sodium hydroxide, and sulfuric acid have been determined. The curves showing the heat of coagulation as a function of the purity vary widely in shape with the nature of the coagulant, the heat effect being usually positive, but with sodium sulfate and sodium chloride at low purities, negative. As the purity increases the heat of coagulation becomes smaller, finally becoming negligible, except in the case of sulfuric acid. The peculiar behavior of the last electrolyte is due to solution of the ferric oxide.

5. When the heat of coagulation is plotted against the concentration of the coagulating electrolyte, smooth curves are obtained showing no "break" at the point of limiting concentration.

6. The heat effects observed on coagulating ferric oxide sols with electrolytes are to be attributed to the action of the electrolytes in the coagulants upon the electrolytes, particularly ferric chloride, present in the sol. The change in dispersity of the ferric oxide on coagulation does not involve a heat change greater than 1 to 2 calories per gram equivalent of ferric oxide.

7. In the case of ferric oxide hydrosol there exists no "heat of peptization" analogous to the heat of solution of crystalloids.

The work described in this paper has been carried out with the assistance of a fellowship established by E. I. duPont de Nemours and Company, to whom the authors wish to express their indebtedness.

MADISON, WISCONSIN.

THE STRENGTHS OF COBALTAMMINE BASES AND WERNER'S THEORY OF BASES.

BY ARTHUR B. LAMB AND VICTOR YNGVE.

The great strength of many cobaltammine bases has attracted the attention and evoked the surprise of investigators in this field. Cobaltic hexammine hydroxide (luteo cobaltic hydroxide), for instance, is a very soluble, deliquescent substance whose solution is caustic in its properties, absorbs carbon dioxide with avidity, and displaces both ammonia and silver oxide from their salts. Werner,[1] estimating the strengths of various ammine bases qualitatively from their chemical behavior and from the properties of their salts, has arranged certain of them in the order of their strengths, and indeed largely on the basis of these considerations has proposed a new theory of bases and of hydrolysis. We have therefore been interested to obtain quantitative measurements of the strengths of these bases. We have used the conductivity method for this purpose, measuring the conductivities of their dilute solutions at various concentrations and comparing the resulting molecular conductivities with the conductiv-

[1] Werner, "Neuere Anschauungen," 3rd edition, Braunschweig, 1913, p. 265.

ities at infinite dilution, as computed from measurements of the conductivities of salts derived from them.

Solutions of the bases were prepared by triturating their bromides with an excess of moist silver oxide, the mortar, pestle, silver oxide and water having all been carefully cooled to zero degrees. The solution was then rapidly filtered by suction into a graduated 250cc. flask, the residue washed several times with 10cc. portions of ice-cold water, and the solution made up to the mark. After thorough mixing, a portion was transferred to conductivity cells and the conductivity measured, first in an ice-bath and then in a 25° thermostat. Aliquot portions of the original solution were diluted successively and lower concentrations were then measured in the same way. The more important details of manipulation were as follows.

Preparation of Materials.—The water was prepared by redistillation using a little barium hydroxide and potassium permanganate. It and the solutions made from it were kept in carefully closed and steam-extracted resistance-glass bottles. Its conductivity was always measured before use.

Most of the ammines were prepared according to the improved methods of Jörgensen.[2] The hexammine bromide was, however, made by precipitation with pure conc. hydrobromic acid of hexammine chloride prepared according to the method of Lamb and Larson.[3] It was then washed several times with dil. hydrobromic acid and with alcohol until all the acid was removed, and finally was dried in an air-bath at 35°. The triethylenediamine bromide was prepared from the hexammine bromide according to the method of Pfeiffer,[4] while the dibromo-diethylenediamine bromide, which on treatment with moist silver oxide gave diaquo-diethylenediamine cobaltic hydroxide was a commercial product.

The silver oxide was prepared by the action of a clear solution of barium hydroxide on an excess of silver nitrate in dilute solution. It was washed with a large amount of conductivity water until no test for barium ion could be obtained. It was kept under conductivity water in a closed vessel.

The Apparatus.—Three of the conductivity cells were flask-shaped vessels of Jena glass, provided with large strongly anchored sealed-in electrodes; one consisted of dip electrodes fitted into a wide-mouthed flask. Each was closed by a rubber stopper and was provided with a thermometer legible to 0.01°. A large ice-bath served for a 0° thermostat, and the water thermostat maintained a temperature of 24.96° constant to within 0.01°. The true temperatures were established by a calibrated thermometer whose ice-point was carefully checked. The constants of the cells were fixed by means of a solution of potassium chloride made up by weight to 0.019894 molar using the density data of Baxter,[5] and taking the conductivity of this solution as 0.002759 mhos at 24.96°. The constants were redetermined at the end of our measurements and found to be identical with the initial values. The slide-wire bridge could be read to one part in 5000 and was carefully calibrated under the conditions of its use. No readings were taken until the contents of the cells had reached precisely the temperature of the thermostat. Successive bridge readings were in most cases

[2] Jörgensen, Z. anorg. Chem., 17, 455–9 (1898).

[3] Lamb and Larson, THIS JOURNAL, 42, 2025 (1920).

[4] Pfeiffer, Ann., 346, 59 (1906).

[5] Baxter et al., THIS JOURNAL, 33, 913 (1911).

constant to within the accuracy of a setting, and the mean of several readings was recorded.

