solution for temperatures at intervals of 10°. The following table shows these values and equivalent values for $Ba(OH)_2.8H_2O$:

	BaO.	$Ba(OH)_2.8H_2O$.
10°	2.17%	4.46%
20°	3.36%	6.91%
30°	4.75%	9.77%
40°	6.85%	14.09%

When these four points are plotted and a smooth curve drawn, the curve-reading for the solubility at 25° is 8.30%, agreeing with the value obtained by direct measurement (Table V).

Hence the Rosenstühl-Rühlmann data may serve as a basis for the calculation,

$$\frac{ds}{dt} = \frac{9.77\% - 6.91\%}{10^\circ} = 0.288\%.$$

The application of the complete data to the equation

$$T\frac{(p_2 - p_1)(v_2 - v_1)}{t_2 - t_1} = Q$$

gives for the left-hand side

$$298 \times 0.288 \times \frac{244}{0.491} \times 10^6 \times 0.0508 = 2.16 \times 10^9$$

and for the right-hand side

$$51.2 \times 4.189 \times 10^7 = 2.14 \times 10^9.$$

The agreement is seen to be excellent.

The writer wishes to acknowledge his thanks to Prof. T. W. Richards, of Harvard University, for valuable advice and assistance in the devising of the pressure bomb employed in this investigation. This apparatus is owned by the Carnegie Institution of Washington and is now being used for other work under the auspices of the Institution.

COLUMBIA, MISSOURI.

[CONTRIBUTION FROM KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

STUDIES ON THE COBALTAMMINES. I.

VARIOUS IONIZATION TYPES AS DETERMINED BY THE FREEZING-POINT LOWERING IN AQUEOUS SOLUTION, TOGETHER WITH CONDUCTANCE MEASUREMENTS.[1]

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The present investigation was undertaken as a starting point in the study of the structure of the cobaltammines. The first point necessary

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[1] The temperature readings were taken to one-twenty thousandth of a degree by means of a 50 couple thermoelement, and a double combination potentiometer specially designed for this work by Dr. W. P. White, and we wish to express our indebtedness to him for this aid.

to establish was the type of salt for the different groups under which the cobaltammines may be classified, *i. e.*, the number of ions which they give in aqueous solution. That it is essential that such an investigation should be undertaken, is indicated by the great divergence, amounting to 100% or more, between the results of various investigators in this field, such as that which exists between the results on freezing-point lowering as obtained by E. Petersen[1] and by Werner and Herty,[2] and by the discrepancies which exist between the various results obtained by any one individual investigator.

Petersen criticized the empirical conductivity comparison method employed by Werner for determining the number of ions from his conductivity data, and proposed, by substituting for γ in the Equation $i = 1 + (n - 1)\gamma$, the value obtained for it from the conductivity ratio λ/λ, to determine n by giving it different integral values (1, 2, 3, etc.), and finding which one would fit for the value of i, determined from freezing-point depressions. This work was done during the latter part of the controversy between Werner and Jörgensen, and the materials for it were furnished by the latter. Petersen used as his λ_0 merely the value of λ derived from his conductivity measurements at the lowest concentration used (1 mol of salt to 3200 liters of water), and did not extrapolate his results to obtain the real λ_0. With the exception of some three of the salts, he was unfortunate, too, in his choice of compounds, as he used substances which hydrolyze quite readily, and were therefore of little value in determining the point in question. About four years later, Werner and Herty replied to Petersen, severely criticizing his work, and gave freezing-point data on a few salts. Table I summarizes the results on the only salt on which both Petersen and Werner and Herty give freezing-point data.

TABLE I.—SUMMARY OF PETERSEN'S AND WERNER AND HERTY'S FREEZING-POINT DATA ON CROCEO COBALTAMMINE.

Petersen. Dinitrotetrammine cobalt nitrate.				Werner and Herty. Dinitrotetrammine cobalt chloride.			
Conc. N[3] × 10^3.	Depression. Δt.	$\Delta t/N$.	i.	Conc. N × 10^3.	Depression. Δt.	$\Delta t/N$.	i.
5.0	0.030	6.00	3.23	4.35	0.015	3.45	1.74
10.0	0.058	5.80	3.12	4.72	0.017	3.60	1.82

While their results on conductivity were in fair agreement, the disparity in the freezing-point measurements was so great that Werner's criticisms on Petersen's method, suggesting, as the cause for the difference, an error in determining the real zero on his Beckmann thermometer because of solubility of the freezing-point vessel in the water, can really

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[1] *Z. physik. Chem.*, **22**, 310 (1897); *Ibid.*, **39**, 249 (1902).

[2] *Ibid.*, **38**, 331 (1901).

[3] N represents the equivalent concentration per 1000 g. of water and Δt the lowering of the freezing point.

serve as no explanation at all. He very justly pointed to the fact that, owing to the small solubility of the salts, the difficulties encountered in freezing-point determinations would lead to uncertain conclusions. When it is considered that the limit of accuracy of the ordinary Beckmann thermometer is 0.001°—and the ordinary Beckmann apparatus was evidently used by both Werner and Petersen—and notes the temperature depressions recorded in Table I, it is not difficult to account for a difference of 5–10% in their measurements. But the disparity amounts to almost 100%—great enough so that while Werner interpreted the croceo salt as one giving two ions in aqueous solution, Petersen designated it a tetraionic salt.

The method of determining freezing-point lowerings by the use of a fifty junction copper-constantan thermoelement[1] can be applied with accuracy to low concentrations of solution, and the use of the interferometer for analysis, while interfered with by the color of the cobaltammines, permits the determination of the concentration of the equilibrium mixture of these complex salts. We therefore decided to determine the freezing-point lowerings of a few of them, choosing for our work those which showed the least tendency to instability in aqueous solution. The well-known series described by Werner[2] meets this requirement very well, and includes salts of the different types of ionization.

