culations. Grateful acknowledgments are also due to the Carnegie Institution of Washington, whose financial assistance has made this work possible.

BOSTON, MASS.

[CONTRIBUTIONS FROM THE HAVEMEYER CHEMICAL LABORATORY, NEW YORK UNIVERSITY.]

AN EQUILIBRIUM IN THE COBALTAMMINES.[1]

BY ARTHUR B. LAMB AND JOHN W. MARDEN.

Received July 20, 1911.

The ammonia compounds of cobalt salts, called the *cobaltammines* to distinguish them from the organic amines, constitute an unusually interesting group of substances. A great number of them have been prepared; they have been arranged in numerous well defined classes, and the systematic correlation of these classes has been well worked out. They exhibit points of marked similarity with organic substances; thus they contain complex radicals entirely analogous in their behavior to organic radicals; they exhibit structural and stereomeric isomerism quite as striking as that of many organic substances; substitutions can be made with an even greater freedom than in organic compounds. On the other hand, these compounds are distinctly inorganic; they are for the most part salts, more or less soluble in water, and more or less electrolytically dissociated.

These unusual substances offer particular advantages for the study of such fundamental chemical problems as valency, the connection between chemical nature and electrolytic dissociation, etc. Indeed, they have already given rise to one theory of valency (Werner's), which, even if it may ultimately prove incorrect, has nevertheless furnished a simple and comprehensive correlation of this group and of other similar groups. However, for a study of any of these problems a knowledge of the *energetic* relationships is important. We ought, for instance, to know the difference in the total and free energy of formation of the different isomers and part isomers in this group; or, if possible, the difference in free or total energy between a partial and principal valency in the sense of Werner's theory. There is at present no information whatever on these subjects, and it was in the hope of making good some of this deficiency that this research was undertaken.

The most promising point of attack appeared to be the spontaneous transformations which many of the cobaltammines undergo either in the dry state or in solution. If these transformations could be shown to approach equilibria, the free energy change, or the affinity of the reactions,

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[1] Presented at the June, 1911, meeting of the New York Section of the American Chemical Society.

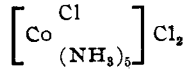
would be known; if the equilibria could be measured at two different temperatures, or if an independent measurement of the heat of reaction could be made, then the total energy change could be calculated.

Of these transformations the one which has been longest known is the change of the *purpureo* salts into *roseo* salts in aqueous solution. In this paper we shall hope to show that a reversible equilibrium is here attained. At a later date we shall hope to furnish the further data necessary for a calculation of the total energy change.

The Transformation of Purpureo Salts into the Corresponding Roseo Salts and Vice Versa.

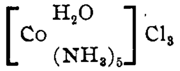
Purpureo and roseo cobalt chloride are both trichloropentammine compounds of cobalt. They were among the original cobaltammines prepared by Genth[1] in 1851. Claudet[2] and Fremy[3] prepared the same substances independently a little later. Gibbs and Genth[4] in 1856 found that these trichloropentammine salts, which till then had all been called roseo salts, really consisted of *two* classes of salts. To one class they gave the old name roseo cobaltammines; to the other, because of the characteristic color of its compounds, they gave the name purpureo cobaltammines. They pointed out that the purpureo salts were in general less soluble in water than the roseo salts; that roseo chloride contained one equivalent of water, while purpureo chloride contained none; and that the purpureo radical behaved as a di-acid, the roseo radical as a tri-acid base. Fremy,[5] and Gibbs and Genth[6] had observed the fact that the chlorine in the purpureo salts was not completely precipitable by silver nitrate in the cold, but Krock[7] first established the fact that it was *exactly* one-third of the chlorine and therefore only one of the chlorine atoms which could not be precipitated.

All these facts, amply confirmed by Jörgensen, are expressed from Werner's point of view by the two following formulas:



$$\left[\mathrm{Co}\begin{matrix}\mathrm{Cl}\\ (\mathrm{NH_3})_5\end{matrix}\right]\mathrm{Cl_2}$$

Purpureo
pentammine cobalt chloride.



$$\left[\mathrm{Co}\begin{matrix}\mathrm{H_2O}\\ (\mathrm{NH_3})_5\end{matrix}\right]\mathrm{Cl_3}$$

Roseo
pentammine cobalt chloride.

Only the chlorine atoms outside the radical can function as ions; only two-thirds, then, of the total chlorine in the purpureo salt can be pre-

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[1] Nordamerikanischer Monatsbericht für Natur- und Heilkunde, 1, Jan., 1851.

[2] *Ann. chim. phys.*, **23**, 483.

[3] *Compt. rend.*, **32**, 509, 808.

[4] "Researches on the Ammonia Cobalt Bases." Smithsonian Contributions to Knowledge. (Washington, 1856.)

[5] *Ann. chim. phys.*, 3, 35, 303.

[6] *Loc. cit.*, p. 5.

[7] Lunds. Univers. Arsskrift, 1870.

cipitated by silver nitrate, while all of it in the roseo salt can be. The purpureo ion is therefore divalent, the roseo trivalent.

Gibbs and Genth[1] observed the easy conversion of roseo salts into the corresponding purpureo salts when heated in aqueous solution, and especially when heated in hydrochloric acid, or in a solution of ammonium chloride.

Jörgensen[2] was the first to observe the reverse change, that is, the change of purpureo into the roseo salt; he found that this took place simply on standing in aqueous solution. The process was a slow one in the case of the chloro, but more rapid in the case of the nitrato salts.[3] Werner and Miolati,[4] in measuring the conductivity of solutions of various purpureo salts, found an increase in conductivity with the time, which indicated a conversion into roseo salts, thus confirming the observations of Jörgensen. Jörgensen also found that while hydrochloric acid and the alkali chlorides readily converted roseo chloride into purpureo chloride, silver oxide, barium hydroxide and ammonia, when not boiled, converted purpureo salts into roseo. If boiled, decomposition of the ammine set in.

Finally, it has been found in this laboratory that in *concentrated* aqueous solution, even at room temperature, roseo chloride is converted into purpureo chloride.

We may summarize these results as follows: In dilute aqueous solutions at low and moderate temperatures and especially in alkaline solutions, purpureo salts change to roseo; in concentrated solutions, or in solutions containing chlorides, or on heating, the reverse change takes place. The evidence, therefore, strongly indicated the existence of a true equilibrium between the roseo and the purpureo modification. In order to study this equilibrium intelligently, it was evidently necessary to know something about the velocity of transformation under different conditions. We therefore first directed our attention to this aspect of the problem, and in particular, since it takes place under the more convenient conditions, to the transformation of purpureo salts into roseo.

The Velocity of Transformation of Purpureo Salts Into Roseo Salts.

Since in the purpureo salts only two-thirds of the negative radical can become ionized, while in the roseo salts all of it can be, it follows that the conductivity of a solution of purpureo chloride, for instance, must increase as the purpureo chloride changes into roseo chloride, provided the mobilities of the two complex ions are approximately the same. Indeed, it was largely upon the measurements of the electrical conductivities of these and similar cobaltammines that Werner based

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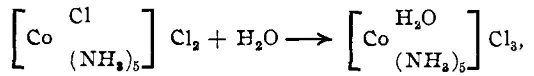
[1] *Loc. cit.*, p. 9.

[2] *J. prakt. Chem.*, 19, 51 (1879).

[3] *Ibid.*, 19, 232 (1879).

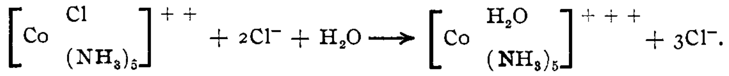
[4] *Z. physik. Chem.*, 14, 520 (1894).

his theory of the structure of these compounds. The transformation would be represented as follows:



$$\left[\mathrm{Co}\begin{matrix}\mathrm{Cl}\\(\mathrm{NH_3})_5\end{matrix}\right]\mathrm{Cl_2} + \mathrm{H_2O} \longrightarrow \left[\mathrm{Co}\begin{matrix}\mathrm{H_2O}\\(\mathrm{NH_3})_5\end{matrix}\right]\mathrm{Cl_3},$$

or in very dilute solution, where ionization could be assumed to be complete, as follows:



$$\left[\mathrm{Co}\begin{matrix}\mathrm{Cl}\\(\mathrm{NH_3})_5\end{matrix}\right]^{++} + 2\mathrm{Cl}^- + \mathrm{H_2O} \longrightarrow \left[\mathrm{Co}\begin{matrix}\mathrm{H_2O}\\(\mathrm{NH_3})_5\end{matrix}\right]^{+++} + 3\mathrm{Cl}^-.$$

The increase in conductivity would evidently amount to 50 per cent. of the original conductivity, assuming an equal percentage dissociation and equal mobilities of the complex ions. This increase is large enough to permit of accurate measurement, and we therefore chose this method for determining the progress of the transformation.

We have assumed in our calculations that the increase in molecular conductivity is *exactly* proportional to the amount of transformation, that is, that $\frac{\mu_t - \mu_0}{\mu_\infty - \mu_0}$ equals the fraction transformed, where μ_0, μ_t and μ_∞ represent respectively the molecular conductivity at the beginning, at the time t and at the end. This must be very nearly the case, for even if the percentage dissociation, or the percentage hydrolysis of the two salts, or the mobilities of the two ions were different, their effect on the conductivity would be nearly proportional to the relative concentration of the two salts. The solutions used were very dilute (1/500 molar); the percentage dissociation must have been nearly the same. The measurements of Werner and Miolati have also shown that the mobilities of the purpureo and roseo ions must be nearly identical.

The solutions were prepared by dissolving a weighed quantity (always less than 1 gram) of the desired salt in exactly one liter of redistilled water previously warmed to precisely 25° (its specific conductivity varied between 1.08 and 2.5×10^{-6} 1/ohms), and shaking vigorously until solution was complete. The temperature was again adjusted exactly, and the solution poured rapidly into the dry conductivity cells already fixed in the thermostat, up to a mark on the narrow neck of the cells. Duplicate runs were made, usually in different cells. The salts were prepared according to the improved methods of Jörgensen.[1] The salts were finely ground before use; nevertheless they went into solution rather slowly, the most insoluble sometimes requiring twenty minutes, the most soluble four or five minutes. Most of the salt would, however, always dissolve in two or three minutes, and the time was therefore counted from one to three minutes after the addition of the salt. Conductivity measurements were taken within a few minutes after complete solution.

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[1] *Z. anorg. Chem.*, 17, 160.

The measurements were made with a Kohlrausch spirally-wound bridge permitting a reading on the bridge wire to one part in ten thousand. A thermostat maintained a temperature of 25° constant to within a few hundredths of a degree. A thermometer which could be read to 0.01° was nevertheless fitted in the large, closed, flask-shaped cells, and the temperature at each reading of the conductivity recorded. The electrodes were firmly fixed in a permanent position and provision was made for stirring.

The following tables contain the result of the velocity measurements. In them the time and the corresponding molecular conductivities are given; when substances other than the cobaltammines were present in the solution the specific conductivities are also given. In the last column of each table are given the values of K, a constant calculated for a first-order reaction, that is, according to the expression

$$K = 1/t \log \frac{\mu_t - \mu_0}{\eta_\infty - \mu_0}.$$

The values of μ_0 and μ_∞ were obtained by extrapolation. It will be seen that these values agree well with one another in the different comparable series.

Table I.—Velocity of Transformation of a 0.004 Molar Solution of Chloropentammine Cobalt Chloride at 25°.

Time. Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.	Time. Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.
0	(259.7)	...	1580	281.3	0.067
40	260.3	0.062	1940	284.3	0.063
345	263.3	0.046	2240	285.5	0.058
470	265.8	0.058	2810	289.3	0.054
790	271.3	0.067	∞	(360.0)	...
1355	278.3	0.066			

Mean value $K = 0.060 \times 10^{-3}$.

Table II.—0.002936 Molar Solution of Chloropentammine Cobalt Nitrate in Water at 25°.

Time. Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.	Time. Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.
0	(253.0)	...	205	256.2	0.054
25.5	253.4	0.043	275	257.0	0.051
55	254.0	0.058	1138	267.8	0.049
108	255.2	0.070	∞	(376.0)	...
185	256.2	0.060			

Mean value $K = 0.055 \times 10^{-3}$.

TABLE III.—0.002978 MOLAR SOLUTION OF CHLOROPENTAMMINE COBALT NITRATE IN WATER AT 25°.