In the case of the dinitro-tetrammine salts, however, a slow decrease in conductivity was noticeable at 25°, while with the carbonato-tetrammine this change was noticeable at 0° and so rapid at 25° as to make measurements of little value. In these latter cases the measurements were made over a period of 2 or 3 hours, and extrapolated to zero time.

The Water Correction.

The correction of our conductivity measurements for the conductivity of the water is of considerable and unusual importance. This is due to the fact that the conductivity of the water, and indeed of any carefully purified water distilled in vessels open to the air is substantially that of the carbonic acid dissolved in it.[6] In acid or neutral solutions the corrections on this account are of no special importance, but here this carbonic acid will neutralize an equivalent quantity of the base and, as the net effect of this is to replace a swift, hydroxyl ion for a sluggish, carbonate ion, a considerable correction, at least in dilute solutions, must be applied. Calling $C_{H_2CO_3}$ the total concentration of the carbonic acid, this correction will be

$$\Delta = \frac{2 \lambda_{OH^-} - \lambda_{CO_3^{--}}}{1000} C_{H_2CO_3}$$

where λ_{OH^-} and $\lambda_{CO_3^{--}}$ are the conductivities of the hydroxyl and carbonate ions at the temperature of the measurements.

Since the specific conductivity of a solution of carbon dioxide is proportional to the square root of the partial pressure of carbon dioxide, and since carbon dioxide is only slightly dissociated even at these concentrations, the specific conductivity must also be proportional to the square root of its total concentration. A solution whose total concentration of carbon dioxide is 2.94×10^{-5} mols has a specific conductivity of 0.65×10^{-6} mhos at 0°.[7] Therefore, calling L_0 the specific conductivity of the water at 0°, $C_{H_2CO_3} = L_0^2 \dfrac{2.94 \times 10^{-5}}{0.65 \times 10^{-6}} = 6.8 \times 10^7 L_0^2$; and therefore $\Delta_0° = 8.3 \times 10^6 L_0^2$; and $\Delta_{25°} = 2.82 \times 10^7 L_0^2$ mhos. These corrections at 0° and 25° have been applied to the specific conductivities at concentrations down to 0.00666 M, and since L_0 varied between 0.94 and 1.48×10^{-6} mhos, the correction varied between 0.73 and 1.8×10^{-5} at 0° and 2.5 and 6.2×10^{-5} mhos at 25°.

This method of correction is rigorous enough at these concentrations. At still lower concentrations the question arises whether the second hydrogen of carbonic acid is sufficiently ionized to react completely with the hydroxyl ions.

[6] Kendall, THIS JOURNAL, **39**, 7 (1917).
[7] Kendall, *ibid.*, **38**, 1494–5 (1916).

If only the first hydrogen were neutralized the decrease in the specific conductivity would be[8]

$\Delta'_{6°} = (\lambda_{OH^-} - _{HCO_3^-})_{0°}C_{H_2CO_3} = 0.080\ C_{H_2CO_3}$ mhos; and similarly $\Delta'_{25°} = 0.146\ C_{H_2CO_3}$ mhos. If the second hydrogen were then neutralized, the further decrease would be $\Delta''_{0°} = 0.042\ C_{H_2CO_3}$ and $\Delta''_{25°} = 0.072\ C_{H_2CO_3}$.

The extent to which these neutralizations will occur can be computed from the ionization constants of carbonic acid and of water. The ionization constant of the first hydrogen of carbonic acid is $K_1 = 2.24 \times 10^{-7}$ at $0°$ and 3.5×10^{-7} at $25°$;[9] that of the second is $K_2 = 6 \times 10^{-11}$ at $18°$.[10] It is evident that at the concentration of hydroxyl ion under consideration ($0.0001\ M$) the neutralization of the first hydrogen ion may be considered as complete.

The neutralization of the second hydrogen will be determined by the equilibrium equations

$$C_{H^+} \times C_{OH^-} = S_{H_2O}, \text{ and } \frac{C_{H^+} \times C_{CO_3^{--}}}{C_{HCO_3^-}} = K_2,$$

where S_{H_2O} represents the ion product of water. Calling C'_{OH^-} the initial concentration of hydroxyl ion, that is, its concentration after the complete neutralization of the first hydrogen of carbonic acid, x the number of mols of the second hydrogen neutralized, and y the number of mols of carbonate ion formed at equilibrium, $C_{H^+} = y - x$ and $C_{OH^-} = C'_{OH^-} - x$. Then $(y-x)(C'_{OH^-} - x) = S_{H_2O}$; and $(y-x)y = K_2(C_{H_2CO_3} - x)$.

The solution of these two equations gives a third degree equation. It is therefore much simpler to solve them by a process of approximation for each set of values of the constants, first guessing a value of y, then solving each equation for x, and finally varying y until each equation gives an identical value for x. After a few trials this solution can be made very rapidly. Values of y computed in this way for $C_{H_2CO_3} = 1.18 \times 10^{-4}$ M, and for a series of hydroxyl-ion concentrations at $25°$ are given in Table I. These values of y divided by $C_{H_2CO_3}$ give the fraction of the total carbonic acid converted into the carbonate ion; that is, the fraction fully neutralized. The resulting figures are entered in the fourth column of Table I. Similar computations were made for the other concentrations

[8] For the conductivity of HCO_3^- see Kendall, THIS JOURNAL, **38**, 1489 (1916).

