

dilution, affects some of the results by 20%. An even more extensive test of the several methods is furnished in the case of sulfuric acid, where satisfactory agreement was obtained over the range from 0 to 20 *M* (66%  $\text{H}_2\text{SO}_4$ ) by three different methods.

Calculations of activity coefficients in mixtures, especially from the solubility of salts in the presence of other salts, lead to an extremely powerful and general rule based upon the new concept of *ionic strength*. Each ion contributes to this ionic strength by an amount which is proportional to its stoichiometrical molality multiplied by the square of its valence. In accordance with this rule the activity coefficient of every strong electrolyte (and the individual activity coefficient of every ion) is the same in all dilute solutions of the same ionic strength. It therefore depends in no way upon the number or the nature of the ions of which the solution is composed.

The general problem of the dissociation of strong electrolytes is discussed from several standpoints.

BERKELEY, CALIF.

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[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY OF NEW YORK UNIVERSITY, AND THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

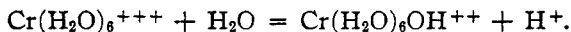
## THE HYDROLYSIS OF DICHLORO AND HEXA-AQUO CHROMIC CHLORIDES.

BY ARTHUR B. LAMB AND GORTON R. FONDA.

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In a paper<sup>1</sup> published in 1906, it was shown that the change of green chromic chloride into the blue (violet) isomer actually takes place through the intermediate formation of an hydrolysis product of the green chloride, presumably  $\text{CrCl}_2\text{OH}$ . Niels Bjerrum,<sup>2</sup> in an able and comprehensive paper published during the same year, arrived independently at the same conclusion, and presented a large amount of quantitative evidence based on kinetic measurements which agreed with it in a striking fashion.

In the course of his investigation Bjerrum measured the degree of hydrolysis of both the green and the blue isomers, obtaining as average values of the hydrolysis constants,  $3.8 \times 10^{-6}$ , for the green, and  $0.89 \times 10^{-4}$  for the blue salt at 25°, the latter hydrolysis taking place according to the equation



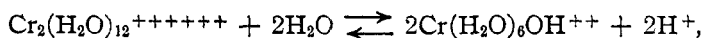
Since then Sand and Grammling,<sup>3</sup> from measurements of the potential

<sup>1</sup> Lamb, *THIS JOURNAL*, **28**, 1710 (1906).

<sup>2</sup> Bjerrum, *Kgl. D. Vid. Selsk. Skr.*, (7) **4**, 1 (1906); also *Z. physik. Chem.*, **59**, 336, 581 (1907).

<sup>3</sup> Sand and Grammling, *Z. physik. Chem.*, **62**, 1, 28 (1908).

of a hydrogen electrode, immersed in a solution of chromic chloride to which sodium hydroxide was slowly added, and from measurements of the velocity with which iodine is liberated from an iodide-iodate mixture containing chromic chloride, have concluded that blue chromic chloride has a double formula, but yields on hydrolysis a simple mono-hydroxo product. That is, instead of the simple equation given above, Sand and Grammling believe that hydrolysis follows the equation



and showed that close agreement with their experimental results was thereby attained. In reply to this Bjerrum<sup>1</sup> showed that Sand's measurements had been vitiated by a time effect, sufficient to invalidate the conclusions based upon them. Meanwhile Denham<sup>2</sup> had measured the hydrolysis of the blue chloride, and obtained a value for the constant about twice as large as that of Bjerrum.

These peculiar salts of chromium, perhaps the most striking exemplifications of Werner's theory of molecular structure, are of such particular interest that it has seemed to us important to secure more exact and certain information as to the extent of their hydrolysis. What follows is an account of the various measurements made for that purpose, and of the results obtained.<sup>3</sup>

### I. Hydrolysis of the Dichloro (Green) Chloride.

Bjerrum's determinations of the hydrolysis of the dichloro chloride were made in two independent ways: first by measurement of the potential of the hydrogen electrode in various of its solutions, and second, by a modification of the Walker method, based on conductivity measurements before and after the addition of acid. Neither of these methods yielded reliable results. In the first method, there was the difficulty of a rapidly changing concentration of hydrogen ions, necessitating a somewhat arbitrary extrapolation, and the results were irregular and uncertain, even the smoothed values varying between  $1.3$  and  $7.5 \times 10^{-6}$ . The second method depended upon the extrapolated initial values of the conductivity, and also involved corrections for the repression of ionization of the hydrochloric acid. The change of the dichloro into the hexa-aquo ion in pure water is so rapid at the start that the error in extrapolation could easily have been twice as great as the quantity measured, that is, the difference between the conductivity with and without the addition of acid.

<sup>1</sup> Bjerrum, *Z. physik. Chem.*, **73**, 724 (1910).

<sup>2</sup> Denham, *J. Chem. Soc.*, **93**, 53 (1908).

<sup>3</sup> The larger part of the experimental work of this paper was performed in 1906-7 at the Havemeyer Chemical Laboratory of New York University, much of it before the appearance of Bjerrum's paper. It was taken up again at Harvard University and completed in 1917, but its publication has been unavoidably delayed until this time.

On the other hand, in the presence of acid, where the transformation is slower and the extrapolation can be made with accuracy, the correction for the repression of ionization is doubtful. In any case, Bjerrum's method of correction for repression of ionization was not rigorous, as will be shown more fully later, and gave results varying between  $1.7$  and  $5.4 \times 10^{-6}$ . The average of these and the previous values is  $3.8 \times 10^{-6}$ . It is evident then that but little significance can be attached to the exact magnitude of the figures obtained in these ways, and indeed Bjerrum claims only that they give the order of magnitude. We have determined the degree of hydrolysis of the dichloro chloride in two ways as follows.

#### Determination of Hydrolysis from the Effect of Different Concentrations of Hydrochloric Acid on the Conductivity.

This method, which so far as we know, is novel, minimizes the difficulties which Bjerrum encountered in his second method. It compares the initial conductivities of two solutions of the dichloro chloride, *both* of which contain hydrochloric acid, but at *different* concentrations. For the more dilute acid solution the lowest concentration is chosen which still permits an accurate extrapolation to zero time: for the more concentrated acid solution a concentration is chosen at which the corrections for the repression of the ionization of the acid and of the salt are small enough to be computed accurately.

An expression connecting the hydrolysis constant of the dichloro with the difference between the conductivities of the chromic chloride in these two solutions and the known concentrations of salt and acids is derived as follows:  $h_1$  and  $h_2$  are the fractions hydrolyzed in the acids of concentration  $S_1$  and  $S_2$ , respectively;  $\lambda_1$  and  $\lambda_2$  the corresponding conductivities of the dichloro chloride corrected for the repressed ionization;  $\lambda_0$  the conductivity of the unhydrolyzed salt, and  $\lambda_{\text{HCl}}$  the conductivity of hydrochloric acid at the concentration it has in the mixture, then

$$h_1 = \frac{\lambda_1 - \lambda_0}{\lambda_{\text{HCl}} - \lambda_0}, \text{ and } h_2 = \frac{\lambda_2 - \lambda_0}{\lambda_{\text{HCl}} - \lambda_0}.$$

Since  $\lambda_{\text{HCl}}$  and  $\lambda_{\text{HCl}}$  in the presence of the slightly hydrolyzed salt of the same concentration are substantially equal,

$$h_1 - h_2 = \frac{\lambda_1 - \lambda_2}{\lambda_{\text{HCl}} - \lambda_0}.$$

By the concentration law

$$\frac{h_1(mh_1 + S_1)}{1 - h_1} = \frac{h_2(mh_2 + S_2)}{1 - h_2} = K_g,$$

where  $m$  is the molecular concentration and  $K_g$  is the hydrolysis constant

of the dichloro salt. Since  $h_1$  and  $h_2$  are very small numbers, we can without sensible error put

$$h_1(mh_1 + S_1) = h_2(mh_2 + S_2) = K_g,$$

from which it follows that

$$h_1 = \frac{1}{2} m (\sqrt{4K_g m + S_1^2} - S_1) \quad \text{and} \quad h_2 = \frac{1}{2} m (\sqrt{4K_g m + S_2^2} - S_2);$$

and hence

$$\frac{\lambda_1 - \lambda_2}{\lambda_{\text{HCl}} - \lambda_0} = \frac{1}{2m} [\sqrt{4K_g m + S_1^2} - \sqrt{4K_g m + S_2^2} - (S_1 - S_2)],$$

which expresses  $K_g$  in terms of known or measurable quantities.

The corrections for the repression of ionization of the acid were not made according to the Arrhenius principle that the conductivity of the acid is the same as in its pure solution of the same total ion concentration, for it has been shown by Bray and Hunt<sup>1</sup> that this principle does not hold for mixtures of sodium chloride and hydrochloric acid, and, therefore, presumably does not hold here. We have used the results of Bray and Hunt simply to correct arbitrarily for the effect of the green dichloro chloride (a salt of the same type as sodium chloride) on the hydrochloric acid. To do this, we first plotted 3 curves based on their experimental results showing the conductivity of the hydrochloric acid in 5, 20 and 100 millimolar concentrations of sodium chloride, assuming that the *sodium chloride* has a conductivity equal to that in the pure solution of the same total *salt* concentration (Table VI, Bray and Hunt). From these curves, other curves could readily be prepared showing the variation of the conductivity of the hydrochloric acid at any desired concentration with the concentration of the sodium (or dichloro chromic) chloride. The conductivity could then be read off from these curves for any particular concentration of the dichloro chloride.