Time. Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.	Time. Minutes.	Molecular conductivity 1/ohms	$K \times 1000$.
0	(244.0)	...	159	245.4	0.031
39	244.7	0.064	316	248.8	0.055
61	244.9	0.051	496	250.5	0.048
81	245.3	0.057	633	252.9	0.052
91	246.1	0.082	1402	263.8	0.054
			∞	(363.9)	...

Mean value $K = 0.055 \times 10^{-3}$.

TABLE IV.—0.003266 MOLAR SOLUTION OF BROMOPENTAMMINE BROMIDE IN WATER AT 25°.

Time. Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.	Time Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.
0	(259.5)	...	196	270.2	0.177
23	260.8	0.174	241	272.0	0.166
28	260.7	0.143	255	272.0	0.157
33	261.5	0.188	575	287.2	0.163
38	261.9	0.155	1311	313.0	0.156
43	262.1	0.184	2030	336.5	0.166
50	262.6	0.190	2713	350.6	0.163
144	267.9	0.183	∞	(402.0)	...

Mean value $K = 0.169 \times 10^{-3}$.

TABLE V.—0.003266 MOLAR SOLUTION OF BROMOPENTAMMINE COBALT BROMIDE IN WATER AT 25°.

Time. Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.	Time. Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.
0	(258.2)	...	255	271.5	0.167
34	260.1	0.165	575	287.2	0.171
44	261.0	0.186	1310	314.5	0.164
51	261.1	0.169	2031	338.1	0.177
145	266.2	0.169	2710	353.1	0.177
197	268.7	0.169	∞	(402.0)	...
240	271.0	0.165			

Mean value $K = 0.170 \times 10^{-3}$.

TABLE VI.—0.002758 MOLAR SOLUTION OF NITRATOPENTAMMINE COBALT NITRATE IN WATER AT 25°.

Time. Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.	Time. Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.
0	(262.4)	...	181	292.2	0.745
25	267.1	0.744	333	310.6	0.755
30	269.8	0.980	423	320.2	0.753
56	273.1	0.784	1015	358.3	0.849
60	273.6	0.800	1383	364.2	0.764
82	276.4	0.704	1658	367.2	0.733
98	279.1	0.728	2530	372.4	0.739
120	281.8	0.675	∞	(374.0)	...
151	287.1	0.729			

Mean value $K = 0.76 \times 10^{-3}$.

TABLE VII.—0.002949 MOLAR SOLUTION OF NITRATOPENTAMMINE COBALT NITRATE IN WATER AT 25°.

Time. Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.	Time. Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.
0	(260.0)	..	638	346.7	0.72
14	263.5	0.83	1358	379.3	0.73
24	265.2	0.72	1478	381.1	0.71
43	270.2	0.81	1607	383.3	0.71
100	279.5	0.69	1838	386.5	0.71
199	296.8	0.71	2678	391.6	0.74
260	304.1	0.67	∞	(393.0)	..
365	323.5	0.79			

Mean value $K = 0.73 \times 10^{-3}$.

TABLE VIII.—0.002949 MOLAR SOLUTION OF NITRATOPENTAMMINE COBALT NITRATE IN WATER AT 25°.

Time. Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.	Time. Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.
0	(255.5)	..	365	329.4	0.99
7	257.6	(1.14)	638	345.2	0.78
16	258.6	0.73	1358	376.2	0.81
23	260.9	0.83	1479	378.1	0.80
45	264.3	0.69	1606	380.4	0.84
73	271.3	0.78	1839	382.4	0.81
198	290.0	0.68	2676	385.5	0.77
260	298.6	0.67	∞	(387.9)	..

Mean value $K = 0.79 \times 10^{-3}$.

TABLE IX.—0.007982 MOLAR SOLUTION OF NITRATOPENTAMMINE COBALT NITRATE IN WATER AT 25°.

Time. Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.	Time. Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.
0	(247.3)	..	173	277.7	0.77
20	251.4	0.79	258	289.7	0.77
29	253.0	0.76	380	304.4	0.78
64	259.0	0.72	1243	336.9	0.52
107	267.0	0.76	∞	(363.0)	..
123	270.1	0.77			

Mean value $K = 0.76 \times 10^{-3}$.

TABLE X.—0.003012 MOLAR SOLUTION OF NITRATOPENTAMMINE CHLORIDE IN WATER AT 25°.

Time. Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.	Time. Minutes.	Molecular conductivity 1/ohms.	$K \times 1000$.
0	(254.5)	..	67	270.0	0.73
10	257.0	0.76	145	287.7	0.78
20	259.8	0.81	223	301.5	0.76
24	260.8	0.80	516	340.7	0.75
28	262.0	0.82	1435	389.1	0.79
48	266.5	0.78	∞	(400.0)	..

Mean value $K = 0.78 \times 10^{-3}$.

Table XI.—0.002651 Molar Solution of Nitratopentammine Cobalt Nitrate in 0.001 Molar Solution of Nitric Acid at 25.°

Time. Minutes.	Specific conductivity 1/ohms.	Molecular conductivity 1/ohms.	$K \times 1000$.
0	0.0	(260.0)	..
11	0.000658	263.8	(1.21)
33	0.000665	266.6	0.71
74	0.000683	273.8	0.68
127	0.000709	284.3	0.73
150	0.000717	287.5	0.71
179	0.000735	294.6	0.74
262	0.000758	303.9	0.71
1144	0.000916	367.2	0.72
1222	0.000919	368.3	0.69
1320	0.000926	371.3	0.70
1505	0.000935	374.9	0.69
2610	0.000959	394.4	0.70
∞	....	(386.3)	..

Mean value $K = 0.71 \times 10^{-3}$.

The specific conductivity of the ammine was obtained by subtracting the specific conductivity of the nitric acid from the observed specific conductivity.

Table XII.—0.002640 Molar Solution of Nitratopentammine Cobalt Nitrate in 0.002 Molar Solution of Nitric Acid at 25°.

Time. Minutes.	Specific conductivity 1/ohms.	Molecular conductivity 1/ohms.	$K \times 1000$.
0	......	(260.0)	..
40	0.000685	267.6	0.65
70	0.000696	271.9	0.59
106	0.000704	275.0	0.50
136	0.000724	282.8	0.61
154	0.000728	284.4	0.59
289	0.000774	302.3	0.59
319	0.000781	305.1	0.58
349	0.000794	310.1	0.60
379	0.000802	313.3	0.60
1047	0.000907	354.3	0.54
1124	0.000918	358.6	0.55
∞	......	(390.0)	..

Mean value $K = 0.58 \times 10^{-3}$.

Table XIII.—0.002644 Molar Solution of Nitratopentammine Cobalt Nitrate in 0.0146 Molar Solution of Sodium Acetate at 25°.

Time. Minutes.	Specific conductivity 1/ohms.	Molecular conductivity 1/ohms.	$K \times 1000$.
0	....	...	..
12	0.000572	222.1	0.66
14	0.000572	222.1	0.56
24	0.000574	224.0	0.69

TABLE XIII (*continued*).

Time. Minutes.	Specific conductivity. 1/ohms.	Molecular conductivity. 1/ohms.	$K \times 1000$.
36	0.000580	226.2	0.74
44	0.000583	227.4	0.73
57	0.000586	228.6	0.66
69	0.000591	230.6	0.69
77	0.000595	232.1	0.71
87	0.000599	234.6	0.78
99	0.000603	235.2	0.71
110	0.000604	235.6	0.66
117	0.000606	236.4	0.66
192	0.000625	244.8	0.64
222	0.000631	246.1	0.59
299	0.000650	255.9	0.64
391	0.000669	261.0	0.59
599	0.000705	275.0	0.58
1364	0.000769	300.0	0.52
1970	0.000805	314.1	0.64
2880	0.000817	318.7	0.73
∞	....	(319.5)	..

Mean value $K = 0.66 \times 10^{-3}$.

TABLE XIV.—SUMMARY OF RESULTS OF VELOCITY EXPERIMENTS AT 25° IN AQUEOUS SOLUTIONS.

No.	Substance.	Concentration molar.	Third substance conc. molar.	Constant $K \times 1000$.
1	$[Co(NH_3)_5Cl]Cl_2$	0.004000	..	0.060
2	$[Co(NH_3)_5Cl](NO_3)_2$	0.002936	..	0.055
3	"	0.002978	..	0.055
4	$[Co(NH_3)_5Br]Br_2$	0.003266	..	0.169
5	"	0.003266	..	0.170
6	$[Co(NH_3)_5NO_3](NO_3)_2$	0.002758	..	0.76
7	"	0.002949	..	0.73
8	"	0.002949	..	0.79
9	"	0.007982	..	0.76
10	$[Co(NH_3)_5NO_3]Cl_2$	0.002918	..	0.78
11	$[Co(NH_3)_5NO_3](NO_3)_2$	0.002651	0.001 HNO_3	0.71
12	"	0.002640	0.002 HNO_3	0.58
13	"	0.002644	0.0146 NaAc	0.66

These experiments show that the change from purpureo is very slow at these concentrations; slow enough to permit of an accurate analytical determination of the relative amounts of roseo and purpureo salts in a given solution at 25°. This was the immediate information desired from these experiments. Nevertheless other interesting relations were found, as follows:

The change to the roseo is a *monomolecular* one. The variations in the constant are relatively small. This indicates that the change is either a slow intramolecular change or a slow process of electrolytic dissociation.

The salts which were studied differ decidedly in their rates of transformation; the bromo changes about three times, the nitrato about ten times as fast as the chloro salt. These differences are much greater than the differences in electrochemical potential of the chlorine, bromine or nitrate ion, or in the differences in the volume of the chlorine, bromine or nitrate radical. However, the stability of the oxalato, carbonato and nitrito pentammine salts indicates that less acidic radicals leave in complex less readily than the more acidic ones.

The rate of transformation is independent of the negative group outside the complex radical; the velocity constants for the chloro chloride and the chloro nitrate are identical within the experimental error (Nos. 1, 2 and 3) and so are the velocity constants for the nitrato nitrate and the nitrato chloride (Nos. 6, 7, 8 and 10).

The velocity constant is independent of the original concentration of the reacting substances, as would be expected for a first order-reaction (Nos. 6, 7, 8 and 9).

The rate of transformation is also nearly, if not quite, independent of the hydrogen ion concentration. Thus the constant for the nitrato nitrate in pure water, 0.001 and 0.002 molar nitric acid and in 0.0146 sodium acetate differed but slightly (Nos. 6, 7, 8, 11, 12 and 13). This is markedly different from the behavior of green chromium chloride solutions, where the rate of transformation to violet chromium chloride was found to be very decidedly dependent on the hydrogen ion concentration.[1]

These experiments on the velocity of transformation showed clearly that equilibrium would not be reached at 25° within a feasible time. We therefore attempted to measure the rate of transformation in a similar fashion at the boiling point of water. We immediately found that decomposition of the cobaltammines occurred within a few moments under these conditions and within a few hours at 70°. It was evident that unless this decomposition could be avoided the equilibrium conditions would become hopelessly complicated. The decomposition of the purpureo salts in aqueous solution was therefore next studied.

The Decomposition of Pentammine Cobalt Salts in Aqueous Solution.

It was observed in the above cases where cobaltammine solutions were heated to 100° or thereabouts that no decomposition was visible for some time, but that suddenly a black precipitate appeared and then decomposition progressed to apparent completion in a few moments, the black precipitate forming in large quantities and leaving an almost colorless supernatant liquid. When the solution was acid, the appearance of the black precipitate was delayed, but once it had appeared, decomposition progressed to apparent completion with equal suddenness. A series of experiments was carried out to test the effect of different concentrations

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[1] Lamb, THIS JOURNAL, 28, 1710 (1906).

of acid on this decomposition. In these experiments weighed quantities of purpureo cobalt chloride were added to a given volume of the different solutions of hydrochloric acid heated to 100° in a water bath. The results are recorded in Table XV.

TABLE XV.—RATE OF DECOMPOSITION OF SOLUTIONS OF CHLOROPENTAMMINE COBALT CHLORIDE AT 100°.