[9] Kendall, *ibid.*, **38**, 1486 (1916).

[10] Johnston, *ibid.*, **37**, 2004 (1915).
  McCoy, *Am. Chem. J.*, **29**, 437 (1903).
  Walker and Cormack, *J. Chem. Soc.*, **77**, 8 (1900).
  Shields, *Z. physik. Chem.*, **12**, 167 (1893).
  Auerbach and Pick, *Arbeiten kais. Gesundheitsamt.*, **38**, 243 (1911).
  Prideaux, *Proc. Roy. Soc.*, **91A**, 535 (1915).

of carbonic acid. Values for intermediate concentrations of hydroxyl ions were found by graphical interpolation.

TABLE I.

ION CONCENTRATIONS.

[$C_{H_2CO_3} = 1.18 \times 10^{-4}$. Temperature $= 25°$.]

Initial conc. OH$^-$ × 10³M.	$C_{OH^-} \times 10^3 M$.	$C_{CO_3^{--}}$ or y ×10³.	$\dfrac{C_{CO_3^{--}}}{C_{H_2CO_3}}$.
6.67	6.54	0.115	0.97
1.33	1.21	0.103	0.87
0.667	0.549	0.087	0.74
0.218	0.100	0.033	0.28
0.133	0.016	0.0064	0.055

It can be seen from this table that the neutralization is nearly complete at the highest concentrations, and corrections for this effect were therefore only applied at concentrations of 0.0013 M and below. With water of the purity used ($L_0 = 0.9 - 1.4 \times 10^{-6}$ mhos) the total correction for water is, however, very large at the lowest concentration, so that any correction is unsatisfactory. This is shown by the large values of the water correction expressed as percentages of the total conductivity (Δ/L) in the tables of data. In any attempt to secure more accurate values for low concentrations much purer water should be used.

Correction for the Solubility of Silver Oxide.—During trituration of the cobaltammine bromide with silver oxide, and the subsequent washing some silver must dissolve, and thus contaminate the solution of the cobaltammine hydroxide. The amount of this contamination can be determined from the known solubility of silver oxide.

The total solubility of silver hydroxide is 2.16×10^{-4} mols per liter at 25°, according to the careful and direct measurements of Noyes and Kohr.[11] The ion concentration of the saturated solution is 1.23 and 1.39×10^{-4} mols at 20° and 25°, respectively, according to Böttger.[12] Assuming that the total solubility has the same temperature coefficient as the ion concentration, it will equal 8×10^{-5} mols at 0°. The total volume of water used during trituration and washing may be taken as 50 cc., and

[11] Noyes and Kohr, *Z. physik. Chem.*, **42**, 338 (1903).

[12] Böttger, *Z. physik. Chem.*, **46**, 602 (1903). It should be pointed out that Böttger's values are somewhat too large for silver hydroxide and lead hydroxide, as he corrected the conductivity of their solutions by simply subtracting the conductivity of the water. This neglects the fact that the carbonic acid which is chiefly responsible for the conductivity of the water will have its first hydrogen completely neutralized, and will therefore have a higher conductivity than when slightly dissociated in the original water. The correction, Δ', for this effect will evidently be

$C_{H_2CO_3} \dfrac{(\lambda_{Ag^+} + \lambda_{OH^-})}{1000}$ or $0.11\ C_{H_2CO_3}$. For the water which he used $C_{H_2CO_3}$

$= 2.8 \times 10^{-5}$, and therefore $\Delta'_{25°} = 3.1 \times 10^{-6}$ and $\Delta'_{20°} = 2.8 \times 10^{-6}$ mhos. These corrections, applied to Böttger's values for the ion concentration give, for 25° and 20°, respectively, 1.39 and $1.23 \times 10^{-4} M$.

assuming its complete saturation and the complete dissociation of the silver hydroxide, the concentration of silver ion would be $1.6 \times 10^{-5} M$. This amount of contamination is wholly negligible in the $3300 \times 10^{-5} M$ solutions which were chiefly studied, and practically negligible in the few $330 \times 10^{-5} M$ solutions. No correction has, therefore, been applied to our results for this effect.

The Conductivity Data.

The conductivity data are collected in the following tables. λ and α signify molecular conductivity and percentage dissociation as usual, L_0, the specific conductivity at $0°$ of the water used; Δ/L, the percentage of the total conductivity which the water correction represents at the various concentrations, and R the molecular conductivity of the hydroxide obtained by subtracting the conductivity of the neutral salt from the observed values.

TABLE II.

HEXAMMINE COBALTIC BROMIDE.

$L_0 = 1.35 \times 10^{-6}$ mhos.

Conc. $M \times 10^3$.	$\lambda_{0°}$.				$\alpha_{0°}$.	$\lambda_{25°}$.				$\alpha_{25°}$.
	1.	Observed. 2.	Mean.	Calc. $n=1.48$.	%.	1.	Observed. 2.	Mean.	Calc. $n=1.45$.	%.
33.23	174.1	174.1	174.1	173.3	58.6	319.1	319.1	319.1	319.9	57.6
6.662	215.3	215.2	215.3	217.4	72.5	397.0	397.0	397.0	397.9	77.1
1.336	253.8	253.8	253.7	251.0	85.4	462.0	461.8	461.9	460.1	83.4
0.2678	272.1	272.1	272.1	273.1	91.6	502.6	502.4	502.5	502.2	90.6
0				(297.1)					(553.5)	

TABLE III.