TABLE I.

The differences between the molar conductivities of the hydrochloric acid in its pure solution and in the mixture, multiplied by the ratio of the concentrations of acid and chloride, that is,

$$\left( \lambda_{\text{HCl}} - \lambda_{2\text{HCl}} \right) \frac{C_{\text{HCl}}}{C_{\text{CrCl}_3}} = \theta_1$$

Hydrolysis of Dichloro-chromic Chloride Computed from the Effect of Different Concentrations of Hydrochloric Acid on the Conductivity.

$$T = 25^\circ. \quad m = 0.008 M.$$

No.	$S_1$ , MM.	$S_2$ , MM.	$\lambda_{1a}$ , mhos.	$\lambda_1$ , mhos.	$\lambda_{2a}$ , mhos.	$\lambda_2$ , mhos.	$K_g \times 10^4$ .
1.....	0.844	4.196	90.7	91.9	84.4	91.3	1.99
2.....	0.878	4.196	90.5	91.7	84.4	91.3	1.39
3.....	0.878	9.815	90.5	91.7	79.1	91.1	1.91
4.....	0.844	9.815	90.7	91.9	79.1	91.1	2.26

$$\text{Mean}^a K_g = 1.8 \times 10^{-4}$$

<sup>a</sup> In taking the mean of these values double weight has been given to pair Nos. 1 and 2, as the correction applied to the conductivity of the more concentrated acid ( $S_2$ ) is presumably subject to only half as great a relative error as is the corresponding correction for pair Nos. 3 and 4.

<sup>1</sup> Bray and Hunt, THIS JOURNAL, 33, 781 (1911).

gives the correction  $\theta_1$  which must be added to the arbitrary value  $\lambda_0$  for the molar conductivity of the chromic chloride in order to correct for the repression of the dissociation of the hydrochloric acid. The effect of the minute amount of hydrochloric acid on the dissociation of the chromic chloride must have been extremely small, and was, therefore, neglected.

This formula has been applied to two pairs of solutions which meet as nearly as possible the above mentioned requirements on which the accuracy of this method depends. The results are collected in Table I.

### Determination of the Hydrolysis from the Rate of Transformation of the Dichloro Chloride (Green) into Hexa-aquo Chloride.

**Outline of Method.**—Adopting Bjerrum's formulas for the kinetics of the transformation, we have studied the effect on the velocity of the addition of small amounts of acid, and have derived an empirical equation connecting these two quantities. From this equation and the observed initial velocity in pure water we have been able to compute the hydrogen-ion concentration in a solution of the dichloro chloride, and hence its hydrolysis.<sup>1</sup>

**The Experimental Procedure.**—The rates of transformation were obtained by observation of the increasing electrical conductivity of the solutions.

The 400 cc. globular conductivity cell used for this purpose, had an opening through which the salt could be introduced, and a mechanically operated stirrer inserted and removed. The thermostat in which the cell was placed maintained a temperature of 25° constant to  $\pm 0.01^\circ$ , and a thermometer fixed rigidly within the cell could be read with at least that accuracy. With solutions of the concentration generally employed, a minimum, accurate to within 1 to 2 mm., on the 7-meter slide-wire bridge could usually be obtained. The water, whose purity was not especially important, had a conductivity varying between 0.8 and  $2.5 \times 10^{-6}$  mhos.

The dichloro chloride was prepared by the method of Higley,<sup>2</sup> and as slight variations in its composition were found, presumably due to a varying water content, each sample was always carefully analyzed for total chlorine. This varied from 39.77 to 40.20% (calculated 39.92) corresponding to a variation in water content from  $\text{CrCl}_3 \cdot 5.845 \text{ H}_2\text{O}$  to  $\text{CrCl}_3 \cdot 6.083 \text{ H}_2\text{O}$ .

The exact quantity required for a measurement was weighed into a special weighing bottle whose neck was ground to fit the curving neck of a small stock bottle containing a supply of the salt. In this way, contact with moist air was almost completely avoided. The salt was then, at a given instant, emptied quickly into the cell, the stirrer started and the bottle rinsed out. Stirring was efficient and the salt went into solution very rapidly, so that the time was reckoned from a few seconds after the salt was introduced. Reliable measurements could usually be obtained after the lapse of one to two minutes.

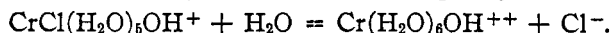
<sup>1</sup> Bjerrum applied substantially the same method, and found in 0.0107 and 0.00322 *M* solutions,  $K_a = 2.1$  and  $2.4 \times 10^{-3}$ , respectively. He did not, however, attach sufficient importance to these results to include them when obtaining the mean of his results, namely,  $K_a = 3.8 \times 10^{-4}$ .

<sup>2</sup> Higley, *THIS JOURNAL*, 26, 613 (1904).

**The Computation of the Velocity Constants.**—The assumptions underlying the kinetic equations used were as follows: first, that a practically instantaneous hydrolysis of the green salt occurs, according to the equation  $\text{CrCl}_2(\text{H}_2\text{O})_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{CrCl}_2(\text{H}_2\text{O})_4\text{OH} + \text{H}^+$ , its extent depending on the concentration of hydrogen ions in the solution; second, that the hydrolysis product reacts slowly with a molecule of water to form a monochloro hydroxide,



which in turn reacts slowly to form the hexa-aquo hydroxide,



The resulting kinetic equations have been formulated by Bjerrum<sup>1</sup>. As we are concerned chiefly with the velocity of the first slow reaction, we will reproduce only the equation for its velocity constant  $k_1$ , namely

$$k_1 = \frac{\ln \left( \frac{\lambda_\infty + \lambda_0}{2} - \lambda'_h \right) - \ln \left( \frac{\lambda_\infty + \lambda_0}{2} - \lambda'_{h_2} \right)}{t_2 - t_1}$$

where  $\lambda_0$  and  $\lambda'_h$  are the initial and final molar conductivities, and  $\lambda'_h$  and  $\lambda'_{h_2}$  the corrected molar conductivities at the times  $t_1$  and  $t_2$ . These corrected molar conductivities are the conductivities which the solutions would have had at the time  $t_1$  and  $t_2$  had the second reaction not occurred. Each differs from the real molar conductivity by an amount  $\Delta$ , which for small values of  $t$  is given by the expression

$$\Delta = \frac{\lambda_\infty - \lambda_0}{2} \left( \frac{k_2}{k_1 - k_2} \right) (k_1 t + e^{-k_1 t} - 1).$$

This expression involves the quantity  $k_1$  which we are endeavoring to compute, but as  $\Delta$  is usually very small, an approximate value may first be assigned to  $k_1$ , the resulting  $\Delta$ s applied and a preliminary value of  $k_1$  thus obtained. This new value may then be used to determine more accurate values for the  $\Delta$ s, if necessary, and so a more accurate value for  $k_1$  itself.

The only variation from this procedure which we have adopted occurs in the case of the experiments in very dilute acid. There, in computing  $\Delta$ , one is no longer justified in assuming, as Bjerrum has done, that  $k_1$  and  $k_2$  are constant throughout the run. The acid concentration increases very considerably, owing to the formation of the more highly hydrolyzed hexa-aquo chloride, and  $k_1$  and  $k_2$  thus become progressively smaller. It is therefore necessary in these cases to compute approximate values for the hydrogen ion concentration for the different stages of the reaction, and use values of  $k_1$  and  $k_2$  corresponding to the average hydrogen-ion concentration over the interval of time during which the reaction has been progressing.

<sup>1</sup> Bjerrum, *Z. physik. Chem.*, **59**, 370-1 (1907).

To correct for the repression of the ionization<sup>1</sup> and so to calculate the actual molar conductivity of the chromic chloride, we have followed the same procedure as on p. 1157. In the present case, the effect of the hydrochloric acid on the chromic chloride is not negligible, so we have also corrected for the repression of its dissociation, assuming it to have the same conductivity in the mixture as in its pure solution of the same total salt concentration. This correction, usually very small, was called  $\theta_2$  and added to  $\theta_1$  gave the total correction  $\theta$ .

As a result of these corrections, we obtained values for the real molar conductivity of chromic chloride in its mixed solution, free from any considerable uncertainty, other than that involved in the assumption that dichloro-chromic chloride and sodium chloride affect the conductivity of hydrochloric acid similarly.

The initial values of  $\lambda_a$  and hence of  $\lambda$  were obtained by extrapolation to zero time in those acid solutions where the change was sufficiently slow to justify this; in the most dilute solutions, and in pure water, this became impracticable and there the initial values have been computed from the values in the more concentrated acid, and from the known hydrolysis constant. Any reasonable error in either of the values has only a slight effect on the value of  $k_1$  during the first interval of time, and no effect on subsequent values.