No.	Concentration of salt. Molar.	Concentration of HCl. Molar.	Time of appearance of black ppt. Minutes.	Retardation. Minutes.	Retardation per equivalent acid. Minutes.	Remarks.
1	0.00966	0	15	0	0	
2	0.00948	0.0050	28	13	2.6	
3	0.01004	0.0100	45	30	3.0	
4	0.00942	0.0133	108	93	6.9	
5	0.00966	0.0200	155	140	7.0	
6	0.00965	0.0244	315	300	12.3	
7	0.00968	0.0400	780	765	19.1	
8	0.00968	0.0800	..	..	..	No apparent decomposition after many hours

The decomposition of the cobaltammine liberates five equivalents of ammonia, and the appearance of the black precipitate (doubtless a hydrated hydroxide of cobalt) marks the point at which this decomposition has produced a certain alkalinity in the solution; once this alkalinity has been attained the decomposition becomes very rapid. If the solution originally contained acid this will require neutralization, and the appearance of the black hydroxide will be retarded; the greater the concentration of the acid the greater the retardation. If the amount of acid originally present is more than equivalent to the ammonia liberated, then the decomposition will proceed to completion without the formation of any hydroxide. These conclusions are all confirmed by the experiments in the above table.

The retardation per equivalent of acid is much greater in the concentrated acid solutions than in the dilute ones. There is then apparently a specific retarding effect of the acid. This cannot, however, be a very marked effect, for the greater retardation must be in part due to the lesser concentration of the cobaltammine in the partially decomposed solution.

This method of following the decomposition is evidently too indirect to be satisfactory. Since ammonia is liberated by the decomposition of the ammine, any method of following the changing acidity of the solution would tell the extent of decomposition at that time. The various indicators which were tried proved to be very unsatisfactory on account of the deep color of the solution. The addition of solid barium carbonate was tried as a means of determining the acidity, but a blank test showed that this simply caused the complete hydrolysis of one chlorine radical.

Electromotive force titrations, using the hydrogen electrode, were tried, but without success. It was found that the cobaltammine solutions lost their color after standing a few hours in contact with the platinized electrode when a current of hydrogen was passing through the solution. When the electrode was removed, or when the current of hydrogen was turned off, this reduction did not take place. This indicated that the reduction was caused by the hydrogen dissolved in, or adsorbed upon, the finely divided platinum. This suggested interesting electromotive force experiments, but the method was evidently unsuited for our purpose. The oxygen electrode was also tried but no constant readings were obtained.

Titrations by means of electrical conductivity measurements were then resorted to, with more success. The solutions after being heated for a specified length of time at a given temperature were cooled and titrated. The alkali was added from a small buret graduated to 0.01 cc. Phenolphthalein was also added to these solutions and the rather indefinit point at which the pink color became evident was noted. The bridge readings were plotted against the number of cubic centimeters of the alkali added and the point of minimum conductivity determined graphically. This could be done with considerable accuracy in all the cases recorded in the tables. The phenolphthalein end point corresponded, as nearly as could be determined, with the electrical one.

TABLE XVI.—ELECTRICAL TITRATION OF SOLUTIONS OF CHLOROPENTAMMINE COBALT CHLORIDE IN WATER.

No.	Concentration of salt molar.	Volume of solution cm³.	Temperature of titration.	Concentration of HCl molar.	Time of heating. Hours.	Temperature of heating.	NaOH 0.1 *M* added at maximum. cm³.	Excess NaOH solution. cm³.
1	0.004100	50.00	25.0°	0	0	..	0	0
2	0.003692	100.00	25.0	0.02	0	..	19.98	—0.02
3	0.003692	100.00	25.0	0.02	0	..	19.91	—0.09
4	0.004140	50.00	25.0	0	2	60°	0.17	0.17
5	0.003996	50.00	16.5	0.02	2	60°	10.02	0.02
6	0.004140	50.00	25.0	0	$2^3/_4$	60°	0.38	0.38
7	0.003996	50.00	16.5	0.02	4	60°	10.30	0.30

The results (Table XVI) show a slight *increase* in the apparent acidity of the solutions which have been heated to 60°, as compared with the unheated solutions. This indicates certainly that no decomposition took place. The slight increase (0.02 to 0.38 cc.) in apparent acidity may be due to the formation of the more largely hydrolyzed roseo salt. Although the minima in the conductivity curves obtained with these solutions in which no decomposition had taken place were fairly sharp, with solutions which were known to have undergone decomposition, the minima became very indefinit, due perhaps to the ammonium and cobalt salts formed. This method then told us when no decomposition had taken place, but was useless to measure the extent of decomposition.

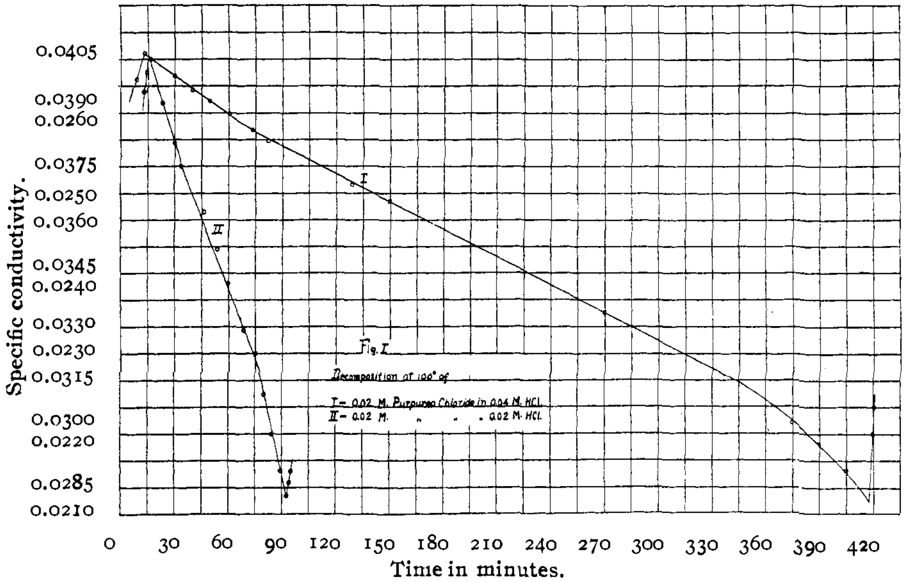
We finally resorted to the same method as was employed at 25° to measure the velocity of transformation, namely, successive measurements of the electrical conductivity. A 400 cc. flask, containing the dilute acid solution, was hung in a thermostat adjusted to the desired temperature, and when the conductivity of the acid had become constant, the salt was dropped in and the solution thoroughly mixed by means of the dip electrode. Readings were then taken at frequent intervals, until the change was complete. A liquid thermostat was used for temperatures below 100°, but a steam jacket was used for the measurements at 100°. The apparatus for this purpose consisted of an inverted bell-jar fitted with a cover from which the flask was hung. Steam was led in at the top of the bell-jar and allowed to flow out at the bottom.

The results obtained with 0.02 *M* purpureo chloride in 0.02 *N* hydrochloric acid are typical of what was observed at 100°. They are given numerically in Table XVII and graphically in Curve II, Fig. I, where the specific conductivity is plotted against the time.

TABLE XVII.—CONDUCTIVITY MEASUREMENTS SHOWING DECOMPOSITION OF A 0.02 MOLAR SOLUTION OF CHLOROPENTAMMINE COBALT CHLORIDE IN 0.02 *N* HCl.

Time. Minutes.	Temperature. °.	Sp. conductivity 1/ohms.	Remarks.
11	96.4	0.02627	
15	98.9	0.02651	
19	99.6	0.02636	
23	99.6	0.02611	
27	99.6	0.02585	
31	99.6	0.02566	
35	99.6	0.02537	
39	99.6	0.02510	
43	99.6	0.02484	
48	99.6	0.02461	
53	99.6	0.02432	
57	99.6	0.02407	
61	99.6	0.02384	
65	99.6	0.02359	
69	99.6	0.02330	
73	99.6	0.02305	
77	99.6	0.02280	
81	99.6	0.02254	
86	99.6	0.02222	
87	99.6	0.02200	
89	99.6	0.02177	
91	99.6	0.02153	Black oxide of cobalt precipitated here.
93	99.6	0.02125	
95	99.6	0.02143	
96	99.7	0.02254	
97	99.7	0.02401	

It will be observed that the conductivity first rizes, then falls at a fairly constant rate, only to rize again very sharply indeed. The beginning of the last very sharp rize always just precedes the separation of the black oxide of cobalt from the solution. It is evident that the initial rize of

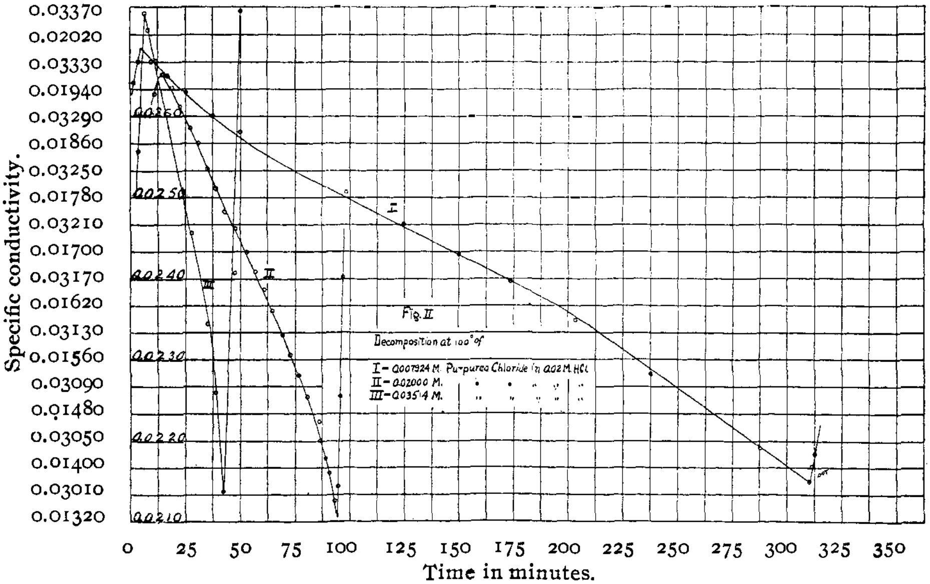


the curve is due largely to the fact that the solution is somewhat cooled by the introduction of the salt; doubtless it is partly due to the formation of the roseo modification and the consequent increase in the number of ions. Decomposition, however, has been going on steadily, setting free ammonia, and this has decreased the original acidity, and hence by the removal of the swiftly moving hydrogen ions has decreased the conductivity. This decomposition soon becomes the dominating factor, increasing slightly in its velocity as the solution becomes less and less acidic. Finally, as the neutral point is reached, the decomposition becomes much more rapid, and since now the rapidly moving hydrogen ions are practically all removed, further decomposition, involving the liberation of rapidly moving hydroxyl ions, increases rather than decreases the conductivity. Moreover, the cobalt hydroxide, one of the products of decomposition, would appear as soon as the neutral point is passed.

The approximately linear course of the main portion of the curve is not without interest. It indicates that the rate of decomposition is approximately constant over a fairly long-time interval. There are evidently two influences at work: the concentration of the cobaltammine is steadily decreasing, which would tend to diminish the rate, and the acid concentration is also decreasing, which would increase the rate. The change in concentration of the cobaltammine is relatively slight, in the case studied, up to the neutral point; the acidity at first decreases slowly, but as the neutral point is reached very rapidly indeed. In fairly acid solutions then, we should expect a very nearly straight curve, but as the neutral point is reached this should drop very rapidly indeed, only to rize still more rapidly when the neutral point is passed. It will be seen that this is actually the case.

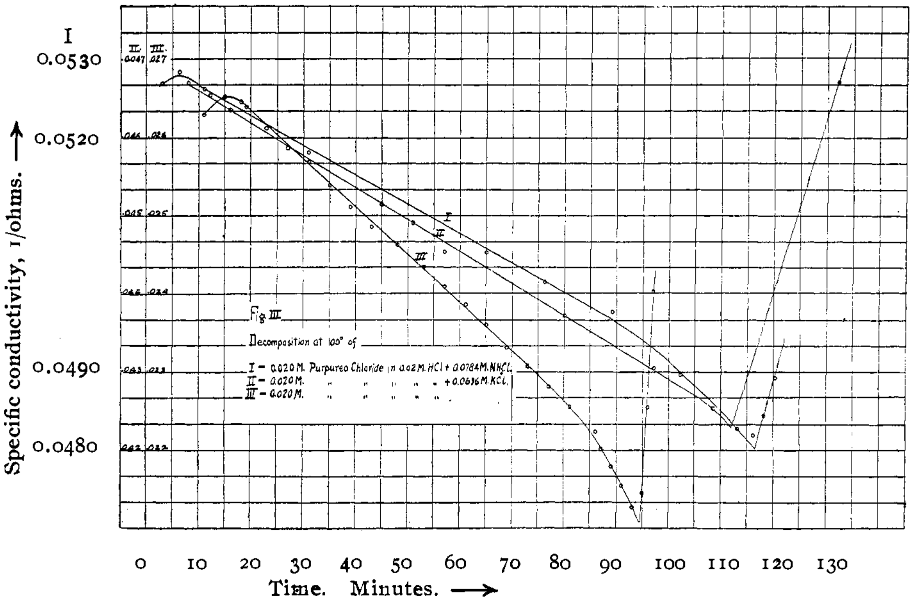
Fiftieth molecular purpureo chloride in twenty-fifth normal hydrochloric acid gives the same form of curve (Curve I, Fig. I) but the time interval is longer. A doubling of the concentration of the acid lengthens by more than four times the time required to reach neutrality. It should lengthen it but twice, assuming an approximately linear decomposition curve and no specific effect of acid on the rate. This confirms our previous conclusion that acid does slightly lessen the rate of decomposition.