We therefore prepared the following salts:

Hexammine (luteo) cobalt chloride	$Co(NH_3)_6Cl_3$
Nitropentammine (xantho) cobalt chloride	$(NO_2)Co(NH_3)_5Cl_2$
Chloropentammine (purpureo) cobalt chloride	$ClCo(NH_3)_5Cl_2$
Dinitrotetrammine (croceo) cobalt chloride	$(NO_2)_2Co(NH_3)_4Cl$
Dinitrotetrammine (flavo) cobalt nitrate	$(NO_2)_2Co(NH_3)_4NO_3$
Trinitrotriammine cobalt	$(NO_2)_3Co(NH_3)_3$
Potassium tetranitrodiammine cobaltate (Erdmann's salt)	$(NO_2)_4Co(NH_3)_2K$
Ammonium tetranitrodiammine cobaltate	$(NO_2)_4Co(NH_3)_2NH_4$
Sodium cobaltic nitrite	$(NO_2)_6CoNa_3$

While some of the salts of this series are rather unstable and hydrolyze readily at higher temperatures, at zero degrees no trouble was experienced, except with dinitrotetrammine cobalt chloride, and with this only on exposure to bright light, and with sodium cobaltic nitrite. To dispense with any error from hydrolysis, all analyses of the equilibrium mixtures were made on the same day as, and immediately following, the determination of the freezing-point lowerings. Only rather limited data on these salts could be obtained, owing to their slight solubility. However, determinations could be made at a sufficient number of concentrations to

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[1] Adams, THIS JOURNAL, **37**, 481 (1915).

[2] *Z. physik. Chem.*, 14, 506 (1894); "New Ideas on Inorganic Chemistry" (English edition), pp. 40, 41, 157, 158; *Ber.*, 40, 26 (1907).

plot the curve for $\Delta t/N$ against a function of the concentration, and to permit comparison of this with the curve of some simple salt.

Preparation of the Salts.

Chloropentammine Cobaltic Chloride, $[Co(NH_3)_5Cl]Cl_2$ was prepared by Sörensen's method.[1] 20 g. of cobalt carbonate were dissolved in the least amount of 1:1 HCl possible. The filtered and cooled solution was added to a mixture of 250 cc. of concentrated ammonia solution and 50 g. of $(NH_4)_2CO_3$ dissolved in 250 cc. of water. This was then put in a large flask and a rapid stream of air passed through it for three hours. 150 grams of NH_4Cl were added and the solution evaporated on a water bath until it became a crystal pulp. The $(NH_4)_2CO_3$ was decomposed by HCl and the solution made alkaline by the addition of 10 cc. excess NH_4OH. Complete precipitation of the salt was accomplished by the addition of 300 cc. of concentrated HCl. After heating on the water bath for an hour to decompose any aquopentammine the salt was collected on a filter and washed with dilute HCl.

For purification the salt was dissolved in a weak solution of ammonia by heating on a water bath. It was precipitated by concentrated HCl heated on the water bath and filtered. This process was repeated four times. After final washing with dilute HCl. redistilled alcohol and ether it was dried in a desiccator and heated to constant weight at forty degrees in an air bath. Scarcely any loss of weight occurred during the heating. An analysis was made by treating a sample with H_2SO_4 and weighing as $CoSO_4$, and gave 0.2113 g. of $CoSO_4$. The amount calculated from the formula was 0.2115.

Hexammine Cobaltic Chloride, $Co(NH_3)_6Cl_3$, was prepared by Jörgensen's method.[2] 10 grams of chloropentammine cobaltic chloride, 100 cc. of 20% ammonia and 8 grams NH_4Cl were placed in a pressure flask which held about 110 cc. The flask was put in a water bath and heated with shaking every hour until no trace of the pentammine could be seen. This required on the average about five hours. After cooling the contents of the flask were poured into an open vessel and the ammonia removed by suction in a vacuum desiccator. The flask contained mostly hexammine with a little chloropentammine and aquopentammine. When the ammonia had been removed, the mixture was diluted to 300 cc. and 50 cc. concentrated HCl were added. It was heated on the water bath for an hour, 0.5 of its volume of concentrated HCl was then added, and the solution cooled and filtered. For purification the hexammine, which is rather soluble in water, was removed from the pentammine by extracting with cold water. The reprecipitation was carried out as above. It was washed and dried in the same way as the pentammine.

Nitropentammine Cobaltic Chloride, $[Co(NH_3)_5NO_2]Cl_2$, was prepared as recommended by Jörgensen. 20 grams of chloropentammine cobaltic chloride were dissolved in 200 cc. H_2O and 50 cc. of 10% ammonia on the water bath. The solution was filtered, acidified with HCl and then heated for some time with 25 grams $NaNO_2$. Complete precipitation was accomplished by the addition of 250 cc. concentrated HCl. It was filtered, washed many times with dilute HCl, alcohol and ether and then dried.

Dinitrotetrammine (croceo) **Cobalt Chloride.**—The method recommended by Jörgensen[2] was followed. Cobalt carbonate was dissolved in the requisite amount of hydrochloric acid; ammonium chloride, sodium nitrite, and ammonium hydroxide were added, and air was drawn through the solution for several hours. The precipitated salt was separated on a Hirsch funnel, and washed repeatedly to remove the small quantities of xantho chloride contaminating it, until no test for the xantho salt was

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[1] *Z. anorg. Chem.*, **5**, 369 (1894).