The final values have usually been obtained by extrapolation from a prolonged experiment; in certain cases in the more concentrated acid solutions they have been calculated from the known values for aqueous solutions at different concentrations and the known hydrolysis constant of the hexa-aquo chloride. Variations in these values have but a slight effect on the value of  $k_1$ . The values of  $k_2$  were usually taken from the tables of Bjerrum, for his data on the final stages of the reaction are more complete than ours.

**The Velocity Measurements.**—The experimental results are tabulated in Tables II and III, and the average values of  $k_1$  are collected in Table IV. The measurements in pure water and in 0.001 *M* acid were made in quadruplicate, but for economy of space only a single typical run is included. All values of  $k_1$  obtained are, however, included in Table IV.

Examination of the experimental results (Tables II and III) shows that, except in water and in the most dilute two acids, there is no noticeable trend in the separate values of  $k_1$ . This indicates the correctness of the kinetic equations, and of the assumptions on which they are based. The

<sup>1</sup> Bjerrum assumed, for this purpose, the Arrhenius principle that the conductivity of the hydrochloric acid in the mixture is the same as it would be in its pure solution of the same total ion concentration. This was probably all that he could do at that time, but since then, as mentioned above, Bray and Hunt (*loc. cit.*) have shown that this principle is by no means valid for mixtures of hydrochloric acid and sodium chloride. It is doubtless equally incorrect here.

TABLE II.  
Velocity of Transformation in Pure Water.

CrCl <sub>3</sub> = 0.00793 M.			
Time Min.	$\lambda$ mhos.	$\Delta$ mhos.	$k_1$ .
0	(98.1)	...	(0.143)
2.17	130.0	0.3	0.133
3.58	143.0	0.5	0.102
4.71	151.4	0.8	0.0927
5.21	154.3	1.1	0.0838
5.75	157.6	1.1	
6.29	161.0	1.3	
7.08	165.5	1.5	0.0826
8.47	172.3	2.0	
10.50	181.2	3.0	
11.47	184.7	3.3	0.0772
12.33	188.0	3.7	
13.42	192.1	4.3	
16.64	200.7	6.1	0.0647
18.33	206.0	...	....
19.25	208.1	...	....
22.42	216.0	...	....
30.75	231.0	...	....
38.88	236.2	...	....
51.75	256.1	...	....
62.75	264.9	...	....
73.83	273.1	...	....
84.50	279.2	...	....
95.50	284.4	...	....
105.9	288.8	...	....
117.1	293.0	...	....
228.8	319.1	...	....
$\infty$	(350.0)	...	....

$k_1$  (extrapolated) = 0.143

average value of  $k_1$  has therefore been taken as the most probable value of  $k_1$  for that particular concentration. In the most dilute two acids, the values of  $k_1$  show a sudden drop during the first few minutes. This effect is even more marked in pure water, and is due to the fact that the kinetic equations do not take into account the change in the concentration of the dichloro hydroxide which results from the formation of the strongly hydrolyzed hexa-aquo salt. In these cases the initial value of  $k_1$  was found by plotting values of  $k_1$  against the first third of each corresponding time interval, and then extrapolating to zero time. The points in general lay on smooth curves.

In order to ascertain the relation between the velocity of transformation ( $k_1$ ) and the concentration of the hydrogen ion on the one hand, and of the dichloro hydroxide on the other in these solutions, these latter quantities were computed on the basis of the previously determined value of the hydrolysis constant ( $K_g$ ) and the added acid ( $s$ ), without making the



TABLE III.

Velocity of Transformation in Presence of Hydrochloric Acid.

No. 1.					No. 2.				
HCl = 0.0000824 M.					HCl = 0.000200 M.				
CrCl <sub>3</sub> = 0.008072 M.					CrCl <sub>3</sub> = 0.008010 M.				
L <sub>HCl</sub> = 0.0000348 mhos.					L <sub>HCl</sub> = 0.0000841 mhos.				
Time	$\lambda_{\alpha}$	$\lambda$	$\Delta$	$k_1$	Time.	$\lambda_{\alpha}$	$\lambda$	$\Delta$	$k_1$
Min.	mhos.	mhos.	mhos.		Min.	mhos.	mhos.	mhos.	
0	(93.9)	(94.0)	0	0.098	0	(93.23)	(93.63)	0	0.066
2.50	121.9	122.0	0.3	0.0876	2.42	113.20	113.60	0.4	0.0706
3.92	133.5	133.6	0.5		3.67	121.34	121.74	0.5	0.0633
4.56	138.1	138.2	0.6		4.25	125.20	125.60	0.6	
5.22	142.2	142.3	0.7	0.0744	5.17	130.71	131.10	0.7	0.0625
6.30	148.5	148.6	1.0		6.08	135.92	136.32	0.9	0.0633
7.92	156.9	157.0	1.4	0.0722	7.17	141.13	141.52	1.1	0.0549
10.08	167.4	167.5	1.8	0.0790	8.75	149.03	149.43	1.4	0.0624
14.58	183.5	183.6	2.8	0.0724	12.17	163.14	163.64	1.8	0.0599
19.83	197.9	198.0	...	....	14.67	171.87	172.37	...	....
30.92	220.6	220.1	...	....	18.75	183.69	184.14	...	....
44.25	243.7	243.9	...	....	22.25	192.78	193.27	...	....
58.42	252.3	252.5	...	....	110.9	276.94	277.44	...	....
70.08	261.5	261.7	...	....	270.0	316.2	316.8	...	....
80.25	267.6	267.8	...	....	1660.0	348.6	349.2	...	....
91.17	273.3	273.5	...	....	...	....	(351.5)	...	....
103.4	278.9	279.1	...	....	$k_1$ (extrapolated) = 0.066				
119.2	285.5	285.7	...	....					
....	...	(349.9)	...	....					
$k_1$ (extrapolated) = 0.098									
No. 3.					No. 4.				
HCl = 0.0008442 M.					HCl = 0.000878 M.				
CrCl <sub>3</sub> = 0.008077 M.					CrCl <sub>3</sub> = 0.0008065 M.				
L <sub>HCl</sub> = 0.0003552 mhos.					L <sub>HCl</sub> = 0.0003626 mhos.				
$k_2$ = 0.0038					$k_2$ = 0.0038				
0	(90.7)	(91.9)	...	....	0	(90.5)	(91.7)	0	....
2.25	95.96	97.16	0	0.0191	2.00	95.38	96.58	0	0.0201
3.50	98.66	99.86	0.1	0.0192	2.75	97.13	98.33	0.1	0.0199
4.75	101.45	102.75	0.2		3.75	99.44	100.64	0.2	0.0205
6.25	104.92	105.22	0.3	0.0207	4.84	101.99	103.29	0.2	
9.50	112.27	113.57	0.5		5.84	104.32	105.62	0.3	0.0204
19.50	132.70	134.10	2.0	0.0212	7.00	106.99	108.29	0.3	
43.25	169.77	171.47	8.4	0.0200	10.75	114.91	116.21	0.6	0.0208
60.00	188.44	190.14	...	....	15.25	124.47	125.87	1.2	
76.50	203.64	205.38	...	....	19.25	132.23	133.63	2.0	0.0204
186	254.6	256.6	...	....	24.17	141.34	142.84	3.0	0.0213
276	274.4	276.5	...	....	29.50	150.25	151.75	4.2	0.0203
344	302.9	305.2	...	....	32.00	154.22	155.72	4.9	0.0206
1500	333.2	335.8	...	....	...	....	(336.4)	...	....
...	....	(336.4)	...	....	$k_1$ (average) =				0.0205
$k_1$ (average) = 0.0204									

TABLE III (Continued.)

Velocity of Transformation in Presence of Hydrochloric Acid.