The effect of a change in the concentration of the purpureo chloride, keeping the acid concentration the same, was tried. 0.007924 and a 0.03514 molar solutions of chloropentammine cobalt chloride were heated to 99.4° in 0.02 molar hydrochloric acid. Their change in conductivity with the time is given in Curves I and III of Fig. II. From this figure one sees that the most concentrated solution evidently reaches the neutral point much sooner. This would be expected, for the more concentrated the cobaltammine the more rapidly it should decompose. If the rate of this decomposition were directly proportional to the concentration of the cobaltammine and was nevertheless kept nearly constant in each case by the decreasing concentration of the acid, since the solu-



tion represented by Curve III is about five times as concentrated as that represented by Curve I, we should expect that the concentrated solution would reach the neutral point in about one-fifth the time of the more dilute, or in about sixty-five minutes. It actually reaches this point in about forty-five minutes.

It was also of interest to determin the effect on the rate of decomposition of an increase in the concentration of the chlorine ion without any change in the acid concentration. Potassium chloride was added to the solution of the purpureo chloride in hydrochloric acid. That the rate of decomposition was but slightly affected by this change can be seen from Curves II and III of Fig. III.

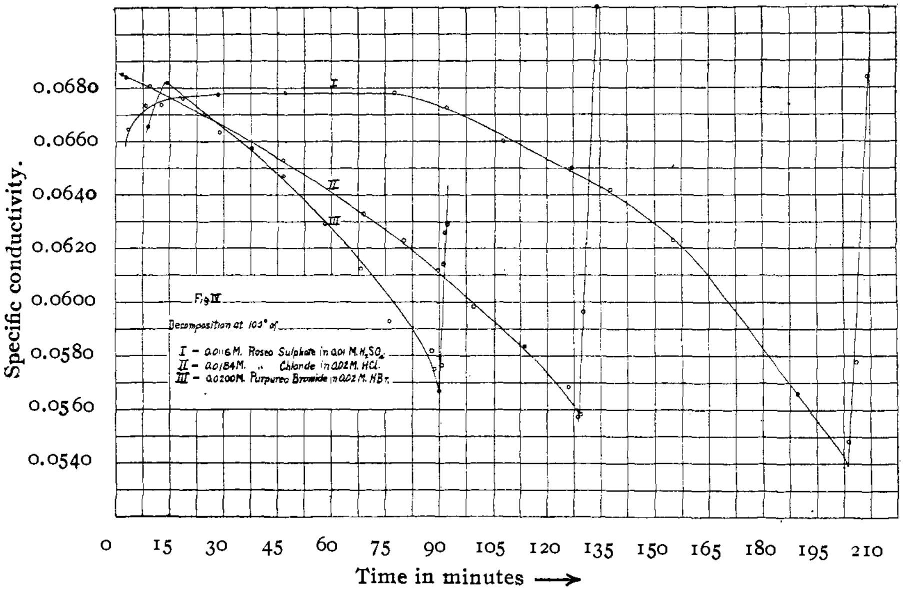


A 0.02 molar solution of chloropentammine cobalt chloride in a 0.02 molar hydrochloric acid solution which contained ammonium chloride at a concentration of 0.0784 molar was also studied and its decomposition was found to follow a curve very similar to that of a potassium chloride solution of the chloropentammine. This shows that the ammonium ion exerts no specific influence.

Solutions of the nitratopentammine cobalt nitrate in dilute nitric acid decomposed so rapidly at 100° that measurements were not undertaken.

A solution of bromopentammine cobalt bromide, 0.02 molar, in 0.02 molar hydrobromic acid gave a curve very similar to that given by the chloro-chloride, and took very nearly the same time to reach neutrality (Curve III, Fig. IV).

A solution of 0.01 molar aquopentammine cobalt sulfate in 0.01 molar sulfuric acid follows a slightly different form of curve (Curve I, Fig. IV). The conductivity remains nearly constant for some time, but finally falls off at an increasing rate until neutrality is reached, when it rapidly increases. The time required to reach neutrality is considerably greater than in the case of the chloride.



A 0.0184 molar solution of aquopentammine cobalt (roseo) chloride in 0.02 molar hydrochloric acid was found to decompose in much the same fashion as the purpureo salt (chloropentammine cobalt chloride). In spite of the lowering of temperature caused by the introduction of the salt there is no initial rise in the curve, indicating that the initial rise observed with the purpureo salt was indeed due to conversion into roseo, as well as to the rise in temperature (Curve II, Fig. IV). The roseo chloride reaches neutrality more slowly than the corresponding purpureo chloride, but this is partly due to the greater dilution of the roseo chloride solution. When the time intervals required by the various purpureo chloride solutions to reach neutrality in 0.02 molar hydrochloric acid are plotted against the concentrations of these solutions and the connecting curve is drawn, it is found that the corresponding time interval for the roseo chloride solution still lies, however, somewhat above this curve, indicating a somewhat slower decomposition even when corrected for the difference of concentration.

Experiments were also undertaken to determin the effect of ammonia on the rate of decomposition; that is, to find whether, if the ammonia were not allowed to escape from the solution after the neutral point was passed, the rate of decomposition would be increased or decreased. First, using small bottles with loosely fitting stoppers, it was found that the 0.02 molar solution of the purpureo chloride in 0.02 molar hydrochloric acid, which, under the above conditions, required about 95 minutes for the appearance of the cobalt oxide, now required in three separate experiments 132–135 minutes. When the same solution was employed, but the whole was sealed in a thick-walled glass tube, the time was lengthened to 201 minutes. This shows that once the neutral point is passed the presence of ammonia lessens the rate of decomposition. This appears reasonable from what we know of the methods of formation of the cobaltammines.

Gaseous Products of the Decomposition.

Bubbles of gas were given off within a few moments after the salt was dropped into the various solutions at 100°. This indicated that aside from the mere decomposition of the cobaltammine, there was also a reduction of the trivalent cobalt to the divalent condition, with a corresponding liberation either of oxygen, or of nitrogen derived as a secondary product from the oxidation of the ammonia. We therefore undertook experiments, first to determin the amount and nature of this gas; and secondly to determin the extent of the reduction.

To determin the amount of the gas a simple apparatus was employed, consisting chiefly of a flask whose volume was 350 cc. when completely filled. The neck of the flask was closed with a stopper whose lower surface had been hollowed out and provided with a capillary outlet tube which could be closed by a stopcock. All bubbles of gas which rose to the top of the liquid made their way easily into this outlet tube. Another outlet tube was sealed into the neck sloping very obliquely downward from the neck, and this in turn was sealed to a vertical U-tube. This U-tube had a volume of fifty cc. and was partly filled with mercury. This arrangement provided for any change in volume of the liquid contained in the closed flask. A thermometer was also fitted into the flask through a hole in the rubber stopper. The flask was first filled nearly full with the acid solution, and heated for some time in a steam bath to 100°, the salt was then dropped in, the stopper inserted, and by blowing on the outer branch of the U-tube the level of the solution was raised in the flask and then all the air forced out. By a suitable arrangement of the stopcocks the gas, as fast as it was formed in the decomposition flask, was similarly forced over into the gas pipet containing acid, and all the ammonia absorbed. Very little gas was given off after the black oxide of cobalt had precipitated and the runs were therefore stopped at that point. This gas was then carefully measured over water in a small buret graduated to 0.02 cc. It was then passed into an alkaline pyrogallol solution and again measured. The residual gas was shown to be nitrogen by adding hydrogen and sparking over sulfuric acid. The decrease in volume corresponded very nearly, after twenty-four hours, to four times the original volume. The volumes of gas found are given in Table XVIII.

TABLE XVIII.—VOLUME AND COMPOSITION OF GAS[1] GIVEN OFF ON HEATING A SOLUTION OF 1.75 GRAMS CHLOROPENTAMMINE COBALT CHLORIDE IN 350 CC. 0.02 MOLAR HYDROCHLORIC ACID. TEMPERATURE 20°.

No.	Time of decomposition. Minutes.	Temperature. °.	Barometric pressure. Mm. Hg.	Volume gas. Total Cc.	Volume N_2. Cc.	Volume O_2. Cc.	Equivalent volume O_2. Cc.
1....	106	99.45	756.4	5.06	4.52	0.54	7.32
2....	106	99.38	757.2	5.10	4.60	0.50	7.40
3....	104	99.45	757.1	4.99	4.44	0.55	7.22
							7.31

Calculated equivalent volume of oxygen if complete reduction had taken place = 42.9 cc.

These experiments showed that both oxygen and nitrogen were given off, but in amounts corresponding to only about one-fifth of the total salt present, assuming complete reduction.

The Determination of Trivalent Cobalt.

Either reduction was not complete in these experiments, or some non-gaseous oxidation product was formed. A method was therefore worked out for determining the amount of unreduced *i. e.*, trivalent cobalt present at any time. It was found namely that the purpureo chloride was completely decomposed by boiling for an hour and a half with hydriodic acid under definit conditions. 0.5 gram of the purpureo chloride was boiled with a solution of 1.5 cc. sulfuric acid and 5 grams of potassium iodide in 100 cc. of water in a small flask provided with a reflux condenser. To the end of the condenser were attached in series two absorption bulbs containing concentrated solutions of potassium iodide. An inlet tube, reaching below the surface of the liquid in the flask was also provided and through this was passed a current of purified carbon dioxide gas. Indeed, the whole apparatus was filled with this gas before heating was begun. The iodide liberated was carried over by the current of gas; the second absorption bulbs were never more than faintly yellow, showing that the absorption was complete. The whole apparatus was of glass. The iodine was titrated by means of a sodium thiosulfate solution. Blank tests were run without the addition of any salt; 0.50 cc. and 0.60 cc., respectively, of the thiosulfate solutions were required. This slight amount of iodine was perhaps formed by the traces of oxygen still present in the solution and in the apparatus or as iodate in the iodide.

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[1] We wish to thank Mr. John F. W. Schulze for his careful execution of these experiments on the gaseous products of decomposition.

Two analyses of pure purpureo chloride were then made (0.4983 and 0.5040 gram) requiring, respectively, 20.15 cc. and 21.00 cc. of the sodium thiosulfate solution. The calculated volumes, taking the blank tests into account, were 20.00 cc. and 21.05 cc. respectively. This agreement is within the experimental error.

This method was now employed to follow the reduction of a purpureo chloride solution at 100°. 0.5000 gram of the purpureo chloride was added to 100 cc. of 0.02 molar hydrochloric acid previously warmed to 100°; this was kept in a steam bath for a specified length of time, then cooled. 5 grams of potassium iodide and 1.5 cc. of sulfuric acid were added. The air was then expelled from the apparatus by means of carbon dioxide and the analysis completed as before. In this way the purpureo chloride was decomposed under exactly the same conditions as in previous experiments, and at the same time the analytical conditions were not altered. The results are given in Table XIX.

TABLE XIX.—RATE OF REDUCTION OF A 0.02 MOLAR SOLUTION OF CHLOROPENTAMMINE COBALT CHLORIDE IN 0.02 HYDROCHLORIC ACID, AT 100°, MEASURED ANALYTICALLY.

No.	Time of heating. Minutes.	$Na_2S_2O_3$ required. Cc.	$Na_2S_2O_3$ corrected. Cc.	Percentage reduction.	Remarks.
1	25	18.70	18.15	10.6	
2	50	18.30	17.75	12.6	
3	77	16.60	16.05	20.9	The oxide of cobalt was precipitated only in No. 5
4	90	15.55	15.00	26.1	
5	105	15.50	14.95	26.4	

The Composition of the Black Oxide of Cobalt.