[2] *Ibid.*. **17**, 455 (1898).

given by ammonium oxalate. To convert this mixture of croceo chloride and nitrate to the pure chloride, it was dissolved in water weakly acidified with acetic acid, and a large amount of ammonium chloride was added; the solution was cooled, and allowed to stand for a few hours. The salt which separated was washed thoroughly first with water, and finally with 90% alcohol. It was dried, and recrystallized from water very weakly acidified with acetic acid. Although Jörgensen recommends recrystallization without acid, it was found impossible to do this without some hydrolysis, and the consequent precipitation of a varying amount of an oxide of cobalt. 150 g. of the pure salt were prepared. The air-dry salt was brought to constant weight at 80°.

Dinitrotetrammine (flavo) Cobalt Nitrate.[1]—The first preparation was carbonatotetrammine cobalt sulfate,[2] which was made by dissolving cobalt carbonate in the requisite amount of sulfuric acid, adding ammonium carbonate and ammonium hydroxide, oxidizing by drawing air through the solution for a few hours, concentrating on the water bath with frequent addition of a little ammonium carbonate, cooling to 0°, and filtering on a platinum cone. This material was then converted into the flavo salt by dissolving in dilute nitric acid, adding sodium nitrite, heating on the water bath for a few minutes, cooling, and leaving in the ice chest for several hours. The acid flavo nitrate which separated was washed with dilute nitric acid, and changed to the neutral salt by further washing with alcohol to neutral reaction. The salt was recrystallized from hot water, very weakly acidified with acetic acid, and was separated on a platinum cone. 140 g. of the pure salt were prepared. The air-dry salt was brought to constant weight at 50°.

Trinitrotriammine Cobalt.[3]—Cobalt carbonate was dissolved in just the requisite amount of hydrochloric acid, and the solution was poured into a solution containing ammonium chloride, sodium nitrite, and ammonium hydroxide. The cobalt was oxidized by drawing air through the mixture for a few hours. After standing for a week in open dishes, the solution had lost its odor of ammonia and had decreased in volume by half. The solid material which had separated consisted of a yellow slime and dark brown crystals. To remove all traces of chloride, repeated washing was necessary, and it was found expedient to do this by decantation, as the crystals were practically chloride-free. This salt was finally dissolved in boiling water containing a little acetic acid, and crystallized by cooling to 0°. The air-dry salt was brought to constant weight at 80°. An analysis for cobalt showed 23.76%; theoretical, 23.77%.

Potassium Tetranitrodiammine Cobaltate.[4]—Cobalt carbonate was converted into the chloride, ammonium chloride was dissolved in the solution, the mixture heated to 50°, and a very concentrated solution of potassium nitrite at the same temperature added. The temperature was maintained at 50° for half an hour. After some hours, a fine yellow powder and dark brown crystals had separated from the solution. Most of the powder was removed by decanting off the original solution, and washing the crystals with cold water in the same manner; the remainder, by dissolving the crystals in hot water, and filtering off the practically insoluble powder. The salt obtained on cooling the solution was recrystallized from pure water, and brought to constant weight at 50°. An analysis for cobalt showed 18.61%; theoretical, 18.65%.

Ammonium Tetranitrodiammine Cobaltate.—The procedure was similar to that used in the preparation of the preceding salt, with the exception that sodium nitrite was used in place of potassium nitrite. An analysis for cobalt showed 20.16%; theoretical, 19.98%.

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[1] *Z. anorg. Chem.*, **17**, 455 (1898).

[2] *Ibid.*, **2**, 282 (1892).

[3] Jörgensen, *Loc. cit.*

[4] *J. prakt. Chem.*, [2] **23**, 249 (1881).

Sodium Cobaltic Nitrite.[1]—The method recommended by Biltz was followed in this preparation. The air-dry salt was brought to constant weight at 50°. An analysis made by weighing the sodium and cobalt as sulfates showed for the cobalt 14.03%. This salt is described in the literature[2] as one of varying amounts of water of hydration. On the basis of the formula $(NO_2)_6CoNa_3$. the theoretical percentage of cobalt is 14.60; for $(NO_2)_6CoNa_3.H_2O$, 13.97. The freezing-point data were figured on the basis of the latter formula. However, the difference in values obtained, using one formula or the other, is of little significance, as the decomposability of the salt in aqueous solutions renders any determination at best merely an approximation.

Freezing-Point Data.

The method followed in this work was the same as will be described in a later paper. On account of the color of the solutions, the analysis with the interferometer proved rather troublesome, and probably a method based on conductivity measurements would be even more satisfactory. The difficulties experienced in the analysis account largely for the slight irregularities of the individual points on the curves as plotted. All data are calculated on the basis of weight normality.