No. 5.					No. 6.				
HCl = 0.00099 M.					HCl = 0.004196 M.				
CrCl <sub>3</sub> = 0.008048 M.					CrCl <sub>3</sub> = 0.008199 M.				
$L_{\text{HCl}}$ = 0.0004198 mhos.					$L_{\text{HCl}}$ = 0.001746 mhos.				
$k_2$ = 0.0033.					$k_2$ = 0.00080.				
Time Min.	$\lambda_a$ mhos.	$\lambda$ mhos.	$\Delta$ mhos.	$k_1$	Time Min.	$\lambda_a$ mhos.	$\lambda$ mhos.	$\Delta$ mhos.	$k_1$
0	(90.4)	(91.8)	...	....	0	(84.4)	(91.4)	...	...
3.25	96.0	97.4	0	0.0207	2.00	85.9	92.9	...	0.00656
3.25	97.8	99.2	0.1	0.0146	3.83	86.8	93.9	...	0.00553
5.50	99.8	101.2	0.1		5.25	87.7	94.8	...	
6.00	102.4	103.8	0.2		8.67	89.9	97.1	...	0.00600
8.00	105.7	107.3	0.3	0.0181	12.25	92.4	99.7	0.1	0.00656
13.00	116.0	117.4	0.5		23.50	99.9	107.0	0.2	0.00624
20.50	129.1	130.7	1.1	0.0179	34.25	106.9	114.4	0.4	0.00715
38.67	155.0	156.8	3.4	0.0181	81.17	132.5	140.8	1.9	0.00677
60.50	180.8	182.8	...	....	156.7	163.2	172.3	7.0	0.00660
88.00	214.8	217.0	...	....	196.2	175.1	184.5	...	...
116	222.9	225.1	...	....	387.7	207.2	217.3	...	...
2675	330.4	333.2	...	....	....	...	(320.0)	...	...
3275	331.5	334.3	...	....	$k_1$ (average) = 0.0064				
...	...	(336.5)	...	....					
$k_1$ (average) = 0.0179									
No. 7.					No. 8.				
HCl = 0.00800 M.					HCl = 0.009815 M.				
CrCl <sub>3</sub> = 0.007933 M.					CrCl <sub>3</sub> = 0.008082 M.				
$L_{\text{HCl}}$ = 0.003338 mhos.					$L_{\text{HCl}}$ = 0.004039 mhos.				
$k_2$ = 0.00050.					$k_2$ = 0.00032.				
0	(79.8)	(90.4)	...	...	0	(79.1)	(91.1)	0	....
2.08	80.2	90.8	0	0.00400	2.50	79.8	91.8	0.0047	0.0047
5.25	82.5	93.3	0		3.25	80.7	92.8		
11.58	84.5	95.4	0		3.75	80.7	92.8		
22.25	90.4	101.7	0	0.00522	4.25	81.2	93.3	0.0028	0.0028
39.92	98.1	110.0	0.1	0.00454	5.25	81.4	93.5		
53.17	104.1	116.4	0.3	0.00494	8.33	81.7	93.9		
68.83	109.6	122.2	0.3	0.00416	13.00	83.6	95.8	0.1	0.0046
83.92	114.8	127.9	0.5	0.00438	34.75	92.9	105.5		
97.50	120.3	133.7	0.7	0.00529	57.50	101.6	114.9	0.3	0.0045
163.8	140.3	155.1	1.8	0.00475	68.00	104.9	118.5	0.3	0.0041
236.7	156.5	172.5	3.4	0.00468	987.0	203.0	224.0	...	....
....	...	(325.6)	...	....	2322	235.1	259.2	...	....
$k_1$ (average) = 0.0047					2653	239.5	263.9	...	....
					3407	252.5	277.8	...	....
					6457	274.2	301.4	...	....
					8407	279.2	306.8	...	....
					9862	282.9	310.8	...	....
					11287	284.9	313.0	...	....
					$\infty$	(288.0)	(316.4)	...	....
					$k_1$ (average) = 0.0042				

simplifying assumption adopted by Bjerrum that the concentration of

TABLE IV.  
 Variation of  $k_1$  with Concentration of Acid.

$m \times 10^3$ , $M$	$s \times 10^3$ , $M$	$k_1$ , observed.	$a-x$ , $\times 10^3$ , $M$	$k_1$ , calculated.	$K_g \times 10^4$ .
7.930	0	0.143	0.1209	(0.133)	2.16
7.987	0	0.144	0.1213	(0.134)	2.18
7.948	0	0.131	0.1210	(0.134)	1.80
8.072	0.0824	0.098	0.0879	0.0967	....
7.978	0.2000	0.066	0.0575	0.0644	....
8.045	0.844	0.0204	0.0173	0.0211	....
8.033	0.878	0.0205	0.0166	0.0205	....
8.016	0.999	0.0179	0.0147	0.0187	....
7.935	1.005	0.0179	0.0145	0.0185	....
7.815	1.005	0.0186	0.0145	0.0185	....
7.950	1.005	0.0190	0.0145	0.0185	....
8.133	4.196	0.0064	0.00346	0.00642	....
7.933	8.000	0.0047	0.00181	0.00463	....
8.050	9.815	0.0042	0.00141	0.00419	....
7.565	10.09	0.0042	0.00141	0.00418	....

$$k_s \text{ (average)} = 2.05 \times 10^{-4}$$

the hydroxide was negligible compared with that of the dichloro ion. In pure aqueous solution, if  $a$  represents the concentration of the hydrogen ion,  $a^2 = K_g(m - a)$ . When  $s$  moles of hydrogen ion are added,  $x$  mols of hydroxide will be converted back to dichloro ion, and then  $(s + a - x)(a - x) = K_g(m - (a - x)) = a^2 + K_g x$ . Therefore, the concentration of hydrogen ion

$$s_1 = (s + a - x) = \frac{1}{2} (\sqrt{(2a + s + K_g)^2 - 4as} + s - K_g),$$

and that of the hydroxide

$$(a - x) = \frac{1}{2} (\sqrt{(2a + s + K_g)^2 - 4as} - (s + K_g)).$$

The values computed by these equations are given in the fourth column of Table IV. When the observed values of  $k_1$  in the acid solutions are plotted against these values of  $(a - x)$  they are found to lie nearly on a straight line represented by the linear equation,

$$k_1 = 0.00265 + 1080 (a - x).$$

The faithfulness with which this formula reproduces the experimental results is shown by the close agreement of the figures in the fifth column with the observed values given in the third column. Indeed, the average deviation is only  $\pm 1.5\%$ .

Since  $a - x = K_g m / (s_1 \times K_g)$ , and since  $s_1$  is always at least 100 times greater than  $K_g$ , no significant error results if we write  $a - x = K_g m / s_1$ ; and then

$$k_1 = 0.00265 + \frac{0.0000142}{s_1}$$

The concentration of hydroxide in pure aqueous solution of the dichloro chloride can now be found by substituting the observed values of  $k_1$  in the first formula. From this, in turn, the values of  $K_g$  given in Col. 6 result. The average of these values ( $2.0 \times 10^{-6}$ ) agrees reasonably well with the value previously obtained by a different method<sup>1</sup> ( $1.8 \times 10^{-6}$ ).

### A General Method for Determining Hydrogen-Ion Concentration.

It is evident that the precise linear relation shown above to exist between the rate of transformation of the dichloro-chloride and the reciprocal concentration of the hydrogen ion offers a convenient method for measuring these concentrations. To make such a determination a small weighed quantity of the dichloro chloride is dropped into a measured volume of the solution to be investigated, the solution stirred and the rate of increase in conductivity observed. To compute the results the above equation for  $k_1$  can be rearranged to

$$s_1 = 1.9 \times 10^{-6} \left[ \frac{1080m + 0.00265 - k_1}{k_1 - 0.00265} \right] - \frac{k_1 - 0.00265}{1080},$$

where  $m$ , the concentration of the dichloro chloride, is preferably in the neighborhood of 0.008  $M$ .

**The Effect of Chloride Ions.**—As we contemplated applying this method to a study of the hydrolysis of the blue chloride, it was of importance to find out whether the rate of transformation is affected by chloride ions. This was accomplished by measuring the velocity of transformation in solutions of potassium chloride. The results are given in Table V.

Here, as in the case of aqueous solutions, there is a decided trend in the values of  $k_1$ . However, when plotted against the time, they were found to lie on smooth curves which could be extrapolated with reasonable certainty to zero time. The resulting initial values were similar in the two parallel experiments, and the mean value of  $k_1$  (0.125) was only slightly smaller than in pure water. Indeed, the difference is scarcely greater than the experimental error, and would correspond according to the above formula, assuming no effect of the potassium chloride, to only  $2 \times 10^{-5}$  molar concentration of hydrogen ion in the potassium chloride solution. The method can, therefore, be applied without hesitation in the presence of an equimolecular concentration of potassium chloride.

<sup>1</sup> It should be noted that this empirical equation violates the fundamental assumptions made in deriving the kinetic equations. According to them, the first term of the right hand member should be zero. Actually it is only negligible in pure or very dilute acid solutions. Bjerrum explains this contradiction reasonably enough by assuming that the *unhydrolyzed* dichloro ion also undergoes a slow direct transformation to the hexa-aquo ion, and from the magnitude of the above term computes a velocity constant for this transformation about a thousand times smaller than  $k_1$ .

TABLE V.

Velocity of Transformation in Potassium Chloride Solutions.

No. 1.					No. 2.				
KCl = 0.00795 <i>M</i> .					KCl = 0.00798 <i>M</i> .				
CrCl <sub>3</sub> = 0.007885 <i>M</i> .					CrCl <sub>3</sub> = 0.008075 <i>M</i> .				
<i>L</i> <sub>KCl</sub> = 0.0011295 mhos.					<i>L</i> <sub>KCl</sub> = 0.001134 mhos.				
Time Min.	λ <sub>α</sub> mhos.	λ mhos.	Δ mhos.	<i>k</i> <sub>1</sub> .	Time Min.	λ <sub>α</sub> mhos.	λ mhos.	Δ mhos.	<i>k</i> <sub>1</sub> .
0	(94.1)	(98.1)	0	(0.124)	....	....	....	...	(0.0125)
2.33	122.5	127.5	0.4	0.1123	2.33	123.1	128.1	0.4	0.1150
3.14	129.7	134.9	0.5	0.0916	3.17	130.1	135.3	0.5	0.0937
3.67	133.6	138.9	0.6	0	3.75	134.9	140.2	0.7	0.0893
5.17	143.9	149.6	0.9	0.0863	4.95	142.8	148.5	0.9	0.0840
5.67	147.4	153.1	1.0		6.92	154.0	160.0	1.4	0.0789
6.50	152.1	158.0	1.3	0.0845	12.17	175.9	182.2	3.6	0.0695
9.25	165.2	171.5	1.7	0.0787	19.08	195.8	202.7	7.8	..
3.50	180.5	187.3	4.2	0.0662	39.42	229.0	237.3	...	..
0.67	199.7	207.0	...	....	47.42	236.2	244.7	...	..
20.67	199.7	207.0	...	....	47.42	236.2	244.7	...	..
34.83	223.1	231.1	...	....	56.33	244.4	253.1	...	..
43.33	233.4	241.8	...	....	72.00	248.8	257.7	...	..
51.67	241.5	250.2	...	....	81.17	260.6	269.8	...	..
62.17	249.7	258.6	...	....	91.08	265.6	275.0	...	..
76.36	258.9	268.1	...	....	97.45	268.2	277.7	...	..
97.25	269.3	278.8	...	....	111.4	274.5	284.2	...	..
114.5	275.8	285.5	...	....	<i>k</i> <sub>1</sub> (extrapolated) = 0.125				
137.2	283.0	292.9	...	....					
∞	...	(350.0)	...	....					
<i>k</i> <sub>1</sub> (extrapolated) = 0.124									