Two samples of the black oxide of cobalt were then prepared by the decomposition of a 0.02 molar solution of purpureo chloride in 0.02 molar hydrochloric acid. They were washed for a long time by decantation, as filtration proved impracticable, and then dried by standing over sulfuric acid. The results are given in Table XX.

TABLE XX.—ANALYSIS OF BLACK OXIDE.

No.	Oxide taken. Gram.	$Na_2S_2O_3$ solution required. Observed. Cc.	$Na_2S_2O_3$ solution required. Corrected. Cc.	$Na_2S_2O_3$ solution calculated Co_2O_3. Cc.	$Na_2S_2O_3$ solution calculated Co_3O_4. Cc.	Percentage reduction.
1	0.2360	19.80	19.25	29.43	20.15	34.59
2	0.1992	16.70	16.15	24.70	17.14	34.62

These analyses confirm our conclusion that the cobalt is only partially reduced during this decomposition. If we consider that the oxide still contained, in all probability, traces of water, the analytical values agree excellently with the requirements of the formula Co_3O_4. This is in exact agreement with the supposition of Gibbs[1] that from a neutral solution

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[1] *Loc. cit.*

of purpureo chloride on boiling, "a dark brown precipitate, probably of the hydrated magnetic oxide, is thrown down."

All these experiments on the decomposition of purpureo chloride indicate that the decomposition of the ammine progresses nearly to completion with only a partial reduction of the cobalt. The gas experiments gave a somewhat smaller percentage reduction than the digestion experiments with hydriodic acid; this would indicate that some gaseous oxidation products are formed in solution which are reduced by the hydriodic acid.

Velocity of Decomposition.

In any case, it was evident that the decomposition at 100° was altogether too rapid to permit of equilibrium experiments at that temperature. The rate of decomposition and transformation at lower temperatures were therefore investigated (Tables XXI, XXII and XXIII).

TABLE XXI.—CONDUCTIVITY MEASUREMENTS SHOWING RATE OF DECOMPOSITION OF A 0.02 MOLAR SOLUTION OF CHLOROPENTAMMINE COBALT CHLORIDE IN 0.02 MOLAR HYDROCHLORIC ACID AT 60°.

Time. Hours.	Temperature. °.	Specific conductivity 1/ohms.
0	60.0	0.01360
0.3	60.0	0.01923
1.9	60.0	0.02032
9.5	60.0	0.02175
26.1	60.0	0.02315
46.1	60.0	0.02315
57.2	60.0	0.02454
72.1	60.0	0.02418
93.9	60.0	0.02301
117.7	60.0	0.02244
143.2	60.0	0.02224

TABLE XXII.—CONDUCTIVITY MEASUREMENTS SHOWING RATE OF DECOMPOSITION OF A 0.02 MOLAR SOLUTION OF CHLOROPENTAMMINE COBALT CHLORIDE IN 0.02 MOLAR HYDROCHLORIC ACID AT 70°.

Time Hours.	Temperature. °.	Specific conductivity 1/ohms.
0	70.0	0.01414
0.05	70.0	0.02115
0.3	70.0	0.02311
12.3	70.0	0.02499
13.4	70.0	0.02520
15.5	70.0	0.02525
17.7	70.0	0.02525
24.7	70.0	0.02520
31.2	70.0	0.02505
50.7	70.0	0.02468

Complete decomposition only after eleven days.

TABLE XXIII.—CONDUCTIVITY MEASUREMENTS SHOWING RATE OF DECOMPOSITION OF A 0.02 MOLAR SOLUTION OF CHLOROPENTAMMINE COBALT CHLORIDE IN 0.02 MOLAR HYDROCHLORIC ACID AT 75°.

Time. Hours.	Temperature. °.	Specific conductivity 1/ohms.
0	75.0	0.01454
0.05	75.0	0.02259
0.17	75.0	0.02330
0.35	75.0	0.02408
9.1	75.0	0.02753
10.2	75.0	0.02746
11.5	75.0	0.02639
13.8	75.0	0.02617
20.5	75.0	0.02573
33.5	75.0	0.02463

These results show that the maximum conductivity, that is, complete conversion into roseo, is not attained at 60° until after some sixty hours, at 70° until after thirteen hours and at 75° until after something less than nine hours. The subsequent decrease in conductivity, that is, the decomposition, is very slow at both 60° and 70°, requiring at 70° some ten or twelve hours to become perceptible. On the other hand, at 75° the rate of decomposition is decidedly more rapid, producing a noticeable change in conductivity within an hour. These results evidently agree with those obtained by the electrical titration measurements. 70° is evidently the optimum temperature for equilibrium measurements.

Measurements on the Roseo-Purpureo Chloride Equilibrium.

We now took up the study of the equilibrium between the purpureo and roseo compounds under these optimum conditions, that is, at 70° and in weakly acid solution. The most suitable method for this purpose in the case of the chloride appeared to be the determination of the precipitable and unprecipitable chlorine in the mixture. This could evidently be accomplished by adding an excess of silver nitrate to the mixture, filtering, converting the purpureo salt in the filtrate into roseo by adding ammonia, boiling, acidifying and again filtering from the precipitated silver chloride. The weight of either precipitate, compared with the total precipitate or the weight of salt taken, tells us the per cent. of roseo salt in the mixture. Since, however, from our conductivity experiments, we know that the transformation takes place with some rapidity at 70°, it was necessary to cool the equilibrium mixture rapidly to room temperature, or lower, before the precipitation, to prevent a shifting of the equilibrium. Even at these lower temperatures we know that a slow transformation takes place and consequently the filtration of the silver chloride must be rapid.

The method of procedure finally adopted to meet these requirements was as follows: 100 cc. of standardized hydrochloric acid solution were measured into Jena glass flasks of that capacity. They were then placed in the thermostat at 70° and when they had reached this temperature, a weighed quantity of salt, usually about 0.5 gram, was added. This dissolved rapidly to a clear, dark-red solution. After given intervals of time the flasks were removed and their contents quickly poured over a mixture of ice and water in Erlenmeyer flasks. A few drops of nitric acid and an excess of silver nitrate were then added, the flasks closed with their ground-in stoppers and shaken. The clear, supernatant liquid was now filtered off rapidly by suction through a porous alundum crucible and transferred to a 600 cc. Erlenmeyer flask, a slight excess of ammonia added and the whole boiled until the conversion into roseo salt was complete. The solution was then acidified and the precipitated silver chloride collected in a platinum Gooch crucible, and heated to constant weight in an electric oven at 140°.

We first carried through a preliminary series of analyses to get a rough idea of the location of the equilibrium. In these experiments both the first and second precipitate of silver chloride were weighed. The results are given in Table XXIV.

TABLE XXIV.—PRELIMINARY MEASUREMENTS OF THE EQUILIBRIUM IN A 0.02 MOLAR SOLUTION OF CHLOROPENTAMMINE COBALT CHLORIDE IN A 0.02 MOLAR HYDROCHLORIC ACID SOLUTION AT 70°.

No.	Wt. purpureo.	Time of heating. Hrs.	Wt. 1st ppt. AgCl from HCl and purpureo.	Wt. AgCl from HCl.	Wt. 1st ppt. AgCl from purpureo.	Wt. 2nd ppt. AgCl.	Total wt. AgCl.	Total wt. AgCl calc.	% roseo calc. from wt. 1st ppt.	% roseo calc. from wt. 2nd ppt.
1	0.5000	1	1.0060	0.2818	0.7242	0.1350	0.8592	0.8600	52.30	52.88
2	0.5000	5.5	1.0548	0.2818	0.7730	0.0862	0.8592	0.8600	68.95	66.53
3	0.5000	17	1.0597	0.2818	0.7779	0.0808	0.8587	0.8600	71.00	71.25
4	0.5000	23	1.0621	0.2818	0.7803	0.0780	0.8583	0.8600	71.74	72.74
5	0.5000	27	1.0698	0.2818	0.7880	0.0716	0.8596	0.8600	75.00	75.10

These preliminary experiments showed a rapid increase in the percentage of roseo salt up to seventeen hours and a very slow increase thereafter, and indicated that in this solution at equilibrium there was approximately 71 per cent. of roseo salt present. The agreement between the weight of the first and the second precipitate of silver chloride establishes the reliability of both methods of analysis; in the following experiments therefore we have only weighed the second precipitate.

It was first necessary to show that the cooling was sufficiently rapid to prevent a shifting of the equilibrium before a low temperature had been reached. For this purpose we carried out a series of experiments identical in every respect among themselves except in the rate of cooling. This difference in the rate of cooling was obtained by using different relative amounts of ice and distilled water in the Erlenmeyer flasks into which the equilibrium mixtures were poured. The results of these experiments are given in Table XXV.

TABLE XXV.—EFFECT OF DIFFERENT RATES OF COOLING ON A 0.02 MOLAR SOLUTION OF CHLOROPENTAMMINE COBALT CHLORIDE IN 0.02 MOLAR HYDROCHLORIC ACID.

No.	Weight purpureo. Gram.	Rate of cooling.	Weight AgCl. Gram.	Per cent. roseo.	Remarks.
6	0.5000	Cooled very slowly. Filtered after 1 hour.	0.0636	77.84	Silver nitrate and nitric acid added to the ice-water.
7	0.5000	Cooled slowly. Filtered after 1/2 hour.	0.0702	75.54	Silver nitrate and nitric acid added one minute after pouring equilibrium mixture.
8	0.5000	Cooled more rapidly	0.0788	72.54	
9	0.5000	15 sec. 40° 30 sec. 40° 60 sec. 40°	0.0822	71.29	
10	0.5000	15 sec. 23° 30 sec. 21° 60 sec. 20.9°	0.0854	70.25	
11	0.5000	15 sec. 9° 30 sec. 3.5° 60 sec. 2°	0.0858	70.10	
12	0.5000	15 sec. 2° 30 sec. 2° 60 sec. 1°	0.0865	69.86	

It will be seen from these results that slow cooling has a decided effect on the equilibrium, but that in the three experiments with the most rapid cooling the difference is not greater than the experimental error. In our further analyses we therefore cooled as in No. 12, added the precipitant at the end of one minute, shook and filtered immediately.

We now repeated our preliminary equilibrium measurements using these precautions as to cooling and obtained the results given in Table XXVI.

TABLE XXVI.—EQUILIBRIUM MEASUREMENTS ON A 0.02 MOLAR SOLUTION OF CHLOROPENTAMMINE COBALT CHLORIDE IN 0.02 MOLAR HYDROCHLORIC ACID AT 70°.

No.	Weight salt. Gram.	Time of heating. Hours.	Weight second precipitate AgCl. Gram.	Per cent. roseo.
13	0.5000	...	0.2685	6.62
14	0.5000	0.90	0.1228	57.21
15	0.5000	3.03	0.0862	69.97
16	0.5000	6.55	0.0858	70.14
17	0.6000	17.72	0.0851	70.35
18	0.5000	24.72	0.0850	70.38
19	0.5000	27.60	0.0821	71.39

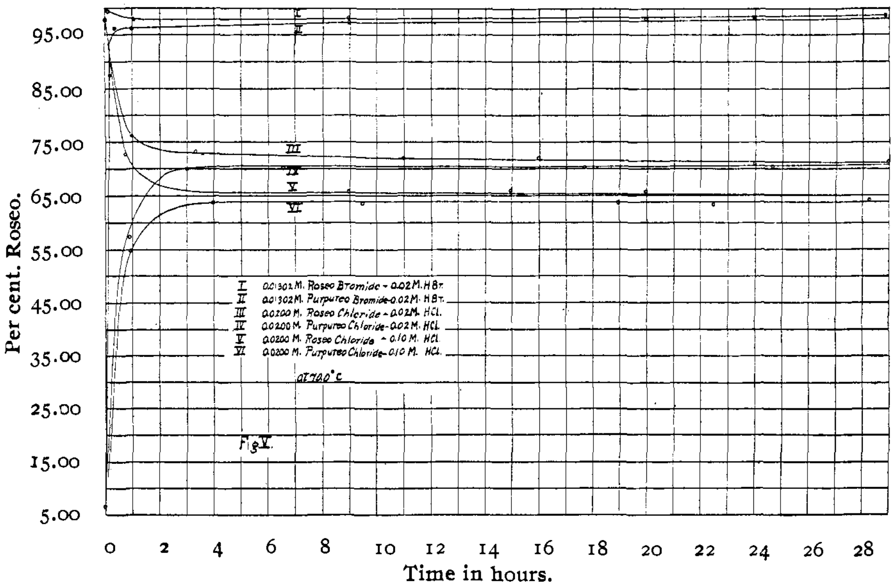
These experiments agree excellently with experiments Nos. 10, 11 and 12. As would be expected, they give results somewhat lower than the more slowly cooled experiments Nos. 3 and 4.