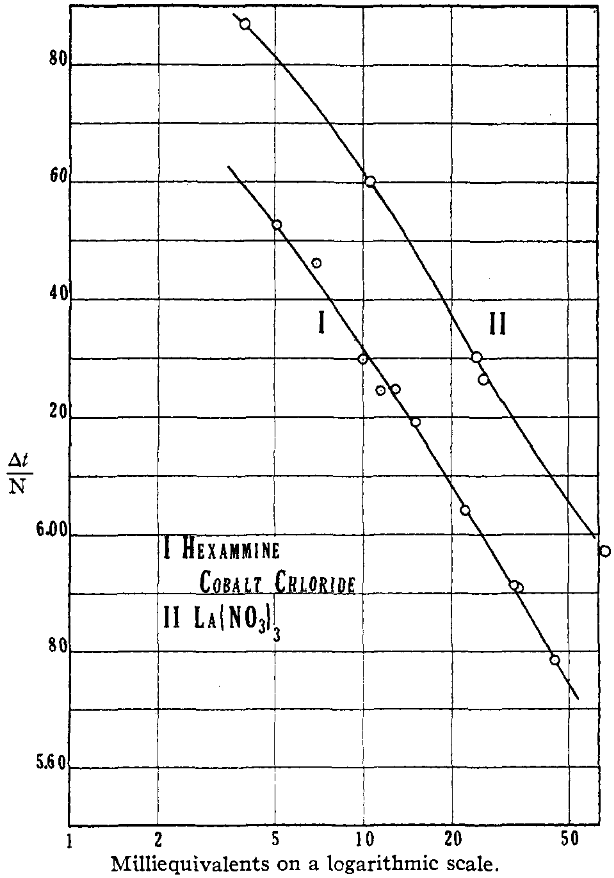

Fig. 1.—Values of $\Delta t/N$ for the freezing-point lowerings of hexammine (luteo) cobalt chloride and of lanthanum nitrate.

Hexammine Cobalt Chloride. — This is one of the most stable salts of the series. Table II comprises the data on this salt, and the values obtained by Werner. Table III includes our data at rounded concentrations, the corresponding *i* values for lanthanum nitrate, and the apparent ionization as obtained from the

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[1] Biltz, "Laboratory Methods of Inorganic Chemistry," 1909, p. 149.

[2] Moissan, *Chim. Minerale*, 4, 206 (1905), and the references listed.

conductivity measurements of Roberts at 0°. The latter are calculated on the basis of volume normality; but the concentrations are small enough so that very little change would be made by recalculating on the basis of weight normality. Fig. 1 shows the curve of $\Delta t/N$ plotted against the logarithm of the concentration, and the corresponding curve for lanthanum nitrate. Fig. 2 plots our values on a smaller scale, in order to include Werner and Herty's data. The freezing-point lowerings, are smaller throughout than those shown by lanthanum nitrate. However, the agreement is such as to leave no doubt that the

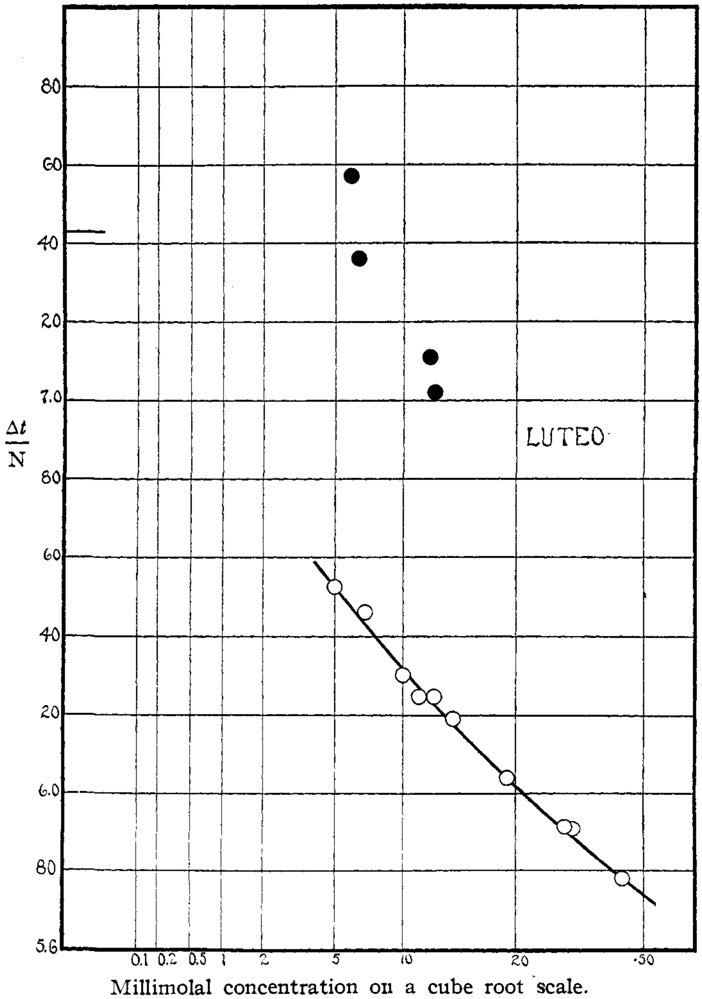

Fig. 2.—Values of $\Delta t/N$ from the freezing-point lowerings of solutions of hexammine (luteo) cobalt chloride, a tri-univalent salt. The black circles represent the results of Werner and Herty.

hexammine salt is of the same type as the lanthanum nitrate—a tetraionic salt.

TABLE II.—SUMMARY OF THE DATA TAKEN ON HEXAMMINE COBALT CHLORIDE, AND OF WERNER AND HERTY'S VALUES.

Conc. $N \times 10^3$.	Equivalents $(10)^3$.	Depression. Δt.	$\Delta t/N$.	
1.69	5.05	0.0110_1	6.527	
2.31	6.92	0.0149_0	6.461	
3.35	10.05	0.0211_0	6.300	
3.84	11.53	0.0240_5	6.247	
4.31	12.92	0.0269_2	6.248	
5.02	15.05	0.0310_7	6.191	
7.43	22.30	0.0449_0	6.040	
10.89	32.67	0.0644_3	5.913	
11.29	33.87	0.0667_2	5.909	
14.95	44.85	0.0864_5	5.783	
		Werner and Herty.[1]		
				i.
1.98	5.94	0.0112	7.57	4.08
2.12	6.36	0.0166	7.36	3.96
4.15	12.44	0.0295	7.11	3.83
4.27	12.82	0.03	7.02	3.78

TABLE III.—DATA ON HEXAMMINE COBALT CHLORIDE AT ROUNDED CONCENTRATIONS.