## II. THE HYDROLYSIS OF THE HEXA-AQUO CHLORIDE.

### 1. Computed from Conductivity at Different Concentrations.

Bjerrum's<sup>1</sup> determinations of the hydrolysis constant of the hexa-aquo chloride (blue) depended on the measurement of the potential of a hydrogen electrode immersed in the solutions, and of the conductivity of these solutions. The former method gave apparently reproducible results, increasing from 0.87 in 0.1 *M* to  $1.18 \times 10^{-4}$  in 0.008 *M* solution at 25°. Denham's<sup>2</sup> similar independent measurements gave values increasing from  $1.0 \times 10^{-4}$  in 0.25 *M* to  $1.5 \times 10^{-4}$  in 0.016 *M*. Bjerrum's latter method gave concordant values averaging  $0.81 \times 10^{-4}$  over a wide range

<sup>1</sup> Bjerrum, *Z. physik. Chem.*, **59**, 336, 581 (1907).

<sup>2</sup> Denham, *loc. cit.*

of concentrations. It depended on correcting the equivalent conductivity at the different concentrations to that at infinite dilution by adding certain average differences ( $\Delta$ ), taken from the computations of Bredig,<sup>1</sup> ascribing to hydrolysis the increase which these values show with increasing dilution, and finding a value of  $K_b$  which would fit them. Bredig's values for  $\Delta$  are based almost wholly on observations on salts of univalent bases with trivalent acids which, moreover, are known to be greatly hydrolyzed. It happens, nevertheless, that the values of  $\Delta$  agree with the careful measurements of Noyes and Johnston<sup>2</sup> of the conductivity of solutions of lanthanum nitrate, a salt of the same type as hexa-aquo-chromic chloride. It is, however, wholly arbitrary to assume that this salt will have the same dissociation curve and mobility as lanthanum nitrate. Indeed, the assumption is unlikely, for it gives  $\lambda_{\text{Cr}(\text{H}_2\text{O})_6^{+++}} = 68$  mhos, a value at least a third larger than 49.5, the best value found by Hopfgartner<sup>3</sup> from transference experiments, and one-half larger than the value 44.9, found by Heydweiller<sup>4</sup> from conductivity measurements.

A much less arbitrary method of treating these data is to adopt the most probable value of  $\lambda_{\text{Cr}(\text{H}_2\text{O})_6^{+++}}$ , and then (by means of the Storch-Bancroft equation,  $1/\lambda_0 = 1/\lambda_1 - k(C_1\lambda_1)^{n-1}$ , which, with the exponent  $n$  equal to 1.5, Noyes and his co-workers have found so generally applicable to salts of this type) by varying  $k$  to compute values for the conductivity of the unhydrolyzed salt which will give a constancy of  $K_b$  at different concentrations. The results of this method are given in Table VI, where  $\lambda_{\text{Cr}(\text{H}_2\text{O})_6^{+++}}$  has been taken as 47.6 mhos, the mean of the values of Heydweiller and Hopfgartner, and  $k = 0.000305$ .

TABLE VI.

Conc. MM.	$\lambda$ Obs. mhos.	$\lambda$ Cal. mhos.	Per cent. Hydrolysis.	$K_b$ $\times 10^4$ .
0.8052	458.3	348.7	33.2	1.33
4.017	381.6	327.2	18.0	1.60
4.015	381.2			
7.369	352.2	315.0	12.2	1.26
7.948	348.4			
8.046	348.5	313.2	11.6	1.23
8.055	348.7			
17.46	320.8	293.8	8.73	1.46
34.89	297.5	273.3	7.93	2.26
Average				$1.52 \times 10^{-4}$

<sup>1</sup> Bredig, *Z. physik. Chem.*, **13**, 191 (1894).<sup>2</sup> Noyes and Johnston, *THIS JOURNAL*, **31**, 987 (1909).<sup>3</sup> Hopfgartner and Marinkovic, *Monatsh.*, **36**, 831 (1915).<sup>4</sup> Heydweiller, *Z. physik. Chem.*, **89**, 281 (1915).

## 2. By Measurements of the Velocity of Transformation of the Dichloro-Chloride.

Having shown above that measurements of the velocity of transformation of the dichloro chloride may be used to determine hydrogen-ion concentrations, even in the presence of potassium chloride, this method was first applied to solutions of the hexa-aquo chloride.

Certain changes had to be made in the method of correcting for repression of ionization. The Arrhenius principle is certainly far from adequate in this instance, as a preliminary computation soon showed. Moreover, no data like those of Bray and Hunt for hydrochloric acid exist for the hexa-aquo salt. The most reasonable method was to apply such corrections at the beginning and end of the transformation as would bring the conductivity up to the corresponding initial and final conductivities in an acid solution giving approximately the same value of  $k_1$ . The intermediate corrections could then be made proportional to the conductivities. This was the method adopted. In other respects the measurements and computations were identical with those made on pure water and hydrochloric acid solution. Duplicate determinations were made at each concentration with one exception, but as the duplicate showed good agreement the observations of only a single determination at each concentration are reproduced in Table VIII. All of the extrapolated or average initial values of  $k_1$  are, however, given in Table VIII.

From the values of  $k_1$  in the various solutions, the concentrations of the added hydrogen ion in these solutions can be readily computed from the formula given in Part I. The hydrolysis constant for the hexa-aquo salt may then be computed from the equation  $K_b = s_1^2/c - s_1$  where  $s_1$  is the concentration of the hydrogen ion and  $c$  the concentration of the hexa-aquo salt. This is, however, only an approximate equation, for the concentra-

<sup>1</sup> Bjerrum's own measurements utilized in a similar way (taking  $k = 0.00032$ ) are given in Table VII.

TABLE VII.

Conc. MM.	$\lambda$ Obs. mhos.	$\lambda$ Cal. mhos.	Per cent. Hydrolysis.	$K_b$ $\times 10^4$ .
0.00080	469.5	348.7	40.3	2.16
0.00097	457.7	346.6	37.0	2.11
0.00190	420.5	337.8	27.6	2.04
0.00390	384.6	326.5	19.7	1.82
0.00779	353.1	312.2	13.6	1.68
0.01559	324.6	294.8	9.9	1.92

Average  $1.96 \times 10^{-4}$

They yield an average value even larger than the one obtained from our own data.

tion of the hydrolysis product is not simply equal to  $s_1$ ; it is in reality somewhat greater.

TABLE VIII.

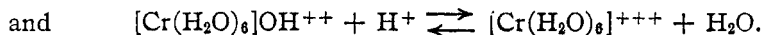
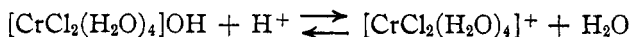
Velocity of Transformation in Hexa-aquo Chloride Solutions.