HEXAMMINE COBALTIC DIBROMIDE HYDROXIDE.   HEXAMMINE COBALTIC BROMIDE DIHYDROXIDE.

$L_0 = 1.48 \times 10^{-6}$ mhos.

Conc. $M \times 10^3$.	λ.		R.		α.		λ.		R.		α.	
	$0°$.	$25°$.	$0°$.	$25°$.	$0°$. %.	$25°$. %.	$0°$.	$25°$.	$0°$.	$25°$.	$0°$. %.	$25°$. %.
33.23	216.9	388.4	101	175	63	58	258.2	449.4	200	343	63	57
6.662	259.5	463.8	116	199	72	66	302.3	529.0	230	397	72	66
1.336	293.8	528.8	125	221	78	73	344.0	603.4	260	448	81	74
0.2678	333.6	621.0	152	286	95	95	387.2	693.2	296	526	93	87
0												

TABLE IV.

HEXAMMINE COBALTIC HYDROXIDE.

$L_0 = 1.48 \times 10^{-6}$ mhos.

Conc. $M \times 10^3$.	$\lambda_{0°}$ mhos.		$\alpha_{0°}$.	$\lambda_{25°}$ mhos.		$\alpha_{0°}$.	Δ/L.
	Obs.	Calc. $n=1.4$.	%.	Obs.	Calc. $n=1.3$.	%.	%.
33.23	347.5	347.5	72.2	591.3	589.9	65.5	0.2
6.662	396.9	396.8	82.4	675.3	672.7	74.8	0.7
1.336	431.1	431.6	89.5	739.0	741.8	81.8	3.2
0.2678	469.0	450.7	97.4	843.0	791.8	93.4	14.0
0		(482.0)			(901.0)		

TABLE V.

AQUO-PENTAMMINE COBALTIC HYDROXIDE.

$L_0 = 1.31 \times 10^{-6}$ mhos.

Conc. $M \times 10^3$.	Obs. $\lambda_{0°}$. mhos.	Calc. $n = 1.11$.	$\alpha_{0°}$. %.	$\alpha'_{0°}$. %.	Δ/L. %.
33.21	223.4	223.9	45.7	70.8	0.2
6.66	244.7	244.6	50.0	77.9	1.1
1.335	261.8	265.5	53.5	82.9	4.1
0.2683	286.8	285.7	58.6	90.7	17.5
0		(475.0)			

TABLE VI.

DIAQUO-TETRAMMINE COBALTIC HYDROXIDE.

$L_0 = 1.04 \times 10^{-6}$ mhos.

Conc. $M \times 10^3$.	$\lambda_{0°}$. mhos.	$\alpha_{0°}$. %.	$\alpha'_{0°}$. %.	Δ/L. %.
6.59	116.4	24.8	74.7	2.5
1.321	115.4	24.6	74.0	6.0
0.265	102.7	21.8	65.9	31.3
0	(469.0)			

TABLE VII.

TRIETHYLENEDIAMINE COBALTIC HYDROXIDE.

$L° = 1.34 \times 10^{-6}$ mhos.

Conc. $M \times 10^3$.	$\lambda_{0°}$ mhos. Obs.	Calc. $n = 1.37$.	$\alpha_{0°}$. %.	$\lambda_{25°}$ mhos. Obs.	Calc. $n = 1.35$.	$\alpha_{25°}$. %.	Δ/L. %.
33.29	304.2	303.0	67.0	519.1	512.3	66.4	0.2
6.674	344.0	344.5	81.2	596.4	594.5	76.3	0.7
1.338	375.4	374.5	88.6	651.6	659.6	83.3	2.8
0.2683	394.4	394.6	93.1	706.8	705.5	90.4	12.7
0		(423.6)			(781.0)		

TABLE VIII.

DIAQUO-DIETHYLENEDIAMINE COBALTIC HYDROXIDE.

$L_0 = 1.34 \times 10^{-6}$ mhos.

Conc. $M \times 10^3$.	$\lambda_{0°}$. mhos.	$\alpha_{0°}$. %.	$\alpha'_{0°}$. %.	$\lambda_{25°}$. mhos.	$\alpha_{25°}$. %.	Δ/L. %.
33.29	107.6	24.6	73.7	185.0	22.7	0.4
6.674	113.9	26.6	79.8	197.4	25.2	2.0
1.338	116.8	27.3	81.8	209.0	26.7	9.0
0.2683	143.1	33.4	100.3	269.4	34.5	33.5
0	(430.0)			(778.5)		

TABLE IX.

CARBONATO-TETRAMMINE COBALTIC HYDROXIDE.

$L_0 = 1.04 \times 10^{-6}$ mhos.

Conc. $M \times 10^3$.	$\lambda_{0°}$. mhos.	$\alpha_{0°}$. %.	Δ/L. %.
33.32	108.7	89.2	0.3
6.674	113.4	93.1	
1.338	119.0	97.6	5.7
0.2683	100.3	85.3	24.0
0	(121.8)		

TABLE X.
1,2-DINITRO-TETRAMMINE COBALTIC HYDROXIDE.
$L_0 = 0.94 \times 10^{-6}$ mhos.

