for accurate experiments on this equilibrium has been represented by a detailed drawing and has been fully described.

The results of this investigation show that the complex chloroplumbic acid has the composition $HPbCl_5$; for with a given chlorine pressure the quantity of this complex acid present in equilibrium with solid plumbous chloride was found to be proportional to the first power of the chloride ion concentration. The hydrogen ion concentration, which would not be involved in the equilibrium if the ionization of the substances were complete, was found to have a small secondary effect, probably owing to an influence on the ionization of the chloroplumbic acid.

The equilibrium constant corresponding to the expression $(PbCl_5^-)/(Cl^-)p_{Cl}$ is given by the expression $K' = 0.055 + 0.07\ c_H$, the concentrations being expressed in mols per 1000 g. of water, the partial pressure of the chlorine being given in atmospheres, and the ionizations of hydrochloric acid and $HPbCl_5$ being assumed equal.

The equilibrium constant of the reaction $PbCl_2(s) + Cl_2(g) + 2H_2O = PbO_2(s) + 4H^+Cl^-$, as given by the expression $K = (H^+)^4(Cl^-)^4/p_{Cl}$ was found to be 2.4×10^{-8}, under the assumption that the ionization of the hydrochloric acid and $HPbCl_5$ is complete.

From these equilibrium constants and from other data existing in the literature the values of the free energy decreases at 25° were calculated for the case that the concentrations of all dissolved substances are one molal (except that of the chlorine whose partial pressure is one atmosphere), and were found to be those expressed by the following free energy equations:

$PbCl_2(s) + Cl_2(g) + Cl^- = PbCl_5^- - 6590$ joules.

$PbCl_2(s) + 2H_2O + Cl_2(g) = PbO_2(s) + 4H^+Cl^- - 43{,}500$ joules.

$Pb(s) + O_2(g) = PbO_2(s) + 219{,}000$ joules.

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[1] THIS JOURNAL, 36, 1992 (1914).