No. 1.					No. 2.				
Hexa-aquo = 0.0008376 <i>M</i> .					Hexa-aquo = 0.004017 <i>M</i> .				
Dichloro = 0.00800 <i>M</i> .					Dichloro = 0.00800 <i>M</i> .				
$L_{\text{Hexa-aquo}}$ = 0.0004049 mhos.					$L_{\text{Hexa-aquo}}$ = 0.001533 mhos.				
$k_2$ = 0.0083 to 0.0054.					$k_2$ = 0.0054.				
Time	$\lambda_d$	$\lambda$	$\Delta$	$k_1$	Time	$\lambda_d$	$\lambda$	$\Delta$	$k_1$
Min.	mhos.	mhos.	mhos.		Min.	mhos.	mhos.	mhos.	
0	(88.0)	(96.0)	...	....	...	(77.8)	(92.4)	...	....
3.67	107.5	116.2	0.8	0.0446	2.75	86.1	101.4	0.1	0.0267
5.17	115.2	124.4	1.3	0.0508	3.42	88.0	103.6	0.3	0.0277
7.00	123.7	132.2	1.7	0.0422	5.08	92.8	109.0	0.4	
11.92	144.1	154.4	3.7	0.0500	10.83	105.6	123.1	1.1	0.0250
19.08	166.7	177.9	7.2	0.0452	12.50	110.3	128.5	1.4	
33.08	196.0	208.4	13.6	0.0444	15.08	115.9	134.6	2.0	0.0243
52.75	221.9	235.5	22.8	0.0513	20.25	127.4	147.5	3.4	0.0280
77.50	242.5	256.9	...	....	26.08	140.0	161.6	5.5	0.0305
118.0	263.2	278.4	...	....	32.33	150.3	173.1	8.2	0.0246
161.7	277.6	293.4	...	....	1260	298.4	338.8	...	....
250.7	296.4	313.0	...	....	...	...	(343.1)	...	....
341.7	307.7	324.8	...	....	$k_1$ (average) = 0.0267				
464.7	316.6	334.1	...	....					
1576.7	330.4	348.3	...	....					
2170.7	339.9	348.8	...	....					
2240									
....	...	(350.0)	...	....					
$k_1$ (average) = 0.0472									
No. 3.					No. 4.				
Hexa-aquo = 0.008384 <i>M</i> .					Hexa-aquo = 0.03487 <i>M</i> .				
Dichloro = 0.00800 <i>M</i> .					Dichloro = 0.00800 <i>M</i> .				
$L_{\text{Hexa-aquo}}$ = 0.002951 mhos.					$L_{\text{Hexa-aquo}}$ = 0.01038 mhos.				
$k_2$ = 0.0035.									
....	(74.2)	(92.2)	0.1	0.0168	....	...	(92.0)	...	....
4.25	81.9	100.8	0.1	0.0167	4.58	59.5	96.5	...	0.0854
5.33	83.3	102.3	0.2		9.25	63.4	101.0	0.1	0.0848
6.25	85.4	104.7	0.3	0.0167	14.83	68.4	106.9	0.2	0.0990
7.17	85.8	105.1	0.5		26.50	77.5	117.4	0.5	0.0894
12.17	95.0	115.4	1.3	0.0160	67.42	102.0	145.7	0.3	0.0796
21.50	108.1	130.2	3.9	0.0178	131.9	130.5	178.8	9.5	0.0787
38.58	130.8	155.5	9.7	0.0171	218.2	147.4	198.4	...	....
66.17	157.4	185.3	...	....	325.9	164.9	218.6	...	....
103.8	181.5	212.4	...	....	451.6	171.5	226.2	...	....
269.1	224.8	261.0	...	....	658.0	181.1	237.4	...	....
456.5	249.6	288.7	...	....	....	...	(327.0)	...	....
....	...	(338.8)	...	....	$k_1$ (average) = 0.0862				
$k_1$ (average) = 0.0168									

The exact relationship must take into account the fact that there are



2 salts present which adjust themselves to hydrolytic equilibria,



Call the concentration of the dichloro hydroxide  $a$  and that of the dichloro ion  $b$ ; that of the hexa-aquo hydroxide  $c$  and that of the hexa-aquo ion  $d$ , when each salt is present by itself in the solution. Then,  $a^2 = K_g b$ , and  $c^2 = K_b d$ . If both are mixed together at the same total concentration of each salt, rearrangement will in general occur;  $a$  will decrease by an amount  $x$  and  $c$  by an amount  $y$ . The equations  $(a - x)(a + c - x - y) = (b + x)K_g$  and  $(c - y)(a + c - x - y) = (d + y)K_b$ , will then hold. Eliminating  $y$  from these two equations, and noting that  $a + b = m$ , and  $c + d = n$ , where  $m$  and  $n$  are the total concentrations of the dichloro and hexa-aquo salts, the following expression is obtained,

$$K_b = \frac{[m - (a - x)](K_g - a - x)^2}{\frac{(a - x)^2[n + (a - x)]}{[m - (a - x)]K_g} - (a - x)},$$

where  $K_b$  is expressed in terms of  $K_g$ ,  $m$  and  $n$ , all known quantities, and  $(a - x)$ , the concentration of the dichloro hydroxide. This last quantity can be computed from the values of  $k_1$  by the formula given in II.

The values of  $k_1$  corresponding to different values of  $n$  have been collected in Table IX. In the third column are given the values of  $K_b$ , the hydrolysis constant of the hexa-aquo salt, calculated from them by means of the above equation.

TABLE IX.

$n$ .	$k_1$ .	$K_b \times 10^4$ .
0.0008376	0.0472	1.96
0.0008376	0.0485	
0.004017	0.0257	
0.004017	0.0267	
0.008055	0.0178	1.63
0.008388	0.0168	1.50
0.03489	0.00862	(2.29)*

$$K_b \text{ (average)} = 1.6 \times 10^{-4}$$

\* The equivalent chloride concentration here is more than 10 times greater than in the experiments with potassium chloride, where a slight accelerating effect was found. It follows that  $k_1$  is doubtless too small and  $K_b$ , therefore, too great at this concentration. This value has, therefore, been omitted in taking the mean.

### 3. Hydrolysis Computed from Velocity of the Inversion of Cane Sugar in the Solution.

Since the use of this method involved measurements of rates of inversion much slower than had heretofore been attempted, every recognized refinement of observation was adopted.

For purposes of comparison, measurements on the velocity of inversion in very dilute acids, at 25°, were first made.

Each solution of sugar was freshly prepared from an unbleached recrystallized cane sugar (rock-candy), was sterilized by boiling, and kept sterile by the use of a trace of camphor. The inversion was carried on in tightly closed, 1-liter, Jena glass flasks which were steamed out before every run. They were kept throughout in a water thermostat maintained at  $25.00 \pm 0.01^\circ$ . The polariscope was the standard Schmidt and Haensch instrument. Its scale corrections were found to be negligible. Readings were made in 20-cm. tubes. The hexa-aquo salt was prepared as before by boiling the dichloro salt and then cooling. The final rotation was computed from the initial rotation by the formula<sup>1</sup>  $\alpha_f = \alpha_i [0.44 - (0.005)25]$ , where  $\alpha_i$  and  $\alpha_f$  are the initial and final rotations. The velocity constants were calculated from the usual formula

$$k_r = 1/t \cdot \ln \left( \frac{a_i - a_f}{a_i + a_f} \right)$$

where  $a_i$  is the rotation at the time  $t$ .

The resulting values of  $k_r$  showed a satisfactory constancy, the average variation from the mean being 0.6%. The results of the three runs made are collected in Table X.

TABLE X.

Velocity of Inversion by Dilute Hydrochloric Acid at  $25.00^\circ$ .

Conc. HCl <i>M</i> .	Conc. Sugar per 100 cc.	$k_r \times 10^4$ Min.	$k_r \times 10^4$ Min. for 0.01 <i>M</i> H <sup>+</sup> .
0.00741	9.916	0.564	0.783
0.00739	9.919	0.572	0.794
0.01477	9.917	1.131	0.793

Average = 0.790

We have not been able to find any measurements using such dilute acid at so low a temperature. The nearest approach is in certain measurements of R. F. Jackson<sup>2</sup> and of Lamble and Lewis.<sup>3</sup> Jackson records a single experiment in 0.01 *M* hydrochloric acid at  $30^\circ$ , where he found a value of  $k = 0.0001886$ . Applying the Arrhenius formula,  $k_{t_1} = k_t$ ,  $c \frac{q}{R} \frac{T_1 - T_0}{T_1 T_0}$ , where  $T_1$  and  $T_0$  are absolute,  $t_1$  and  $t_0$  Centigrade temperatures,  $c$  the concentrate and  $q$  a constant, which he found in excellent agreement with observations up to  $90^\circ$ , we get  $0.923 \times 10^{-4}$  for 0.01 *M* acid or  $0.961 \times 10^{-4}$ , for 0.01 *M* hydrogen ions. This is larger than our value.

Lamble and Lewis made a series of measurements on hydrochloric acid at  $25^\circ$  at concentrations from molar down to 0.05 *M*. On plotting their values of  $k_r$  against the concentration we found that the relationship was far from linear, and that extrapolation was consequently uncertain; but the logarithms of these variables proved to be very nearly linear functions of each other, so it was not difficult to obtain an empirical, 3-constant

<sup>1</sup> Ostwald-Luther, "Physiko-chemische Messungen," p. 529, 3rd Ed., Leipzig, 1910.

<sup>2</sup> Jackson, "The Temperature Coefficient of the Inversion of Cane Sugar," *Dissertation*, Harvard University, 1917.

<sup>3</sup> Lamble and Lewis, *J. Chem. Soc.*, 107, 1, 240 (1915).

equation which followed the experimental results with great fidelity. This equation,  $\log c = 1.085 + 0.980 \log k_r + 0.04272 \log^2 k_r - 0.03672 \log^3 k_r$ , gave calculated values whose maximum deviation from the experimental values was 0.4%, and whose average deviation was only 0.2%. Solving this empirical equation for an acid concentration of 0.01029 *M*, corresponding to a hydrogen-ion concentration of 0.01, the value  $k_r = 0.842 \times 10^{-4}$  was obtained. This is in reasonable agreement with our directly measured values of  $0.794 \times 10^{-4}$ .