The next logical step was to find whether or not this was a true equilibrium. This was done by starting with the roseo instead of the purpureo salt in a solution of the same molecular concentrations. The results are recorded in Table XXVII.

TABLE XXVII.—EQUILIBRIUM MEASUREMENTS ON 0.02 MOLAR SOLUTION OF PENTAMMINE COBALT CHLORIDE (ROSEO) IN 0.02 MOLAR HYDROCHLORIC ACID AT 70°.

No.	Weight salt. Gram.	Time of heating. Hours.	Weight of second precipitate AgCl. Gram.	Percentage roseo.
20	0.5360	...	0.0082	97.64
21	0.5360	0.97	0.0682	76.24
22	0.5360	3.33	0.0770	73.14
23	0.5360	11.0	0.0798	72.20
24	0.5360	16.0	0.0802	71.99
25	0.5360	24.0	0.0840	70.78

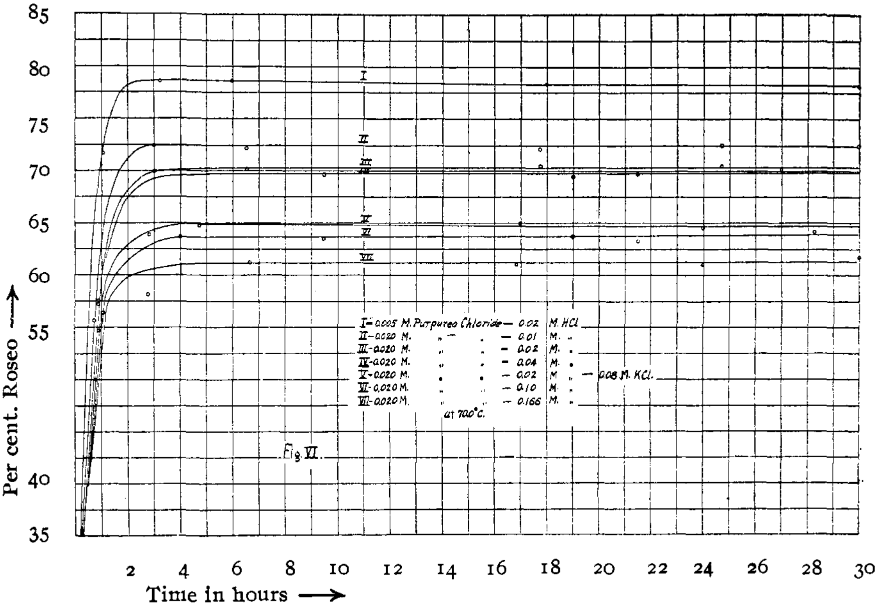
These results are plotted against the time in Fig. V, Curves III and IV. It is seen that the two curves come very nearly together. The slight difference between the two curves is probably only apparent; it may be due to a trace of moisture present in the roseo salt. This experiment demonstrates that a real equilibrium exists in these solutions between the roseo and the purpureo salts. Further proof of this will also be found in the experiments on 0.02 molar purpureo and roseo chloride in 0.10 molar hydrochloric acid and in the experiments on 0.01302 molar roseo and purpureo bromide in 0.02 molar hydrobromic acid (see Curves I, II, V and VI in Fig. V).



Similar experiments were now made on the equilibrium in a 0.02 molar solution of purpureo chloride in 0.01 molar hydrochloric acid. The results are given in Table XXVIII, Curve II, Fig. VI.

TABLE XXVIII.—EQUILIBRIUM MEASUREMENTS ON A 0.02 MOLAR SOLUTION OF CHLOROPENTAMMINE COBALT CHLORIDE IN 0.01 MOLAR HYDROCHLORIC ACID AT 70°.

No.	Weight of salt. Gram.	Time of heating. Hours.	Weight of second precipitate AgCl. Gram.	Percentage roseo.
13	0.5000	0	0.2685	6.62
26	0.5000	0.78	0.1275	55.58
27	0.5000	3.03	0.0793	72.37
28	0.5000	6.55	0.0799	72.17
29	0.5000	17.72	0.0802	72.07
30	0.5000	24.72	0.0792	72.40
31	0.5000	30.0	0.0791	72.43



The concentration of roseo salt is seen to be distinctly higher at this lower concentration of hydrochloric acid. Experiments were made in still more concentrated hydrochloric acid; namely in 0.04, 0.1 and 0.1660 molar acid, respectively. This latter acid was the most concentrated acid which would dissolve the purpureo chloride completely at the concentration used (0.02 molar). The results are given in Tables XXIX, XXX, XXXI, and XXXII, and Curves IV, VI and VII, Fig. VI. The equilibrium was approached from both sides in the case of the 0.1 molar acid (Curves V and VI, Fig. V).

Table XXIX.—Equilibrium Measurements on a 0.02 Molar Solution of Chloropentammine Cobalt Chloride in 0.04 Molar Hydrochloric Acid at 70°.

No.	Weight purpureo salt. Gram.	Time of heating. Hours.	Weight of second precipitate AgCl. Gram.	Percentage roseo.
13	0.5000	0	0.2685	6.62
32	0.5000	0.78	0.1431	50.00
33	0.5000	3.97	0.0938	67.30
34	0.5000	9.47	0.0871	69.65
35	0.5000	19.0	0.0878	69.41
36	0.5000	21.47	0.0870	69.67
37	0.5000	27.0	0.0855	70.19

Table XXX.—Equilibrium Measurements on a 0.02 Molar Solution of Aquopentammine Cobalt Chloride (Roseo) in 0.10 Molar Hydrochloric Acid at 70°.

No.	Weight roseo. Gram.	Time of heating. Hours.	Weight of second precipitate AgCl. Gram.	Percentage roseo.
20	0.5360	0	0.0082	97.64
38	0.5360	0.75	0.0785	72.63
39	0.5360	3 (?)	0.0811	71.72
40	0.5360	9	0.0985	65.69
41	0.5360	15	0.0978	65.94
42	0.5360	20	0.0986	65.62

Table XXXI.—Equilibrium Measurements on a 0.02 Molar Solution of Chloropentammine Cobalt Chloride in 0.10 Molar Hydrochloric Acid at 70°.

No.	Weight purpureo salt. Gram.	Time of heating. Hours.	Weight of second precipitate AgCl. Gram.	Percentage roseo.
13	0.5000	0	0.2685	6.62
43	0.5000	0.93	0.1302	54.63
44	0.5000	4.0	0.1043	63.66
45	0.5000	9.50	0.1050	63.41
46	0.5000	19.0	0.1043	63.66
47	0.5000	21.5	0.1056	63.20
48	0.5000	28.28	0.1030	64.11

Table XXXII.—Equilibrium Measurements on a 0.02 Molar Solution of Chloropentammine Cobalt Chloride in 0.166 Molar Hydrochloric Acid at 70°.

No.	Weight purpureo salt. Gram.	Time of heating. Hours.	Weight of second precipitate AgCl. Gram.	Percentage roseo.
13	0.5000	0	0.2685	6.62
49	0.5000	1.08	0.1252	56.38
50	0.5000	2.78	0.1201	58.16
51	0.5000	6.69	0.1117	61.08
52	0.5000	16.85	0.1120	60.98
53	0.5000	24.0	0.1120	60.98
54	0.5000	30.0	0.1100	61.67

These experiments show clearly that the percentage of roseo salt, and hence its concentration, decreases steadily as the concentration of the hydrochloric acid is increased. To determin whether this was due to the hydrogen ion or the chlorine ion an experiment was carried out with a 0.02 molar solution of the purpureo salt in 0.02 molar hydrochloric acid to which enough potassium chloride was added to bring the concentration of the chlorine ions up to approximately 0.1 normal. The results are given in Table XXXIII, and in Curve V, Fig. VI.

TABLE XXXIII.—EQUILIBRIUM MEASUREMENTS ON A 0.02 MOLAR SOLUTION OF CHLOROPENTAMMINE COBALT CHLORIDE IN 0.02 MOLAR HYDROCHLORIC ACID PLUS 0.08 MOLAR POTASSIUM CHLORIDE SOLUTION AT 70°.

No.	Weight of purpureo salt. Gram.	Time of heating. Hours.	Weight of second precipitate AgCl. Gram.	Percentage roseo.
13	0.5000	0	0.2685	6.62
55	0.5000	0.92	0.1207	57.64
56	0.5000	2.84	0.1036	63.90
57	0.5000	4.75	0.1012	64.74
58	0.5000	17.0	0.1007	64.91
59	0.5000	24.0	0.1019	64.48

This experiment shows that the equilibrium concentration of the roseo salt in this solution is identical with that in a 0.1 molar solution of hydrochloric acid. This demonstrates that it is the concentration of the chlorine ion and not of the hydrogen ion which affects the equilibrium. This is what would be expected from the equation already given for the change.

The effect of a change in the concentration of the ammine itself was then tried. 0.005 and 0.05361 molar solutions of the purpureo salt in 0.02 molar hydrochloric acid were taken. The results are given in Tables XXXIV and XXXV, and in Curve I, Fig. VI.

TABLE XXXIV.—EQUILIBRIUM MEASUREMENTS ON A 0.005 MOLAR SOLUTION OF CHLOROPENTAMMINE COBALT CHLORIDE IN 0.02 MOLAR HYDROCHLORIC ACID AT 70°. (A 400 CC. SAMPLE INSTEAD OF A 100 CC. SAMPLE WAS TAKEN.)

No.	Weight of purpureo salt. Gram.	Time of heating. Hours.	Weight of second precipitate AgCl. Gram.	Percentage roseo.
13	0.5000	0	0.2685	6.62
60	0.5000	1.08	0.0956	71.69
61	0.5000	3.25	0.0616	78.54
62	0.5000	6.0	0.0616	78.54
63	0.5000	18.0	0.0622	78.30
64	0.5000	30.0	0.0630	78.05

TABLE XXXV.—EQUILIBRIUM MEASUREMENTS ON A 0.05361 MOLAR SOLUTION OF CHLOROPENTAMMINE COBALT CHLORIDE IN 0.02 MOLAR HYDROCHLORIC ACID AT 70°.

No.	Weight purpureo salt Gram.	Time of heating. Hours.	Weight of second precipitate AgCl. Gram.	Percentage roseo.
13	0.5000	0	0.2685	6.62
65	0.6713	14.1	0.1291	66.38
66	0.6713	17.3	0.1289	66.44
67	0.6713	22.7	0.1292	66.35

These experiments show the more dilute the solution of the cobaltammine the greater the percentage of roseo salt at the equilibrium. This agrees with our previous inferences stated at the outset of the paper.

Just the opposit shifting of the equilibrium took place when ammonium nitrate instead of the chloride was added to the solution. To a solution of fiftieth molar hydrochloric acid ammonium nitrate was added in sufficient quantity to make a tenth-normal solution. It will be seen from Table XXXVI that the results was a large increase in the percentage of roseo salt present at equilibrium. This would indicate that some nitratopentammine salt is formed, which is, of course, equivalent to a decrease in the total concentration of the chloropentammine salt plus the roseo pentammine salts; we have just seen that such a decrease in concentration results in a greater relative concentration of the roseo salt at equilibrium. There is then no evidence of any specific effect of the ammonium ion.

TABLE XXXVI.—EQUILIBRIUM MEASUREMENTS ON A 0.02 MOLAR SOLUTION OF CHLOROPENTAMMINE COBALT CHLORIDE IN A SOLUTION 0.02 MOLAR WITH RESPECT TO HYDROCHLORIC ACID AND 0.1 MOLAR WITH RESPECT TO AMMONIUM NITRATE.

No.	Weight of purpureo salt. Gram.	Time of heating. Hours.	Weight of second precipitate AgCl. Gram.	Percentage roseo.
13	0.5000	0	0.2685	6.62
68	0.5000	1.08	0.0947	67.00
69	0.5000	3.17	0.0589	79.48
70	0.5000	19.0	0.0595	79.27
71	0.5000	20.0	0.0601	79.10
72	0.5000	27.0	0.0600	79.07

The measurements on the purpureo-roseo chloride equilibrium are collected in Table XXXVII.