Conc. Equivalents $(10)^3$.	$\Delta t/N$.	i.		γ.	
		Hexammine.	$La(NO_3)_3$.	F.-P. L.	(Roberts) Cond.
5	6.527	3.513	3.666	83.8	82.8
10	6.317	3.399	3.562	80.0	78.7
20	6.085	3.275	3.429	75.8	73.6
50	5.741	3.089	3.261	69.6	65.2

Nitropentammine and Chloropentammine Cobalt Chloride.—Fig 3 shows the curves for these salts in relation to the curve of cobalt chloride. It will be seen that they are very much steeper over the range possible to investigate than that of the cobalt chloride. The points taken by Werner and Herty on the xantho salt are also plotted. Table IV collects our data. and that of Werner and Herty; Table V includes the data at rounded concentrations, the i values of cobalt chloride, and the ionization values determined by Roberts' conductivity measurements at 0°. The salts, especially the purpureo, show high ionization values. Evidently they are quite comparable to cobalt chloride, and are therefore of the three ion type.

Dinitrotetrammine Cobalt Salts. Croceo Chloride and Flavo Nitrate.—Fig. 4 plots the curves of these salts, shows the points determined by Werner and Herty, and gives also the curve for potassium iodate, as a representative- di-ionic salt. The difference in the slope of the curves for the croceo and flavo salts is only slightly greater than that between potassium chloride and potassium nitrate (Fig. 5 of the following paper).

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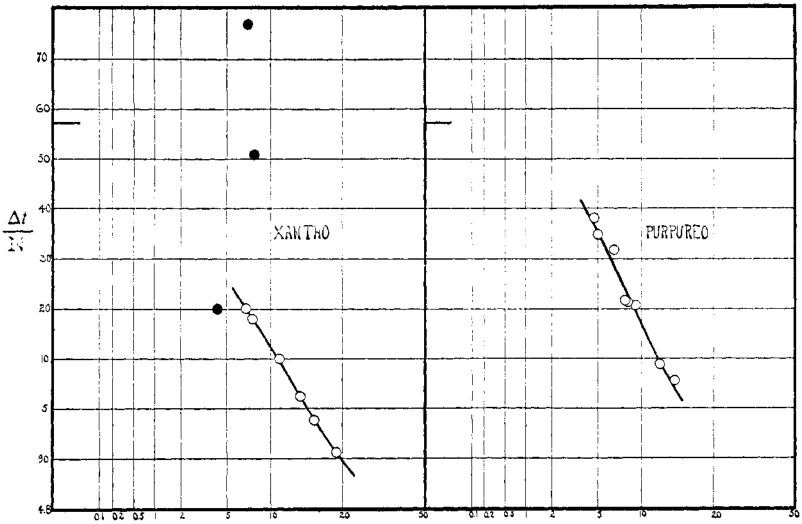
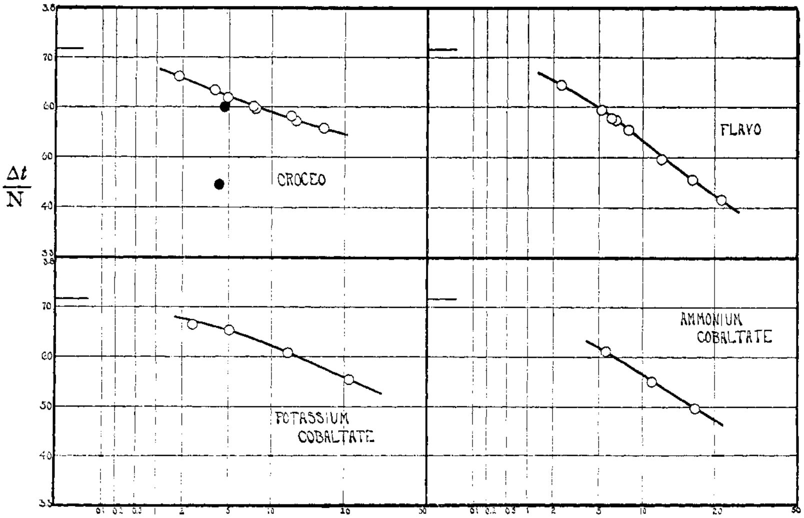
[1] The data given by Werner and Herty, *Z. physik. Chem.*, 38, 352 (1901), have been recalculated on the basis of 1.858 for the molal lowering.



Milliequivalents on a cube root scale.

Fig. 3.—Values of $\Delta t/N$ for nitropentammine (xantho) cobalt chloride and chloropentammine (purpureo) cobalt chloride. The black circles give the results of Werner and Herty.



Concentrations in milliequivalents on a cube root scale.

Fig. 4.—Values of $\Delta t/N$ from the freezing-point lowerings of dinitrotetrammine (croceo) cobalt chloride, dinitrotetrammine (flavo) cobalt nitrate, two isomeric compounds, and of potassium and ammonium tetranitrodiammine cobaltates, a series of uni-univalent salts. The black circles give the values of Werner and Herty. The bottom line in each of these four plots represents a value of 3.30 for $\Delta t/N$.

TABLE IV.—SUMMARY OF THE DATA TAKEN ON XANTHO AND PURPUREO COBALT CHLORIDES, AND OF WERNER AND HERTY'S VALUES.