For measuring the inversion produced by the opaque chromic chloride solutions, a somewhat different procedure had to be followed than with the transparent acid solutions. At suitable intervals 50 cc. samples of the solution were transferred by means of a pipet to a narrow bottle, and 10 cc. of a sodium carbonate solution added of just the strength required to precipitate completely the chromic chloride and leave a slight excess of the carbonate. The time was reckoned to the moment of the addition of the sodium carbonate. After settling, the solution was run through a triple filter, the first few cc. of the filtrate rejected, and the inversion tube filled. Readings on a solution treated in this way taken over a period of 3 days were identical, showing that no further inversion occurred under these conditions. They were corrected for the 5/6 dilution. The results of a representative run are given in the following table.

TABLE XI.

Velocity of Inversion in a 0.00787 *M* Solution of Hexa-aquo Chromic Chloride.  
Temperature 25.0°. 9.992 g. of Sugar per 100 cc.

Time, min.	Observed Rotation, Degrees.	$k_r \times 10^6$ .
0	11.01	....
6091	10.31	8.14
9963	9.90	8.03
17414	9.21	7.64
$\infty$	(-3.46)	....

$$k_r (\text{average}) = 7.94 \times 10^{-6}$$

After several unsuccessful preliminary runs, seven final runs of this sort were made. All the averaged values of  $k_r$  thus obtained are collected in Table XII, page 1173.

Before computing the hydrogen-ion concentration, and from it the hydrolysis constant, the velocity constants were first corrected for the slight accelerating effect of the neutral salt. It was assumed that the chromic chloride would produce the same effect as sodium chloride of the same concentration. Kullgren<sup>1</sup> has shown that a normal solution of this salt increases the velocity constant by 67.3%, irrespective of the temperature or the concentration of the acid.

The uncorrected and corrected values of the velocity constant are

<sup>1</sup> Kullgren, *Z. physik. Chem.*, **85**, 471 (1913).

TABLE XII.

Hydrolysis Computed from the Velocities of Inversion of Cane Sugar in Solutions of Hexa-aquo Chromic Chloride at 25.00°.

Run No.	Conc. Hexa-aquo. Salt M.	Average $k_r \times 10^6$ .	Average $k_r \times 10^6$ . Corrected.	$K_b \times 10^4$ .
1.....	0.00787	7.94	7.82	1.42
2.....	0.00789	11.99	11.80	3.48 <sup>a</sup>
3.....	0.00800	8.89	8.76	1.78
4.....	0.00796	7.28	7.17	1.17
5.....	0.00785	8.94	8.80	1.84
6.....	0.01662	12.32	11.95	1.57
7.....	0.01649	11.04	10.71	1.22

$$K_b \text{ (average)} = 1.6 \times 10^{-4}$$

<sup>a</sup> This value because of its exceptional discordance is given only half weight in taking the average.

given in the third and fourth columns of Table XII. The hydrolysis constants calculated from these velocity constants and from the experiments on hydrochloric acid are given in the fifth column. The average value  $1.6 \times 10^{-4}$  is substantially independent of the concentration and in good agreement with the values obtained by other methods.

#### 4. Hydrolysis Determined from the Decrease in Its Conductivity Produced by Hydrochloric Acid.

The hydrolysis of the hexa-aquo chloride can be calculated easily and with a good deal of certainty from the decrease in its molecular conductivity produced by the addition of small amounts of hydrochloric acid, that is by the modification of the well-known Walker<sup>1</sup> method. It is necessary, as Bjerrum pointed out when he applied this method to solutions of the green chloride, to correct for the slight hydrolysis which will occur even in the acid solution. It is not necessary, however, to employ the laborious and complicated formula developed by Bjerrum for this purpose; we need only make a preliminary computation of the hydrolysis constant, assuming no appreciable hydrolysis in the acid solution, then correct the molar conductivity in the acid solution on this basis and repeat the computation for an accurate value of the hydrolysis constant.

One must, of course, correct the apparent molecular conductivity of the chromic chloride in the hydrochloric acid solution for the repression of the ionization of both the hydrochloric acid and the chromic chloride. There is also the possibility of the existence of mono- or dichloro salt, particularly in the hydrochloric acid solution, which would result in a decreased conductivity. No data bearing on this point have previously been secured for such dilute solutions as are here involved and we have therefore carried out a series of experiments to make good this deficiency.

For these experiments, an approximate 0.01 M solution of hydrochloric

<sup>1</sup> Walker, *Z. physik. Chem.*, **4**, 319 (1889).

acid was prepared and carefully analyzed. To it was then added enough dichloro chloride to give an approximately 0.008 *M* solution, and the mixture placed in a thermostat kept at 25.00°. 250-cc. samples of this solution were removed at intervals and analyzed for chloride ion. They were then made ammoniacal and warmed for half an hour on the steam-bath, to convert any chloro salt into aquo, and were again analyzed for chloride ion. The results are given in the following table. The percentage of complex chlorine present is based on the weights of the second precipitate.

TABLE XIII.  
Conversion of Dichloro Chloride into Hexa-aquo Chloride.

No.	Time Hours.	Conc. Dichloro <i>M.</i>	Conc. HCl. <i>M.</i>	Wt. of 1st AgCl Precipitate. Total. G.	Wt. of 2nd AgCl Precipitate. G.	Complex Chlorine. %.	Uncon- verted. %
	0	...	...	....	....	66.67	100.0
1.....	30	0.00811	0.01028	1.0456	0.1946	22.28	33.40
2.....	144	0.00811	0.01028	1.2282	0.0139	1.59	2.38
3.....	204	0.00811	0.01028	1.2300	0.0121	1.39	2.08
4.....	528	0.00756	0.01009	0.2341	0.0022	1.04	1.56

It is evident from the above table that there is some complex chlorine in this solution at equilibrium. The amount may reasonably be estimated at 1.0%, which would correspond to 1.5% of unconverted dichloro salt, or since the molecular conductivity of the hexa-aquo at this concentration is greater than that of the dichloro by 215 mhos, to a decrease of 3.2 mhos.

The amount of complex chlorine which will be present in pure aqueous solution will, of course, be very much less; indeed it has been assumed by previous investigators that the conversion of the dichloro into the hexa-aquo is complete at this low concentration. To make certain of this point, we prepared a 0.008 *M* solution of an analyzed sample of dichloro, placed it in a thermostat at 25.00° and analyzed successive portions of the solution as before for complex chlorine at intervals of 2 days. The ionized chlorine was removed by precipitation, as before, and the complex chlorine remaining was liberated simply by prolonged digestion on the steam-bath with an excess of silver nitrate and a little nitric acid. The percentages of uncorrected dichloro salt still present after 2, 4 and 6 days were 0.38%, 0.23% and 0.26%.

The solutions we have compared by this method were prepared from portions of the same sample of chromic chloride, and the measurements were made at very nearly the same time. The corrections for the repression of ionization were computed as described above. The correction for hydrolysis in the acid solution was obtained by a preliminary approximate computation as explained above. The molecular conductivity of the pure aqueous solution was 348.5 mhos; that of the solution

containing acid was 285.1 mhos. The various corrections, as above mentioned, which are to be applied to these figures, are collected in the following table.

TABLE XIV.  
Corrections to be Applied to the Observed Conductivity.  
Corrections in Mhos.

	Pure Aqueous Solution 0.008046 <i>M</i> .	0.01 <i>M</i> HCl Solution 0.007565 <i>M</i> .
To exactly 0.008 <i>M</i> .....	+0.1	-1.0
For complex chlorine.....	+0.5	+3.2
For repression of ionization, HCl.....	...	+19.6
For repression of ionization, CrCl <sub>3</sub> .....	...	+8.2
For hydrolysis.....	- <i>q</i>	-4.1
Total.....	- <i>q</i> +0.6	+25.9

Applying these corrections the conductivities become  $349.1 - q$  and 311.0 mhos, respectively, and since these should be equal, except for hydrolysis,  $q = 38.1$  mhos. This, divided by the increase which would take place were hydrolysis complete,  $[(350)(0.974) - (47.6)(0.836) = 301 \text{ mhos}]$  gives 0.1266 as the fraction hydrolyzed at this concentration, and therefore  $K_b = 1.47 \times 10^{-4}$ . This value agrees well with our previously determined values.

##### 5. The Hydrolysis of Hexa-Aquo Chloride as Indicated by the Change in Conductivity of Its Solution Caused by Sodium Acetate.

The relatively slight hydrolysis (12% at 25°) of the hexa-aquo salt at 0.008 *M* concentration will, of course, become much greater, if the hydrogen ions are removed by the addition of a salt of a weak acid, sodium acetate for instance. The accompanying extensive formation of the slightly dissociated weak base and weak acid results in a considerable decrease in the conductivity of the mixed solution below what would have obtained had no hydrolysis taken place.

Bjerrum<sup>1</sup> has already shown that the observed decrease in conductivity due to the presence of sodium acetate is about what would be expected from his computed value of the hydrolysis constant of the hexa-aquo chloride, namely,  $0.9 \times 10^{-4}$  at 25°. But a very small change in conductivity corresponds to a large change in the hydrolysis constant, so that reversing his computation it is found that his observed change in conductivity corresponds to a hydrolysis constant of  $57 \times 10^{-4}$ , a value 60 times larger than his, and 30 times larger than our computed value. This discrepancy is so great that we have thought it worth while to examine, from this point of view, a series of experiments we had previously made for another purpose.