Conc. $M \times 10^3$.	$\lambda_{0°}$. mhos.	$\alpha_{0°}$. %.	$\lambda_{25°}$. mhos.	$\alpha_{25°}$. %.	Δ/L. %.
6.657	102.5	83.3	176.8	79.2	1.1
1.335	99.9	81.2	179.0	78.4	5.4
0.2676	102.8	84.7	201.8	89.4	21.0
0	(123.1)		(228.3)		

TABLE XI.
1,6-DINITRO-TETRAMMINE COBALTIC HYDROXIDE.
$L_0 = 0.94 \times 10^{-6}$ mhos.

Conc. $M \times 10^3$.	$\lambda_{0°}$. mhos.	$\alpha_{0°}$. %.	$\lambda_{25°}$. mhos.	$\alpha_{25°}$. %.	Δ/L. %.
3.329	116.2	94.6	201.4	88.3	1.9
0.6675	117.2	95.4	209.0	91.6	9.0
0.1339	123.2	100.3	256.0	112.2	30.3
0	(122.9)		(228.1)		

TABLE XII.
DINITRO-AQUO-TRIAMMINE COBALTIC HYDROXIDE.
$L_0 = 0.94 \times 10^{-6}$ mhos.

Conc. $M \times 10^3$.	$\lambda_{0°}$. mhos.	$\alpha_{0°}$. %.	$\lambda_{25°}$. mhos.	$\alpha_{25°}$. %.	Δ/L. %.
5.413	52.4	39.0	92.1	37.0	5.4
1.085	48.6	36.0	90.2	36.0	13.7
0.2176	54.2	40.0	120.0	48.0	48.0
0	(134.5)		(251.6)		

In view of Werner's conclusion[13] that in alkaline solutions of the ammines *hydroxo* compounds are present in equilibrium with the aquo hydroxide we have computed from the observed conductivities of all the aquo hydroxides the percentage ionization of the remaining hydroxide, assuming that all of the complexly bound water has been replaced by hydroxyl groups. The results obtained are collected in the columns headed $\alpha'_{0°}$ in the above tables.

The Conductivities at Zero Concentration.

The conductivities at zero concentration, required to compute the degree of ionization, can, in the case of the most highly ionized bases, be computed with considerable certainty from the actually observed conductivities; but in other cases and in general, on account of the serious effect of dissolved carbonic acid on conductivity measurements of bases, it is advantageous to compute these conductivities from measurements of the conductivities of salts of these bases. This is the method we have adopted. In most cases the necessary data were found in the literature. The values adopted for the conductivities of the various anions used in these com-

[13] Werner, Ref. 1, p. 264.

putations,[14] and the resulting conductivities of the various cobaltammine ions are collected in Table XIII.

TABLE XIII.

CONDUCTIVITIES OF THE VARIOUS COBALTAMMINE IONS.

Cobaltammine cations.	λ.		Anions.	λ.	
	0°. mhos.	25°. mhos.		0°. mhos.	25°. mhos.
$[Co(NH_3)_6]^{+++}$	167.0	327.0	Br^-	43.1	75.6
$[Co(NH_3)_5H_2O]^{+++}$	160.0	314.0	Cl^-	41.1	75.5
$[Co(NH_3)_4(H_2O)_2]^{+++}$	154.0	300.0	OH^-	105.0	192.0
$[Co(en)_3]^{+++}$	108.6	205.5	NO_3^-	40.4	70.6
$[Co(en)_2(H_2O)_2]^{+++}$	115.0	219.0	HCO_3^-	25.0	46.2
$[Co(NH_3)_4CO_3]^+$	16.8	33.8	$CO_3^=$	88.0	166.4
$1,2-[Co(NH_3)_4(NO_2)_2]^+$	18.1	36.3			
$1,6-[Co(NH_3)_4(NO_2)_2]^+$	17.9	36.1			
$[Co(NH_3)_3(H_2O)(NO_2)_2]^+$	29.5	59.6			

Hexammine Cobaltic Ion.—Although numerous measurements of the conductivity of hexammine salts have been made by Werner and Miolati[15] and Werner and Herty,[16] the results are discordant and much lower than those obtained more recently for the chloride by Harkins, Hall and Roberts.[17] We have, therefore, measured the conductivity of hexammine bromide at both 0° and 25°, and the results are collected in Table II. Values for the conductivity at zero concentration have been obtained by the well-known method,[18] based on the Storch-Bancroft equation, of plotting $1/\lambda$ against $(C\lambda)^{n-1}$ and varying n until the points lie as closely as possible to a straight line. The values of the exponent and the limiting conductivities thus obtained and of the molar conductivities computed inversely from them are included in the table. The close agreement of the computed and observed conductivities indicates the probable reliability of the extrapolation. The data of Harkins, Hall and Roberts on the chloride have been computed in a similar fashion; satisfactory concordance was obtained using $n = 1.50$ and 1.48 at 0° and 25°, respectively; giving 165.2 and 326.7 mhos for the conductivity of the hexammine ion, as compared with the 167.8 and 327.3 mhos which we obtained above from our measurements on the bromide. We have, therefore, adopted 167 and 327 mhos for our further computations. The reliability of these values is further attested by the close agreement of the conductivities of the hydroxide computed from them with the observed conductivities (Table IV).