Concentration. $N \times 10^3$.	Equivalents $(10)^3$.	F.-P. depression, Δt.	$\Delta t/N$.	i.
Xantho Cobalt Chloride.				
1.54	3.09	0.00803	5.201	
3.54	7.08	0.01841	5.203	
3.86	7.72	0.02000	5.180	
5.71	11.41	0.02910	5.102	
7.45	14.89	0.03740	5.023	
8.71	17.41	0.04330	4.976	
10.92	21.83	0.05363	4.912	
Werner and Herty.				
2.12	4.23	0.011	5.20	2.63
3.64	7.28	0.021	5.77	2.92
4.08	8.16	0.0225	5.51	2.79
Purpureo Cobalt Chloride.				
2.45	4.90	0.01319	5.380	
2.49	4.97	0.01330	5.350	
3.40	6.80	0.01809	5.318	
3.98	7.96	0.02075	5.216	
4.16	8.33	0.02171	5.215	
4.62	9.24	0.02405	5.207	
6.44	12.88	0.03277	5.088	
7.76	15.51	0.03931	5.056	

TABLE V.—DATA ON XANTHO AND PURPUREO COBALT CHLORIDES AT ROUNDED CONCENTRATIONS.

Concentration. Equiv. $(10)^3$.	$\Delta t/N$.	i.		γ.	
		Cobaltammine.	$CoCl_2$.	F.-P. D.	(Roberts) Cond.
Xantho Cobalt Chloride.					
5	5.263	2.832	2.840	91.6	91.2
10	5.127	2.760	2.796	88.0	87.8
20	4.939	2.658	2.749	82.9	....
Purpureo Cobalt Chloride.					
2	5.44	2.93		96.0	95.6
5	5.357	2.883		94.2	92.8
10	5.178	2.787		89.4	89.3

TABLE III.—DATA TAKEN ON CROCEO AND FLAVO COBALT SALTS, AND ALSO WERNER AND HERTY'S AND PETERSEN'S VALUES.

Concentration.		F.-P. depression.	
$N \times 10^3$.	Equivalents $(10)^3$.	Δt.	$\Delta t/N$.
Croceo Cobalt Chloride.			
1.82	1.82	0.00665	3.661
3.92	3.92	0.01426	3.635
4.88	4.88	0.01766	3.619
6.63	6.63	0.02399	3.621
7.62	7.62	0.02745	3.602
7.93	7.93	0.02852	3.596
12.86	12.86	0.04607	3.583
13.70	13.70	0.04894	3.573
18.79	18.79	0.06687	3.559

TABLE VI (*continued*).

Concentration.				
$N \times 10^3$.	Equivalents $(10)^3$.	F.-P. depression, Δt.	$\Delta t/N$.	i.
	Werner and Herty.			
4.35	4.35	0.015	3.45	1.74
4.72	4.72	0.017	3.60	1.82
	Flavo Cobalt Nitrate.			
2.35	2.35	0.00857	3.643	
4.40	4.40	0.01596	3.630	
5.14	5.14	0.01846	3.594	
6.17	6.17	0.02208	3.579	
6.67	6.67	0.02383	3.575	
8.25	8.25	0.02931	3.555	
12.86	12.86	0.04495	3.495	
18.57	18.57	0.06421	3.457	
25.00	25.00	0.08539	3.416	
	Petersen's Data.			
5	5	0.035	7.00	3.77
10	10	0.066	6.60	3.55
20	20	0.123	6.15	3.31

TABLE VII.—DATA ON THE CROCEO AND FLAVO SALTS AS COMPARED WITH KIO_3 AND KNO_3 AT ROUNDED CONCENTRATIONS.

		i.		γ.	
Concentration. Equiv. $(10)^3$.	$\Delta t/N$.	Cobaltammine.	KIO_3.[1]	From F.-P. D.	(Roberts) from conductivity.
		Croceo Cobalt Chloride.			
2	3.66	1.97	1.94	97.0	95.4
5	3.622	1.949	1.929	94.9	93.2
10	3.590	1.932	1.912	93.2	90.7
20	3.556	1.914	1.889	91.4	....
		Flavo Cobalt Nitrate.	KNO_3.		
2	3.65	1.964	1.967	96.4	96.6
5	3.595	1.935	1.958	93.5	93.8
10	3.531	1.900	1.937	90.0	91.2
20	3.446	1.855	1.908	85.5	....

Croceo and Flavo Salts.—These interesting isomeric inorganic salts are evidently di-ionic, and correspond very closely to the ordinary di-ionic salts in their freezing-point lowerings.

Trinitrotriammine Cobalt.—The insolubility of this salt renders accurate freezing-point determinations very difficult. The greatest temperature depression noted, as shown in Table VIII, was a little more than 0.005°. This, in conjunction with the difficulty of analyzing the equilibrium mixture, as mentioned above, serves to explain the discrepancies in the i values given in the table. It is interesting to note that this is the only case in which our values are in agreement with those of Petersen. So far as can be shown by freezing-point measurements, the salt is a non-electrolyte.

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[1] L. H. Adams, THIS JOURNAL, **37**, 495 (1915).

TABLE VIII.—SUMMARY OF THE DATA TAKEN ON TRINITROTRIAMMINE COBALT AND PETERSEN'S VALUES.

Concentration. N × 10³.	F.-P. depression. Δt.	Δt/N.	i.
1.83	0.00351	1.92	1.03
1.86	0.00346	1.86	1.00
2.13	0.00394	1.85	1.00
2.14	0.00367	1.72	0.93
2.74	0.00489	1.79	0.96
2.97	0.00532	1.79	0.96
	Petersen's Values.		
4.35	0.008	1.84	0.99
4.17	0.0085	2.04	1.10

Potassium and Ammonium Tetranitrodiammine Cobaltates.—Fig. 4 and Tables IX and X collect the data on these salts. They are highly ionized, and evidently di-ionic.