TABLE XXXVII.—SUMMARY OF MEASUREMENTS ON PURPUREO-ROSEO COBALT CHLORIDE EQUILIBRIUM AT 70°.

	Concentration molar.				Concentration molar.				
No. Equilibrium.	Total ammine.	HCl.	Roseo. Per cent.	Purpureo. Per cent.	Roseo. Total.	Purpureo. Total.	Roseo ion.	Purpureo ion.	Chlorine ion.
1	0.02	0.01	72.3	27.7	0.01446	0.00554	0.00940	0.00387	0.0449
2	0.02	0.02	70.8	29.2	0.01416	0.00581	0.00888	0.00401	0.0531
3	0.02	0.04	69.7	30.3	0.01394	0.00606	0.00832	0.00398	0.0694
4	0.02	0.10	63.7	36.3	0.01274	0.00726	0.00677	0.00430	0.1182
5	0.02	0.166	61.0	39.0	0.01220	0.00780	0.00591	0.00422	0.1716
6	0.005	0.02	78.5	21.5	0.003925	0.001075	0.00271	0.000804	0.02844
7	0.05361	0.02	66.4	33.6	0.03560	0.01801	0.01963	0.01103	0.0989
8	0.02	0.02+0.08 KCl	64.8	35.2	0.01296	0.00704	0.00686	0.00414	0.1181

The Equilibrium Constant.

Our analytical results only tell us the total concentration of roseo and of purpureo compounds in the equilibrium mixtures. Both of these substances are certainly present in a dissociated as well as an undissociated condition, and any one or more of these individual molecular species may be the direct factor in the equilibrium. There is the further uncertainty that while the transformation of purpureo to roseo is almost certainly an intramolecular rearrangement, that of the roseo to purpureo may be either an intramolecular rearrangement of the undissociated or partially dissociated roseo salt, or it may be a direct combination of the wholly or partially dissociated roseo salt with the chlorine ion.

To determin which of these alternative possibilities actually exists, evidently requires, in addition to the above analytical data, information regarding the degree of dissociation of the substances present in the equilibrium mixtures at 70°. In the case of hydrochloric acid we have for this purpose the adequate and excellent conductivity data of A. A. Noyes and his colleagues. The only pertinent information regarding the two ammines is found in two dilution experiments of Werner and Miolati[1] on the purpureo chloride and the roseo bromide. We applied the method of Noyes[2] to these results and obtained for the roseo bromide a constant value of 1.52 for the exponent n, in excellent agreement with the values found by Noyes and Johnson[3] for salts of the same type. The data for the purpureo chloride gave no satisfactory value of n, apparently because of the inaccuracy produced by the steady transformation of purpureo into roseo salt. In view of the general similarity found by Noyes and his colleagues between salts of the same type and of the agreement of the roseo with these salts, we have simply taken the accurate measurements of Noyes and Johnston on barium and lanthanum nitrates and used them to calculate the dissociation of the purpureo and roseo chloride respectively in the various mixtures. To do this we have recalculated the values n and K for these two salts at 50°, 75°, 100°, and by interpolation have found the value of these parameters at 70°. We have carried out the same calculation for hydrochloric acid using the measurements of Noyes and Cooper.[4] The resulting expressions were as follows:

$$\text{for the roseo chloride } \overset{1.49}{C}_{R}{+}{+}{+}/R_{RCl_3} = 0.375;$$

$$\text{for the purpureo chloride } \overset{1.52}{C}_{P}{+}{+}/C_{PCl_2} = 0.471;$$

$$\text{for the hydrochloric acid } \overset{1.40}{C}_{H}{+}/C_{HCl} = 3.51;$$

all at 70°.

We now solved all of the three equations for each mixture by a process of successive approximation making the assumption that the per-

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[1] *Z. physik. Chem.*, 12, 35 (1893) and 14, 520 (1894).

[2] *Carnegie Institution Publication*, 63, p. 50.

[3] THIS JOURNAL, 31, 987–1010 (1909).

[4] *Carnegie Institution Publication*, 63, 115–149.

centage dissociation of each substance in the mixture was the same as it would have been alone at an equivalent ionic concentration equal to the sum of the equivalent ion concentrations of the three substances present.[1]

The resulting values for the concentrations of the various ions and undissociated molecules are given in Table XXXVII. This assumption of Arrhenius is evidently equivalent to the statement that the percentage dissociation is the same in the mixtures as in pure solutions containing the same concentration of free electricity. As a variation of this we tried the assumption that the percentage dissociation of each substance would be the same in the mixture as when alone at a total *molar* ionic concentration equal to the total molar ionic concentration of the mixture. The resulting values were nearly identical with those obtained on the original assumption.

The simplest assumptions regarding the nature of the equilibrium are that it is determined solely either by (1) the total concentrations of the roseo and purpureo compounds, or (2) the concentrations of the roseo and purpureo ions or (3) the concentrations of the undissociated roseo and purpureo molecules. In each of these cases one of the following equations would apply:

$$\text{For (1)}\quad C_R/C_P = K_1,$$
$$\text{For (2)}\quad C_{R^{+++}}/C_{P^{++}} = K_2,$$
$$\text{For (3)}\quad C_{RCl_3}/C_{PCl_2} = K_3,$$

where C_R and C_P represent the total concentrations of roseo and purpureo compounds, $C_{R^{+++}}$ and $C_{P^{++}}$ the concentrations of the corresponding ions, C_{RCl_3} and C_{PCl_2} of the corresponding undissociated molecules and K_1, K_2 and K_3 equilibrium constants. A brief inspection of the calculated values of these constants as given in Table XXXVIII shows that no one of these equations is adhered to, the values of each K varying two or three times.

Table XXXVIII.—Values of Equilibrium Constant for Purpureo Roseo Cobalt Chloride Equilibrium at 70° Calculated on Various Assumptions.

No.	K_1.	K_2.	K_3.	K_4.	K_5.	K_6.	K_7.
1	2.61	2.43	3.03	0.117	0.109	0.86	0.63
2	2.44	2.21	2.94	0.129	0.117	0.90	0.63
3	2.30	2.09	2.70	0.159	0.145	1.04	0.67
4	1.76	1.57	2.02	0.208	0.186	1.20	0.66
5	1.56	1.40	1.78	0.268	0.240	1.40	0.69
6	3.65	3.37	4.48	0.104	0.096	1.22	0.71
7	1.98	1.78	2.29	0.196	0.176	0.90	0.68
8	1.89	1.66	2.10	0.223	0.196	1.25	0.69
Average deviation, per cent	21	22	23	22	26	15	3

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[1] Arrhenius, *Z. physik. Chem.*, 31, 218 (1899).

None of these simple assumptions contains an explicit expression of the chlorine ion concentration; when this is introduced, still assuming the simple concentration law, we would have

$$C_R \times C_{Cl'}/C_P = K_4$$

or

$$C_{R^{+++}} \times C_{Cl'}/C_{P^{++}} = K_5$$

where $C_{Cl'}$ represents the total concentration of the chlorine ion in the mixture. The values of K_4 and K_5 are given in Table XXXVIII and it will be seen that there is still no constancy among them.

This lack of constancy and the general similarity between this transformation and an ordinary electrolytic dissociation led us to apply the Storch-Bancroft modification of the concentration law to our results. We first plotted the logarithmic form of the equation and obtained an approximate straight line which gave a value of $n/2 = 0.73$. The original equation would then become

$$(C_R \times C_{Cl'})^{0.73}/C_P = K_6.$$

The values of K_6 calculated for each mixture are given in Table XXXVIII. It will be seen that an approximate constancy is now attained. The constancy is particularly marked in those experiments where the concentration of the hydrochloric acid is relatively small and the inaccuracy of our method of calculation correspondingly less (Nos. 1, 2 and 7). This value of $n/2 = 0.73$, or $n = 1.46$ agrees excellently with the values 1.40–1.50 which Noyes and his co-workers have found to apply to the dissociation of all types of strong electrolytes.

Influenced by the somewhat arbitrary procedure of assigning exactly the same exponent to both anion and cation in the Storch-Bancroft equation when applied to mixtures, we tried varying the exponents of C_R and $C_{Cl'}$, keeping their sum equal to 1.46—since this total exponent would be expected when the equivalent concentrations of the two ions is the same; that is, when no foreign chlorine ions were present. The values calculated from this equation

$$C_R \times C_{Cl'}^{0.46}/C_P = K_7$$

are given in Table XXXVIII and show a very decided constancy. Its significance cannot be definitly settled until similar calculations have been made on ordinary dissociations.

The above calculations certainly indicate that the equilibria between roseo and purpureo chloride are comparable with the dissociation equilibria of strong electrolytes. It seems to differ from them only in the fact that the rate of reaction is measurably slow. It is because of this slowness of reaction that we are able to get the roseo salt out of solution and study it, without the chlorine ion getting back into the complex.

As a result it has been shown that the splitting off of an additional chlorine ion from the purpureo molecules or ion is necessarily accompanied by a substitution of a water molecule in its place within complex.

By analogy, then, a similar process would be predicted for the dissociation of electrolytes in water, that is, hydration would necessarily accompany dissociation. This conclusion is in agreement with much recent work on aqueous electrolytes. A more rigorous test of all of these conclusions will only be possible when more certain information can be secured regarding the dissociation of the roseo and purpureo chlorides in the equilibrium mixtures.

The Free Energy Change.

This free energy change per mole for an ordinary reversible reaction is given by the simple expression RT *ln K*. That this also represents the free energy change in the present case where the equilibrium is not governed by the ordinary concentration law can be seen from the following consideration:

The free energy gain of the system when a mole of the purpureo compound changes from unit concentration at constant temperature to the equilibrium concentration C_P is equal to RT *ln* C_P. The energy required to bring one mole of chlorine ion and one mole of roseo salt from the equilibrium concentration C_R to unit concentration is equal to $2\int_1^{C_R} P_R dC_R$, or since P_R is a function of C_R to $2\int_1^{C_R} f(C_R)dC_R$. (We cannot assume the gas law to apply to these charged ions.) The free energy gained by the system when one mole of purpureo salt is converted into roseo and chlorine ion is then

$$W = -2\int_1^{C_R} f(C_R)dC_R + RT\, ln\, C_P. \qquad (1)$$

$$\text{But } C_R^{1.43}/C_P = K. \qquad (2)$$

$$\therefore \quad W = -2\int_1^{C_R} f(C_R)dC_R + RT\, ln\, C_R^{1.43} - RT\, ln\, K.$$

Differentiating

$$2f(C_R)dC_R = 1.43\ RTdC_R/C_R$$

or

$$2f(C_R) = 1.43\ RT/C_R.$$

Substituting in (1)

$$W = -1.43\ RT\int_1^{C_R} dC_R/C_R + RT\, ln\, C_P$$

or

$$W = -RT \ln K.$$

K in the above calculation can be either K_6 or K_7—for the expressions containing these two constants become identical when a pure solution of the ammines is used. At present then, since K_7 gives the better constancy, we may substitute it in an approximate calculation of the free energy change. We should then have

$$W = -RT \ln K_7$$
$$= 275 \text{ cal.}$$

The affinity of the reaction would then be —275 cal. This can, of course, only be considered a preliminary calculation, pending a more accurate knowledge of the dissociation conditions in the equilibrium mixtures.

Measurements of Other Equilibria.

Several other pentammine cobalt salts were studied in the same way as the chloride. Attempts were made, for instance, with the nitratopentammine nitrate to discover whether or not an equilibrium existed between it and the corresponding roseo salt. We found that "nitron" was an excellent precipitant of the free nitrate ion, but it was difficult to filter and wash the precipitate rapidly. Our previous experiments have shown that the first filtration must be immediate and rapid. For the time being, therefore, the study of this equilibrium has been abandoned.

The purpureo bromide-roseo bromide equilibrium was, however, measured with more success. When a 0.01302 molar solution of purpureo bromide in 0.02 molar hydrobromic acid at 70° was analyzed by the precipitation of silver bromide, an equilibrium was found corresponding very nearly to pure roseo salt. Similar results were obtained starting with an equivalent solution of the roseo salt. The data is given in Tables XXXIX and XL, and in Curve II, Fig. V.

TABLE XXXIX.—EQUILIBRIUM MEASUREMENTS ON A 0.01302 MOLAR SOLUTION OF BROMOPENTAMMINE COBALT BROMIDE IN 0.02 MOLAR HYDROBROMIC ACID AT 70°.