These experiments consisted of measurements of the rate of conversion

<sup>1</sup> Bjerrum, *Z. physik. Chem.*, **59**, 354 (1907).

of the chloro chloride into hexa-aquo chloride in the presence of sodium acetate. It had previously been shown<sup>1</sup> that sodium acetate greatly accelerated the conversion, and a more careful kinetic study of this effect was made. The results of a representative experiment are given in Table XV.

TABLE XV.

Transformation of Dichloro-chromic Chloride in 0.00804 *M* Solution of Sodium Acetate.  
Dichloro-chromic chloride = 0.00795 *M*. Temp. = 25°.

Time, min.	<i>L</i> , mhos.	Time, min.	<i>L</i> , mhos.
0	0.000670	8.42	0.002632
2.00	0.002338	15.50	0.002673
2.75	0.002414	21.58	0.002682
3.75	0.002498	39.25	0.002681
4.15	0.002523	61.35	0.002677
4.83	0.002548	92.17	0.002675
6.05	0.002590	151.2	0.002665

These measurements confirm the marked accelerating effect previously noted, and in addition disclose a subsequent slow *decrease* in the conductivity of the hexa-aquo chloride presumably caused by the slow formation of an acetato complex. The final value for the unchanged hexa-aquo salt was found by graphical extrapolation of the slow transformation to zero time.

This extrapolated value of the specific conductance (*L*) of the mixed solutions of chloride and acetate can be expressed as a function of the concentrations and mobilities of the respective ions. To evaluate this function the nearly rigorous assumption can be made that the total concentration of hydrolyzed hexa-aquo salt [ $\text{CrCl}_2\text{OH} + \text{Cr}^{++}\text{OH} = x$ ] is equal to the concentration of the undissociated acetic acid. The function then becomes

$$1000 L = t_{\text{Ac}}\alpha_1\lambda_{\text{Na}^+} + (t_{\text{Ac}} - x)\alpha_1\lambda_{\text{Ac}^-} + (t_{\text{Cr}} - x)\alpha_3\lambda_{\text{Cr}(\text{H}_2\text{O})_6^{+++}} + x\alpha_2\lambda_{\text{Cr}(\text{H}_2\text{O})_6\text{OH}^{++}} + \Sigma\lambda_{\text{Cl}^-},$$

where  $t_{\text{Ac}}$  and  $t_{\text{Cr}}$  = total concentration of acetate and chromic salt;  $\alpha_1$ ,  $\alpha_2$  and  $\alpha_3$  = fraction ionized of NaAc,  $\text{CrOHCl}_2$  and  $\text{CrCl}_3$ ,  $\Sigma$  = total  $\text{Cl}^- = x(\alpha_1 + 2\alpha_2 - 3\alpha_3) + 3\alpha_3t_{\text{Cr}}$ .  $x$  can be computed from this equation as follows.

$1000L = 2.693$ ;  $\lambda_{\text{Na}^+} = 51.2$ ;  $\lambda_{\text{Ac}^-} = 44.3$ ;  $\lambda_{\text{Cl}^-} = 75.8$  mhos. The dissociation of the sodium acetate ( $\alpha_1$ ) can be found on the Arrhenius principle by interpolation from the data of Noyes and Cooper<sup>2</sup> at the same ion concentration (0.024 *M*). The molar conductivity of the hexa-aquo ion ( $\lambda_{\text{Cr}(\text{H}_2\text{O})_6^{+++}}$ ) can be taken as the mean of the values of Heydweiller<sup>3</sup> and of Hopfgartner and Marinkovic<sup>4</sup> or 142.9

<sup>1</sup> Lamb, *loc. cit.*

<sup>2</sup> Noyes and Cooper, *Carnegie Inst. Pub.*, 63, Pt. V, p. 134.

<sup>3</sup> Heydweiller, *loc. cit.*

<sup>4</sup> Hopfgartner and Marinkovic, *ibid.*

mhos. The percentage dissociation of the chromic chloride ( $\alpha_3$ ) computed from this value, using the formula of Storch and Bancroft, is 0.836.  $\lambda_{\text{Cr}(\text{H}_2\text{O})_6^{3+}} + \alpha_2$  can be taken as  $\frac{2}{3} \lambda_{\text{Cr}(\text{H}_2\text{O})_6^{3+}}$  and  $\alpha_2$  as approximately intermediate between  $\alpha_1$  and  $\alpha_3$ .

Substituting these values in the above expression  $x = 0.00606 M$  and therefore, since  $K_{\text{HAc}} = 1.73 \times 10^{-5}$  at  $25^\circ$ ,<sup>1</sup>

$$K_b = \frac{(K_{\text{HAc}})(x\alpha_2)^2}{\alpha_1(t_{\text{Ac}} - x)(\alpha_3)(t_{\text{Cr}} - x)} = 1.68 \times 10^{-4}.$$

This also agrees reasonably well with the values obtained by the other methods.

**6. Comparison of Results of Different Methods.**—The results obtained by the five different methods are shown in the following table.

TABLE XVI.

The Hydrolysis Constant of Hexa-aquo chromic Chloride at $25^\circ$ .	
Method.	$K_b \times 10^4$ .
Change of conductivity with concentration.....	1.52
Rate of transformation of dichloro-chloride.....	1.65
Rate of inversion of cane sugar.....	1.60
Conductivity with and without hydrochloric acid.....	1.47
Addition of sodium acetate.....	1.68

Mean  $K_b = \dots\dots\dots 1.58 \times 10^{-4}$

It can be seen that the agreement of the results is excellent, the average deviation from the mean being less than 5%.

### Summary.

1. The uncertainty of the present values of the hydrolysis constants of the dichloro and hexa-aquo chromic chlorides has been pointed out.

2. The hydrolysis constant of the dichloro chloride has been measured by two methods. The first is a modification of the Walker method and involves a comparison of the conductivities of solutions of the dichloro salt containing different amounts of hydrochloric acid. The second is a method already applied by Bjerrum to this problem, and involves a study of the kinetics of the transformation of the dichloro into hexa-aquo, and in particular of the variation of the velocity constant of this reaction with the concentration of the hydrogen ion in solutions to which acid had been added. Knowing this variation, it is possible to compute the hydrolysis constant from the observed values of the velocity constant in pure aqueous solution. The value obtained by the first method is  $K_g = 1.8 \times 10^{-6}$ ; by the second  $K_g = 2.0 \times 10^{-6}$ . The mean value therefore is  $K_g = 1.9 \times 10^{-6}$ .

3. It has been pointed out that the addition of small amounts of dichloro-chromic chloride to a solution and the observation of its change in conductivity offer a convenient method for the determination of hydrogen-ion concentrations—particularly when they are small—and that the re-

<sup>1</sup> Noyes and Sosman, *Carnegie Inst. Pub.*, **63**, Pt. VII, 228.



sults are not affected by the presence of chloride ions at a concentration equal to that of the dichloro chloride (0.008 *M*).

4. The hydrolysis constant of the hexa-aquo chloride at 25° has been measured over a wide range of concentrations by five methods. An average value of  $K_b = 1.58 \times 10^{-4}$  at 25° was obtained, with an average deviation of less than 5%.

5. Incidentally, in applying the method depending on the rate of inversion of sugar, it was necessary to determine the acceleration produced by 0.0074 *M* acid at 25°, a much lower concentration than had previously been worked with at this temperature. A satisfactory empirical equation representing the results of Lambie and Lewis was also derived.

6. In applying the Walker method to the hexa-aquo chloride, it was also necessary to determine the location of the equilibrium between the dichloro and the hexa-aquo chloride at a concentration of 0.008 *M*, both in the presence and absence of hydrochloric acid. It was found that in the former case 1.5% and in the latter 0.25% of dichloro salt was present in the equilibrium at 25°.

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### NOTES

**A Method for Producing Dry Ammonia.**—In the work described previously in this number of *THIS JOURNAL*, it was desirable to have a source of dry ammonia gas which could be used at variable pressures up to two atmospheres. For this purpose, we have modified the method for producing ammonia used by Keyes and Brownlee,<sup>1</sup> consisting of warming a solution of ammonium nitrate in ammonia, by substituting ammonium thiocyanate for the nitrate. The thiocyanate has the advantage of taking up more ammonia than the nitrate at a given pressure, but its chief advantage lies in the extreme rapidity with which it absorbs ammonia.

The apparatus consists merely of a heavy-walled salt-mouth bottle holding about 500 cc., with a stopper provided with an outlet tube, and with an inlet tube for charging. The bottle is nearly filled with dry ammonium thiocyanate to act as an absorbent. The inlet and outlet tubes may be provided with glass stopcocks or even with heavy-walled rubber tube and screw pinchcocks.

The apparatus is stored with ammonia by passing in the dry gas, keeping the bottle cooled with ice during the process. When saturated with ammonia at 0° and atmospheric pressure, the solution contains about 45% ammonia. The gas is absorbed with a rapidity comparable to that of ammonia in water, so that a very rapid current can be run in with almost no loss. By placing the bottle, after being stored, in a water-bath, and keeping at room temperature or slightly above, the ammonia can be drawn off as desired. The ammonia in this generator is nearly the equivalent of liquid ammonia as purchased in tanks, except that its

<sup>1</sup> Keyes and Brownlee, *THIS JOURNAL*, 40, 25 (1918).