TABLE IX.—SUMMARY OF THE DATA TAKEN ON POTASSIUM AND AMMONIUM COBALTATES.

Concentration. N × 10³.	Equivalents (10)³.	F.-P. depression. Δt.	Δt/N.
	Potassium Tetranitrodiammine Cobaltate.		
2.54	2.54	0.00931	3.665
5.15	5.15	0.01883	3.651
12.36	12.36	0.04463	3.609
24.90	24.90	0.08847	3.554
	Ammonium Tetranitrodiammine Cobaltate.		
2.38	2.38	0.00862	3.625
5.74	5.74	0.02075	3.612
11.54	11.54	0.04096	3.550
19.21	19.21	0.06714	3.495

TABLE X.—DATA AT ROUNDED CONCENTRATIONS FOR POTASSIUM AND AMMONIUM COBALTATES, AND FOR POTASSIUM IODATE USED FOR COMPARISON.

Concentration. Equiv. (10)³.	Δt/N.	i.		γ.
		Cobaltammine.	KIO_3.	F.-P. D.
	Potassium Tetranitrodiammine Cobaltate.			
2	3.68	1.98	1.94	98.0
5	3.652	1.965	1.929	96.5
10	3.620	1.948	1.912	94.8
20	3.573	1.923	1.889	92.3
	Ammonium Tetranitrodiammine Cobaltate.			
2	3.66	1.97		97.0
5	3.620	1.948		94.8
10	3.564	1.918		91.8
20	3.492	1.879		87.9

Sodium Cobaltic Nitrite.—The instability of this salt in aqueous solution rendered any accurate determination of the freezing-point depression an impossibility. The salt was dissolved and introduced into the freezing-point jars as quickly as possible, and the temperature depression noted as soon as equilibrium was attained. With the introduction of the salt, the temperature fell rapidly for a short time, and from then on, slowly but continuously. The attainment of equilibrium evidently occurred when this slow change commenced, and the temperature reading was taken at this point. The concentration of the freezing-point mixture was controlled by a gravimetric determination of the cobalt and sodium as sulfates. The *i* values indicate that the salt is tetra-ionic.

TABLE XI.

Concentration.		F.-P. depression. Δt.	Δt/N.	*i*.
$N \times 10^3$.	Equivalents $(10)^3$.			
16.3	48.9	0.1098	6.74	3.63
31.2	93.5	0.2146	6.89	3.71

The values of the apparent ionizations of the cobaltammines, as determined by the conductivity and freezing-point methods, are nearly the same, with one exception, and that is in the case of the salt of highest type, hexammine cobaltic chloride, a tetra-ionic salt, which gives a value for the freezing-point lowering 1.2% higher at 0.005 *N*, and 6.7% higher at 0.050 *N*. These deviations are in the same direction as those found in this laboratory between the two sets of results for lanthanum nitrate, a salt of the same type. These are given in Table XII.

TABLE XII.—VALUES OF THE APPARENT IONIZATION OF LANTHANUM NITRATE AS CALCULATED FROM FREEZING-POINT AND CONDUCTIVITY DATA.

Concn. in equivalents.	Apparent ionization.		Per cent. deviation.
	Conductivity.	Freezing point.	
0.005	85.83	88.9	3.58
0.01	81.77	85.4	4.44
0.05	69.91	75.4	7.86
0.1	64.38	71.6	11.21
0.2	58.51	68.8	14.46

With both of these tri-univalent salts the value of the apparent ionization calculated from the freezing-point results rapidly increases above that determined by conductivity as the concentration of the solution increases. This suggests that the cause of this change is to be sought in some factor which rapidly increases in value with the concentration of the solution. This result is very different from that which is found in the case of salts of simpler types, so even after making allowance for the fact that the freezing-point result depends upon the activity of the constituents of the salt, and the conductivity upon the number and speed of the ions, it still seems as though a large part of the deviation remains to be explained. It is interesting that this deviation is in the direction which would be predicted from the intermediate ion hypothesis as advanced by Harkins.[1]

Conductivity Measurements (by W. A. ROBERTS).

None of the salts whose conductivity was measured showed appreciable decomposition at 0° with the exception of trinitrotriammine. At 25°

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[1] See the fourth paper in this number of THIS JOURNAL.

all with the exception of the hexammine showed some change, but not enough to be considered in the time taken for measurement.

The cells used were the type devised by Kraus and used by Noyes, Melcher, Washburn and others. The cell used for the more concentrated solutions had a constant of 4.745 at 0°, and the one used for the more dilute solutions had a constant of 0.09710 at 0°. The conductivity of $N/50$ KCl was taken as 1.521×10^{-3}.

For the calculation of the equivalent conductivities the hexammine was considered to have four, the pentammines three, and the tetrammines two ions, as determined by the freezing-point measurements. The value of Λ_0 was found by plotting $1/\Lambda$ against $(C\Lambda)^{n-1}$. The range of $(n - 1)$ was found to be from 0.4 to 0.8.

Measurements were begun upon sodium cobalt nitrite, but such rapid decomposition took place that the data were not recorded. Trinitrotriammine which is supposed by Werner not to be ionized showed the following molecular conductivities which are only about 1/20,000 that of the di-ionic croceo and flavo salts:

Molar concentration..........	0.000328	0.000737
Molar conductivity...........	0.004	0.003

TABLE I.—VALUES OF Λ AT 0° AND 25° WITH THE CORRESPONDING DENSITIES OF THE SOLUTIONS AT 25°.