[14] See Johnston, THIS JOURNAL, **31**, 1015 (1909); and Landolt u. Börnstein, "Tabellen."

[15] Werner and Miolati, Z. physik. Chem., **12**, 41 (1893); **14**, 511 (1894); **21**, 237 (1896).

[16] Werner and Herty, Z. physik. Chem., **38**, 336 (1901).

[17] Harkins, Hall and Roberts, THIS JOURNAL, **38**, 2656 (1916).

[18] See Noyes and Coolidge, Carnegie Inst., Pub., **63**, p. 50.

Aquo-pentammine and Diaquo-tetrammine Ions.—The conductivities of various salts of these ions have been measured at 25° by Werner and Miolati.[19] These measurements have shown that the aquo-pentammine and the diaquo-tetrammine salts have conductivities 12 and 25 mhos smaller than the hexammine ion at 0.0005 M concentration. We have, therefore, adopted 160 and 154 at 0° and 314 and 300 mhos at 25° for these values.

Triethylenediamine Cobaltic Ion.—The conductivities of the chloride and nitrate of this ion have been measured at 25° by Werner and Hertz.[16] Their measurements, extrapolated to zero concentration in the usual way give 196 and 214 mhos, respectively, for the conductivity of the triethylene-diamine ion. We have adopted the mean of these results, namely 205.5 mhos. This value is confirmed by the close agreement of the conductivities of the hydroxide computed from it with the observed conductivities. No measurements of the conductivities of these salts at zero degrees have been found in the literature; we have, therefore, adopted the value 108.6 mhos, computed from the conductivity of the hydroxide at zero concen-tration (423.6 mhos) found by direct extrapolation. The approximate, at least, correctness of the result is confirmed by the close agreement of the temperature coefficient, derived from it, and the known value at 25°, (0.0357) with the similar coefficients of the hexammine, aquo-pentammine and diaquo-tetrammine ions, namely 0.0384, 0.0364 and 0.0360.

Diaquo-diethylenediamine Ion.—No measurements of the conductivities of the salts of this ion have been made, nor are our measurements of the conductivity of the hydroxide at different concentrations sufficiently concordant to permit extrapolation. We have, therefore, merely esti-mated the conductivity of this ion by assuming that the replacement of 4 ammonia groups in diaquo-tetrammine will produce the same change per mol. of ammonia as when all 6 ammonia groups are replaced in the hexammine to form the triethylenediamine ion. On this basis the con-ductivity becomes 115 at 0° and 219 mhos at 25°.

Carbonato-tetrammine Cobaltic Ion.—The conductivity of this ion at 25° was determined by extrapolation, taking $n = 1.33$, of the conductivity data on the nitrate obtained by Werner and Miolati.[20] The value thus obtained, 33.8 mhos, is only a few per cent. less than the corresponding value for the closely related 1,2-dinitro-tetrammine ion at the same temper-ature. We have assumed that the values at zero degrees will bear the same proportionate relation. This gives the conductivity of the carbonato ion as 16.8 mhos.

1,2- and 1,6-Dinitro-tetrammine Ions.—The conductivities of these ions

[19] Werner and Miolati, *Z. physik. Chem.*, **12**, 42 (1893); **14**, 520 (1894); and **21**, 237 (1896).

[20] Werner and Miolati, *Z. physik. Chem.*, **21**, 234 (1896).

have been obtained by extrapolation of the measurements of Harkins, Hall and Roberts[17] on the nitrate and chloride. The exponent n was found to be 1.4 for the 1,2-dinitro nitrate and 1.5 for the 1,6-dinitro chloride, giving 18.1 and 17.9 at $0°$, and 36.3 and 36.1 mhos at $25°$ for the 1,2- and 1,6-dinitro ions, respectively.

Dinitro-aquo-triammine Ion.—The conductivity of this ion at $25°$ has been computed by extrapolation of the measurements of Werner and Miolati[21] on the chloride, taking $n = 1.40$, as 59.6 mhos. The value at $0°$ was found, as in the case of the carbonato, by comparison with the 1,2-dinitro ion, giving the value 29.5 mhos.

The Degrees of Ionization.

The degrees of ionization, computed for the different concentrations in the usual way, are included in the columns headed $\alpha_{0°}$ or $\alpha_{25°}$ of the above tables (II–XII). To facilitate comparison the values for 0.00133 M have been collected in the following table (XIV). This concentration rather than the most dilute has been selected because it is not so subject to the uncertainties involved in the water correction.

TABLE XIV.

THE PERCENTAGE IONIZATION OF THE COBALTAMMINE BASES AT $0°$ AND 0.00133 M.

Base.	$\alpha.$ %.	$\alpha'.$ %.
$[Co(NH_3)_6]^{+++}$	89.5	
$[Co(NH_3)_5H_2O]^{+++}$	53.5	82.9
$[Co(NH_3)_4(H_2O)_2]^{+++}$	24.6	74.0
$[Co(en)_3]^{+++}$	88.6	
$[Co(en)_2(H_2O)_2]^{+++}$	27.3	81.8
$[Co(NH_3)_4CO_3]^+$	97.6	
$1,2\text{-}[Co(NH_3)_4(NO_2)_2]^+$	81.2	
$1,6\text{-}[Co(NH_3)_4(NO_2)_2]^+$	95.0	
$[Co(NH_3)_3(H_2O)(NO_2)_2]^+$	36.0	

These results bring out clearly the following facts.