No.	Weight of purpureo Salt. Gram.	Time of heating. Hours.	Weight of second precipitate of AgBr. Gram.	Percentage roseo.
73	0.5000	0.16	0.0221	85.25
74	0.5000	0.33	0.0093	96.12
75	0.5000	1.00	0.0093	96.20
76	0.5000	9.0	0.0062	97.46
77	0.5000	20.0	0.0046	98.11
78	0.5000	24.0	0.0047	98.10

TABLE XL.—EQUILIBRIUM MEASUREMENTS ON A 0.01302 MOLAR SOLUTION OF PENTAMMINE COBALT BROMIDE (ROSEO) IN A 0.02 MOLAR SOLUTION OF HYDROBROMIC ACID AT 70°.

No.	Weight roseo Salt. Gram.	Time of heating. Hours.	Weight of second precipitate of AgBr. Gram.	Percentage roseo.
79	0.5237	0.10	0.0015	99.39
80	0.5237	1.05	0.0057	97.62
81	0.5237	9.0	0.0047	98.10
82	0.5237	14.0	0.0044	98.23
83	0.5237	30.0	0.0039	98.40

It will also be observed that the adjustment of equilibrium is much more rapid here than in the case of the chloride. This agrees with the velocity experiments described at the beginning of this paper. There is also a very slight decomposition indicated by the slight steady increase in the percentage of roseo salt during the last 21 hours.

We have also made some preliminary determinations upon the pentammine sulfato-sulfate equilibrium, but we are somewhat in doubt regarding the purity of the salts used. An equilibrium is, however, undoubtedly reached. The results obtained are given in Tables XLI and XLII and in Curve I, Fig. V.

TABLE XLI.—EQUILIBRIUM MEASUREMENTS IN A 0.0087 MOLAR SOLUTION OF SULFATOPENTAMMINE COBALT SULFATE IN 0.01 MOLAR SULFURIC ACID AT 70°.

No.	Weight of purpureo salt. Gram.	Time of heating Hours.	Weight of second precipitate of $BaSO_4$. Gram.	Percentage roseo.
84	0.5000	10	0.2281	43.8
85	0.5000	24	0.2294	43.5
86	0.5000	30	0.2274	44.0

TABLE XLII.—EQUILIBRIUM MEASUREMENTS ON A 0.00865 MOLAR SOLUTION OF SULFATOPENTAMMINE COBALT SULFATE (ROSEO) IN 0.01 MOLAR SULFURIC ACID AT 70°.

No.	Weight of roseo salt. Gram.	Time of heating. Hours.	Weight of second precipitate of $BaSO_4$. Gram.	Percentage roseo.
87	0.5266	3	0.2298	42.9
88	0.5266	24	0.2282	43.3
88	0.5266	30	0.2282	43.3

The Transformation in the Dry State.

Gibbs[1] in his original communication states that roseo chloride changes on standing into purpureo chloride. Jörgensen[2] has made use of a similar change in the case of the roseo nitrate to prepare purpureo nitrate.

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[1] "Researches on the Ammonia Cobalt Bases." Smithsonian Contributions to Knowledge. Washington (1856), p. 9.

[2] *Z. anorg. Chem.*, 17, 160.

This change of roseo into purpureo must be accompanied by an evolution of water vapor. We wished to find whether this water came off with a definit pressure at a given temperature; whether, in other words, the roseo salts possessed a definit aqueous vapor pressure. If this proved to be the case, we wished also to find out whether the process was reversible, *i. e.*, whether the roseo could be made from the purpureo salt in the dry state.

To measure first the aqueous vapor pressure we exposed weighed samples of roseo chloride, freshly prepared, over solutions of sulfuric acid of various concentrations. The weighed portions of the salt were placed upon small watch glasses supported by glass triangles over the sulfuric acid solutions in small stender dishes. Ground-glass covers were fitted tightly on the stender dishes and they were placed in desiccator jars, which were completely submerged in a thermostat, kept at 25°. If the change from purpureo to roseo salt, and *vice versa*, is analogous to the formation and dehydration of a salt hydrate, then the roseo salt at a constant temperature should exhibit a constant vapor pressure, and should steadily lose water to any solution of sulfuric acid having an aqueous vapor pressure lower than this. The purpureo salt, on the other hand, should steadily gain in weight when exposed to any solution of sulfuric acid having a higher aqueous vapor pressure than that of the roseo salt.

Two series of such experiments were carried out, the results of which are given in Tables XLIII and XLIV. The weighings in the second series (Table XLIV) are the more accurate, having been made on an assay balance and the differences in the concentration of the sulfuric acid are much less.

TABLE XLIII.—CHANGE OF ROSEO TO PURPUREO CHLORIDE IN THE DRY STATE AT 25°.
TOOK 0.2000 GRAM.

No.	H_2SO_4. Per cent.	Loss in weight. (Milligrams.)				Per cent. conversion by loss.	Weight 1st AgCl. Gram.	Weight 2nd AgCl. Gram.	Total weight AgCl. Gram.	Per cent. conversion by analysis.	Remarks.
		2 days.	4 days.	37 days.	68 days.						
1	92.4	0.4	0.6	10.4	11.7	92	0.2272	0.086	0.3140	91.0	There was a marked color change between 4 and 5.
2	77.4	0.5	0.5	..	12.4	98	0.2305	0.0844	0.3149	78.8	
3	68.1	0.5	0.5	8.5	11.5	87	..	0.0828	..	77.7	
4	58.3	0.3	0.2	3.2	11.5	87	0.2314	0.0825	0.3139	77.9	
5	46.9	0.4	0.3	2.9	..	..	..	..	..	..	
6	33.3	0.2	0.1	0.5	3.5	28	0.2745	0.0405	0.3150 (calc. = 0.3160)	37.2	

TABLE XLIV.—CHANGE OF ROSEO TO PURPUREO CHLORIDE IN DRY STATE AT 25°. TOOK 0.2000 GRAM.

No.	H_2SO_4. Per cent.	Loss in weight. (Milligrams.) 4 days.	7 days.	12 days.	24 days.	27 days.	Per cent. conversion (27 days).	Remarks.
7	65	0.42	0.84	1.84	6.04	8.14	64	There was a marked color change between 9 and 10.
8	61	0.48	0.94	2.64	4.54	6.28	50	
9	57	0.02	0.32	0.90	1.56	4.28	34	
10	53	0.02	0.02	0.20	1.40	1.90	15	
11	49	0.02	0.02	0.38	0.78	1.38	11	
12	44	0.10	0.12	0.32	0.80	1.04	8	

There is evidently a steady loss taking place over all the different strengths of sulfuric acid. There is, however, a very marked change in the amount lost between Nos. 4 and 5. There was also a very decided difference in color between these two samples; Nos. 5 and 6 retained the characteristic red color of the roseo salt, while Nos. 4, 3, 2 and 1 had all acquired the purple color of the purpureo salt. Similarly (Table XLIV) there was a marked color change between 9 and 10. This indicates that the critical point lies at about 55 per cent. sulfuric acid, and this acid solution has an aqueous vapor pressure of 5.1 mm. Hg. There is apparently then a definit pressure of water vapor from the roseo salt at this temperature, but a slow loss of water seems to take place at a much higher aqueous vapor pressure. It will be observed that the analytical results for the extent of the conversion agree with those calculated from the loss in weight as closely as could be expected. A similar experiment was tried to study the change from purpureo to roseo over the same strength of acid. The result is given in Table XLV.

TABLE XLV.—CHANGE OF PURPUREO ROSEO CHLORIDE IN DRY STATE AT 25°. TOOK 0.2000 GRAM.

No.	H_2SO_4. Per cent.	Loss in weight, 49 days. Milligram.	Remarks.
13	65	0.38	
14	61	0.38	
15	57	0.36	No change in color evident.
16	53	0.36	
17	49	0.35	
18	44	0.04	

It is seen that instead of a gain in weight over the more dilute acid there is a loss equal to that over the stronger. This indicates either that at 25° the reverse change does not take place in the time interval covered by the experiment or the equilibrium lies very near pure purpureo. The slight loss in weight was probably due to a trace of adsorbed moisture in the original salt. The reaction then, between roseo and purpureo chloride in the dry state is not a reversible one. It is possible, however, that the change to roseo salt, for instance, occurs in two stages; an intramolecular rearrangement and a subsequent combination with water. If this is the case, a pure sample of purpureo salt might change into roseo, even in the absence of water. We had fortunately an old sample of purpureo chloride of known purity, having been prepared in this laboratory by the sodium pyrophosphate method of Jörgensen in 1908. Two analyses of this salt gave respectively 98.5 and 98.7 per cent. purpureo modification. The very small percentages of roseo, 1.5 and 1.3, may well have been caused by the slight unavoidable transformation which takes place while getting the salt into solution, even though the temperature was kept at 0° during the process. Thanks to the courtesy of Professor G. P. Baxter, we also examined a sample of purpureo chloride prepared by Gibbs (probably about 1875). It was unfortunately very evidently impure, containing particles of a black substance. Two analyses showed that it contained 84.9 and 85.1 per cent. respectively of purpureo chloride. We can, however, draw no inferences from this sample. We must conclude then that in the absence of water no change to roseo salt results, even after a very long time, and that therefore the change to roseo salt and the absorption of water are necessarily concomitant processes.

Similarly, an experiment was made in order to find out whether roseo chloride would change to purpureo when no water was allowed to escape. For this purpose a freshly prepared sample of roseo chloride was first analyzed for purpureo, then sealed in a small glass tube, allowed to stand for a month, and then again analyzed. The first analysis gave 98.83 per cent., the second 98.84 per cent. roseo. This shows again that the transformation is necessarily connected with the liberation of the water.

Vapor pressure experiments with the roseo bromide and roseo nitrate indicated an aqueous vapor pressure about 4 mm. Hg each.

Summary.

In this paper we have studied the mutual transformation of the acidopentammine cobalt salts (purpureo) into the corresponding aquopentammine salts (roseo).

The velocities of transformation of various of these ammines in dilute aqueous solution were measured and it was found that they agreed with the requirements for a monomolecular reaction. They were but little affected by the acidity of the solution, thus distinguishing these transformations from the color changes of chromium salts. The velocity of transformation of the acido radical was also found to be independent of the radicals outside of the complex.

The rate of decomposition of these ammines was determined at various temperatures and in different solutions, and the amount of reduction which accompanied this decomposition was also determined both by a specially designed analytical method and by a study of the gaseous products of the decomposition.

On the basis of this study of reaction and decomposition velocities, we selected 70° as the optimum temperature for equilibrium measurements. Working at this temperature we showed that our method of analysis was efficient, and that a true equilibrium was established in the solution. Selecting the chloride for a more extended study we varied the concentrations both of the reacting substances and of the other chlorides present and showed that the equilibrium is affected both by the total concentration of the salt and by the concentration of the chlorine ion; it is, however, independent of the acidity of the solution.

We calculated the concentrations of the various molecular species present in the equilibrium mixtures and applied the simple concentration law to the various possible equilibria which might exist between them. No satisfactory equilibrium constant was obtained. When, however, the equilibrium was viewed as an electrolytic dissociation of purpureo compounds into roseo compounds and chlorine ions, and their concentrations were substituted in the Storch-Bancroft modification of the concentration law, an approximate constant was obtained; a further modification of this law gave an excellent constant. We pointed out that if this view is correct we have the interesting case of a *slow* electrolytic dissociation. Furthermore, we know that the chlorine ion given off by the purpureo radical is replaced by a water molecule; by analogy the same thing would be expected in the dissociation of an ordinary electrolyte.

Finally, it was shown that in the dry state the roseo salts have a critical aqueous vapor pressure above which only a very slow loss of water occurs. The change does not appear to be reversible. It was further shown that the change is necessarily connected with the absorption or evolution of water.

We are carrying out measurements, similar to those described in this paper, on the ammines of chromium, iridium and rhodium and on the complex salts of cobalt and other metals with ethylenediammine.

NEW YORK CITY.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF CLARK UNIVERSITY.]

A RE-INVESTIGATION OF THE VELOCITY OF SUGAR HYDROLYSIS.

FIRST COMMUNICATION.

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1. Introductory.

The mechanism of sugar hydrolysis is as yet scarcely understood. Even as to the number of molecules that take part in the hydrolysis physico-chemical literature contains but incomplete information. Most investigators have, namely, found the reaction to be monomolecular with respect to sugar. There is some evidence also that the process in-