C.	Λ 25°.	Λ 0°.	Densities 25°/4°.
	Hexammine Cobalt Chloride.		
0.1107	101.3	56.09	1.0022
0.07722	109.2	58.90	1.0003
0.05293	117.2	63.27	0.99955
0.02015	130.2	69.8	0.99775
0.002032	160.0	85.7	0.99720
0.0004315	172.0	91.0	.....
	Nitrotetrammine Cobalt Nitrate.		
0.01014	94.56	51.69	0.99870
0.004724	97.22	53.54	0.9977
0.002493	99.81	54.53	0.9974
0.0009658	101.9	55.71	0.9972
0.0004720	102.5	56.04	.....
	Nitrotetrammine Cobalt Chloride.		
0.009693	100.8	53.8	0.99810
0.004710	103.8	55.3	0.9976
0.002389	105.6	56.4	0.99730
0.001107	106.8	57.0	.....
0.0005205	108.9	57.8	0.9972
0.0001100	110.0	58.3	.....
	Chloropentammine Cobalt Chloride.		
0.0178	120.7	65.00	0.99821
0.008384	130.2	69.15	0.99760
0.003728	136.8	72.8	0.99729
0.0008891	142.8	75.25	0.99710
0.0003021	144.7	77.0	.....

TABLE I (*continued*).

C.	Λ 25°.	Λ 0°.	Densities 25°/4°.
	Nitropentammine Cobalt Chloride.		
0.02061	116.0	62.25	0.9984
0.009910	122.4	.....	0.9977
0.004612	129.6	68.60	0.9973
0.001801	134.3	71.0	0.9972
0.001078	135.7	72.25	.....
0.0005492	137.5	72.70	.....

TABLE II.—APPARENT IONIZATION OF HEXAMMINE CHLORIDE AND LANTHANUM NITRATE.

Concentration.	Λ/Λ_0.	$\sqrt[3]{\text{Concentration}}$.
	Hexammine Cobaltic Chloride, $CO(NH_3)_6Cl_3$.	
0.05	63.8	0.3684
0.02	72.0	0.2714
0.01	76.9	0.2154
0.005	81.0	0.1709
0.002	85.8	0.1260
0.001	88.8	0.0794
0.0005	91.4	....
	Lanthanum Nitrate.	
0.2	58.5	....
0.1	64.4	....
0.05	69.9	....
0.01	81.8	....
0.005	85.8	....
0.002	90.3	....

Magnesium Sulfate.—The material used was "Zur Analyse" salt, which was recrystallized twice from conductivity water. The original solution was made up and analyzed. The other solutions were dilutions made at 25°.

TABLE III.—THE VALUES OF Λ AND Λ/Λ_0 AT 18° AND 25° FOR $MgSO_4$ AND THE DENSITIES OF THE SOLUTIONS AT 25°.

Equiv. concn.	Λ25°.	$\Lambda/\Lambda_0$25°.	Λ18°.	$\Lambda/\Lambda_0$18°.	Densities 25°/4°.
0.0	135.0	.....	114.4	91.3	....
0.00050635	123.3	91.33	104.4	87.4	....
0.001067	117.4	86.96	100.1	82.7	....
0.0020134	110.8	82.07	94.67	73.7	0.9972
0.0050635	99.0	73.33	84.35	66.5	0.9974
0.010067	88.85	65.82	76.15	58.7	0.99765
0.020134	78.98	58.50	67.23	49.3	0.9983
0.050635	66.05	48.90	56.54	43.3	1.000
0.10067	57.79	42.81	49.58	37.6	1.0033
0.20135	49.82	36.90	43.12	30.8	1.0092
0.50635	40.72	30.16	35.25	25.2	1.0269
1.0067	33.37	24.72	28.81	....	1.0559

Summary.—The freezing-point lowerings of nine cobaltammines of different types have been determined. These salts, with the exception of sodium cobaltic nitrite, were prepared by methods proposed by Jörgensen. On the whole, the results obtained from the freezing-point measurements, correspond very closely with those given by simple salts of like ionic types. Our results show that the type of each salt is the same as that assumed by Werner and his co-workers, but on the other hand they do not agree well with Werner's own freezing-point measurements. No explanation can be offered for the erroneous results given by Petersen's work, other than that his thermometric measurements must have been approximately 100% in error, except in the work on triamminotrinitro cobalt.

Conductance measurements have also been made on the same series of cobaltammines.

In conclusion, we wish to thank L. H. Adams and John Johnston of the Geophysical Laboratory in Washington, for the loan of the freezing-point apparatus and the interferometer, and to express our indebtedness for a grant of two hundred dollars from the Wolcott Gibbs Fund of the National Academy of Sciences.

CHICAGO, ILL.

[CONTRIBUTIONS FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE FREE ENERGY OF DILUTION AND THE FREEZING-POINT LOWERINGS IN SOLUTIONS OF SOME SALTS OF VARIOUS TYPES OF IONIZATION, AND OF SALT MIXTURES.

BY RALPH E. HALL AND WILLIAM D. HARKINS.[1]

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I. Experimental.

The experimental work outlined in this paper was begun for the purpose of obtaining accurate freezing-point data from which the free energy of dilutions of dilute salt solutions can be determined. It seemed particularly desirable that accurate measurements should be carried out on higher type salts, in order that the results for salts of different types might be compared. It was found, too, that, while it is well known how mixtures of common ion salts in aqueous solution behave with respect to the conductivity of the separate salts, there are no similar data for the freezing-point lowerings of mixtures. This paper gives data for the freezing-point lowerings of uni-univalent, uni-bivalent, uni-trivalent, and bi-bivalent salts, and for mixtures containing two uni-univalent salts.

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[1] This paper forms the basis for a part of a dissertation presented to the University of Chicago by Ralph E. Hall in part fulfilment of the requirements for the degree of Doctor of Philosophy.