(1) These bases are very strong. The univalent bases, carbonato-1,2- and 1,6-dinitro hydroxide, are quite as highly dissociated as the alkali, hydroxides, while the hexammine and triethylenediamine hydroxides have no parallels among the simple tri-acid inorganic bases as regards solubility and extent of ionization.

(2) The replacement of ammonia by ethylenediamine has no noticeable effect on the extent of ionization. Thus, the hexammine and triethylenediamine, on the one hand, and the diaquo-tetrammine and the diaquo-diethylenediamine on the other, show almost identical ionization.

(3) The replacement of ammonia or ethylenediamine by water produces a marked decrease in the degree of ionization. This is apparent on com-

[21] Werner and Miolati, *Z. physik. Chem.*, **12**, 46 (1893); and **21**, 228 and 234 (1896).

paring hexammine with aquo-pentammine and diaquo-pentammine, triethylenediamine with diaquo-ethylenediamine, and the dinitro-tetrammine with dinitro-aquo-triammine. The magnitude of the change is also substantially the same, per water molecule, in each case.

(4) The substitution of acido groups for ammonia or ethylenediamine has no marked effect on the ionization; the carbonato and 1,6-dinitro appear slightly more, the 1,2-dinitro slightly less ionized than the original unsubstituted ammine. It certainly does not produce the weak base which might perhaps be expected from the usual conceptions of organic chemistry. But it must be remembered that the mere decrease in valence, such as any complexly bound acido group would produce, would tend to favor the ionization of the hydroxyl group attached by a polar valence. What little effect there is on the ionization, if it is real, would indicate that the weakest acido group (CO_3) gave the strongest base, as would be expected. This flatly contradicts Werner's qualitative conclusions and seriously invalidates his discussion of the theory of bases.

(5) The ionization of the 1,2-dinitro- is decidedly less than that of the 1,6-dinitro-tetrammine hydroxide. This agrees with Werner's qualitative estimate.[22]

(6) The values of α'_0° are in all cases possible; that is, the assumption that *all* the complexly bound water is replaced by hydroxyl groups does not lead to values of α'_0° greater than 100, though, of course, this does not *prove* that any such replacement has indeed taken place.

The Relative Ionization of the Successive Hydroxyl Groups of Hexammine Cobaltic Hydroxide.

It appeared of interest to ascertain whether there is any marked difference in the degrees of ionization of the successive hydroxyl groups of the hexammine cobaltic hydroxide. This was tested not very conclusively by triturating, in one case, one-third of the requisite quantity of the hexammine bromide with silver oxide as above described, and adding the resulting solution to a solution of the remaining two-thirds; in another case, the proportions were reversed. From the observed molecular conductivity 2/3 or 1/3 of the conductivity of the hexammine bromide was subtracted, the remainder, given in the columns headed R, presumably representing the conductivity of the hydroxide. These values divided by the conductivity of the uni- or di-hydroxide at infinite dilution give the percentage ionization (α). These results are collected in Table III, above. They indicate no marked difference for the three hydroxyl groups.

Werner's Theory of Bases.

As mentioned at the beginning of this article Werner has proposed a

[22] Werner, Ref. 1, p. 265.

theory of bases and of hydrolysis founded largely on considerations connected with the cobaltammine hydroxides. This theory has apparently found such scant acceptance that only a brief discussion of it, and of the bearing of our observations upon it is required. It had its origin in the discovery by Pfeiffer among the ammines of chromium, and later by Werner among the ammines of cobalt and other metals, of the *hydroxo*-ammine salts. These substances, formed by salting out ammoniacal solutions of certain ammines, appear to contain a complexly bound hydroxyl group. Dissolved in strong acids they give solutions from which ordinary aquo salts can be isolated, while with carbon dioxide they yield carbonato salts. On this specific, and on other general evidence, Werner concludes that all bases may be divided into two classes, "anhydro" and "aquo" bases. Ordinary metallic hydroxides, such as sodium, calcium, and aluminum hydroxides, ammonia and the hydroxo-ammines are anhydro bases; while aqueous solutions of these substances contain aquo bases, in equilibrium with the anhydro bases. Only the aquo bases are ionized. Finally, neutralization, according to Werner, is not the simple union of a hydrogen ion with an hydroxyl ion, but the addition of hydrogen ion to the hydroxo group of the anhydro base.

Examined carefully there appear to be two separate and novel hypotheses in this theory. The first is that the hydroxyl group in the free base is complexly bound and must be replaced by a water (or solvate) molecule before ionization can occur. The view that ionization is due to the combination of the solvent with the solute or to the loosening of the bonds of the solute by the residual valences of the solvent, as it is variously expressed, is an old, widespread and multiform theory. Werner's modification simply is that a stoichiometric relation always exists, one molecule of water actually replacing the hydroxyl group. The water then becomes complexly bound, while the hydroxyl group is now held only by polar valences and will therefore dissociate.

Now while this precise replacement of the acido group by the water molecule does indeed occur in the slow ionization of chloro-pentammine cobalt chloride and similar compounds, and presumably also occurs in the ionization of hydroxo compounds, and while it might also occur with a metallic hydroxide which forms a hydrate containing precisely one molecule of water for each hydroxyl group, it is a gratuitous and arbitrary assumption not only in the case of ammines such as the hexammine, the dinitro-tetrammine, etc., for which no hydroxo base and no aquo compounds corresponding to the hydroxo base have been found, but also in the case of metallic hydroxides which either do not form hydrates at all or form them containing more than one molecule of water per hydroxyl group. Thus, for instance, in the case of the hexammine base Werner would have to assume the existence of the particular ion,

$[Co(NH_3)_6(H_2O)_3]^{+++}$, for which there is to our knowledge no evidence whatever.[23]   A more probable view would be that acido groups, including the hydroxyl group, may or may not be held complexly, that is, by non-polar bonds.   If held complexly, they will not be ionized until displaced by a solvate or other neutral molecule.   If not held complexly, that is, if held by electrostatic or polar valence, they will ionize at once up to an equilibrium condition, when dissolved in a suitable solvent.   The ionization in each case is presumably brought about by the chemical interaction of the solute and solvent, but how definite the compositions of the resulting compounds or solvated ions are is an open question.   Presumably there is a quite definite and fixed orientation of at least a few molecules of the solvent about each ion.

The second novel feature of this theory is that neutralization occurs, not by the direct combination of hydrogen ions with hydroxyl ions, but by the addition of a hydrogen ion to the complexly bound hydroxyl group of the anhydro base.   That is, instead of imagining that water is first formed, the equilibrium between aquo and anhydro bases upset and hydroxo thus converted into aquo base, Werner prefers to imagine substantially the reverse procedure.   The hydrogen ion, adding to the hydroxo-ammine ion, forms the aquo ion directly; this causes the re-formation of more hydroxo-ammine ion from the aquo ion with the liberation of water and the binding of the hydroxyl ion.   There is no direct evidence in support of this inverted picture.   It must lead to the same equilibrium conditions as the usual interpretation, and it seems unlikely that hydrogen ion would add rapidly to an hydroxo group, but not at all to an hydroxyl ion bearing an opposite electric charge.

The only evidence which Werner presents in support of this radical proposal is that hydroxo-nitro-tetrammine and hydroxo-dinitro-tetrammine react more strongly basic in solution than do the corresponding hydroxo-pentammine and hydroxo-aquo-tetrammine salts, which is the opposite to what would be expected from the usual point of view.   This could, however, be predicted from his theory because, he alleges somewhat darkly, the acido group would increase the affinity of the complex hydroxyl group for the hydrogen ion.

Our measurements do show that dinitro-tetrammine is indeed stronger than diaquo-tetrammine hydroxide.   But, in the first place, as indicated above, these comparisons between bases of different valences, or acidities, to use the older term, are not justifiable, for it is recognized that, other things being equal, mono-acid bases will be stronger than di-acid bases and very much stronger than tri-acid bases.   In the second place, these comparisons are between nitro and aquo groups; if similar comparisons

[23] The nearest approach to such evidence is that hydrates of hexammine chloride containing 3 molecules of water have been prepared.

are made between nitro and ammonia or ethylenediamine groups the result is wholly different. In spite of the handicap of greater acidity (valence) there is no significant difference in their strengths; dinitro-tetrammine, hexammine, and triethylenediamine hydroxides exhibit practically the same ionization. What little difference there is accords with the usual interpretation; thus, as pointed out above, carbonato-tetrammine hydroxide is a stronger base than the stereochemically similar 1,2-dinitro-tetrammine hydroxide. Finally, it should be pointed out in this connection that the marked decrease in the strength of the bases produced by the replacement of ammonia and ethylenediamine by water, the outstanding result of our measurements, is also in accord with the usual views.

Summarizing regarding this theory we would say that, while it may well be true that any complexly bound hydroxyl group, or acido group, must first be replaced by a water molecule before ionization can occur, it is improbable that this is a necessary or sufficient mechanism for all ionization; nor can the idea that neutralization takes place exclusively by addition of the hydrogen ion to a hydroxo group be seriously entertained.

Summary.

(1) The strengths of 9 cobaltammine bases have been determined by measuring their conductivities over a range of concentrations in dilute solutions and comparing these with the conductivities at zero concentration, as computed from measurements of the conductivities of salts derived from these bases.

(2) The determinations have shown (a) that these bases are very strong, certain of them are as highly ionized as the alkali hydroxides; (b) that the replacement of ammonia by ethylenediamine has no noticeable effect; (c) that the replacement by water molecules produces a marked and progressive decrease in the strength; (d) that the substitution of acido groups has no marked effect on the strength, the electrostatic effect of a decrease in valence perhaps offsetting the chemical effect of the acid radical; the stronger acid radical produced the weaker base; (e) that there is no marked difference in the ionization of the successive hydroxyl groups in hexammine cobalt hydroxide.

(3) The improbability of the distinctive features of Werner's theory of bases has been brought out, and a more probable interpretation suggested.

(4) Equations giving the important correction of the conductivity of solutions of bases for the conductivity of the carbon dioxide dissolved in the water have been derived and applied.

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