

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE CONSTITUTION OF CERTAIN COBALTAMMINE BASES

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In contrast with the simple hydroxides of cobalt many of the complex bases of cobalt are easily soluble and relatively strong. Triethylenediamine cobaltic hydroxide $[\text{Co}(\text{C}_2\text{H}_4(\text{NH}_2)_2)_3](\text{OH})_3$, for instance, is a very soluble, deliquescent substance which displaces both silver oxide and ammonia from their respective salts and whose solution is caustic, absorbing carbon dioxide from the air.

The conductivities of some nine of these cobaltamine bases were measured some time ago,¹ and it was found, in agreement with the above behavior, that these bases are highly ionized. Thus in 0.00133 molar solution at 0° triethylenediamine cobaltic hydroxide appeared to be 88.6%, while the univalent base, 1,6-dinitro-tetrammine hydroxide, 1,6- $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{OH}$, appeared to be 95% ionized.

These measurements disclosed a further important regularity. When water molecules were present within the complex of the bromide from which the bases were prepared, the ionization of the bases was decidedly less than when they were absent. Thus in solutions of the above concentration, one such molecule of water in the complex lowered the percentage ionization of the base by about 30%, two molecules by about 60%. The assumption was then made that every molecule of water in the complexation was replaced by an hydroxyl group as soon as the free base was formed. In other words, for every molecule of water in the complex, one hydroxyl ion was eliminated from the outer sphere. Percentage ionizations were calculated on this basis and were very large, but in no case did they exceed 100%.

Werner² long before had assumed the existence of such hydroxo or "anhydro" bases as he called them. Job³ from observations of the change in conductivity of solutions of aquo-pentammine cobaltic sulfate upon the addition to it of solutions of baryta showed that in this case the first hydroxyl group liberated by the precipitation of barium sulfate became complexly bound, apparently replacing the single water molecule in the complex. The two additional hydroxyl groups liberated remained in an ionized condition. Job made similar observations with diaquo-tetrammine cobaltic sulfate, but in this case, while evidently considering that the two water molecules in the complex were also replaced by the first two hydroxyl

¹ Lamb and Yngve, *THIS JOURNAL*, **43**, 2352 (1921).

² Werner, "Neuere Anschauungen," Braunschweig, 1913, pp. 264-268.

³ Job, "Recherches sur Quelques Cobaltamines," Paris and Lyon (1921); *Compt. rend.*, **174**, 615 (1922).

ions liberated, Job concluded that the resultant ion $[\text{Co}(\text{NH}_3)_4(\text{OH})_2]^+$ was unstable and underwent polymerization of some kind.⁴

In this situation it appeared to us desirable to ascertain more definitely whether such a replacement of complexly bound water molecules by hydroxyl ions does in general take place and, if so, to what extent. To this end we have prepared solutions of some five cobaltamine bases by the action of silver oxide on cobaltamine bromides, containing either 0, 1 or 2 molecules of water in the complex cation, and have titrated them with a relatively concentrated solution of hydrochloric acid by means of conductivity measurements. From the changes in conductivity thus observed it has been possible to infer, as did Job in an analogous case, whether the hydroxyl groups originally present are ionized or un-ionized. Moreover, it has also been possible, from the numerical values of the conductivity at the breaks in the titration curves corresponding to the exact neutralization of one or more hydroxyl groups, to check the correctness of the above inferences, since the conductivities of the corresponding substances are either known or can be computed with reasonable accuracy.

Experimental

Preparation of Materials.—The hexamine and the carbonato tetrammine cobaltic bromides were the same materials as had previously been used by Lamb and Yngve.¹ The aquo-pentamine and diaquo-tetrammine cobaltic bromides were prepared by the methods of Jörgensen;⁵ the aquo-pentamine chromic bromide by the method of Christensen.⁶ The specific conductivity of the water used varied between 0.8 and 1.5×10^{-6} mhos. The solutions prepared from these were all 0.004 molar.

Apparatus.—The conductivity cell consisted of dip-electrodes of platinized platinum held at a fixed position in a closed 200-cc. Pyrex glass test-tube which was almost wholly submerged in an ice-bath (or in a water thermostat maintained at $25.00 \pm 0.02^\circ$). A thermometer legible to 0.01° was placed in the solution itself. The Wheatstone bridge was of the usual spirally-wound type. The uncertainty of the minimum was always less than would correspond to an error of $\pm 0.1\%$ in the conductivity. The cell was standardized against a 0.02 *M* solution of potassium chloride, the specific conductivity of this solution being taken as 0.002768 mhos at 25.00° . The standardization was repeated frequently in the course of the measurements and no variations greater than $\pm 0.1\%$ were observed.

Procedure.—It was necessary not only to guard the solutions of the free bases from contact with the air but also both to prepare and to measure them expeditiously since they undergo a slow decomposition even at 0° , particularly in contact with platinum electrodes. A procedure was therefore adopted to meet these requirements as follows.

A pestle and a small mortar containing a slight excess of moist silver oxide were cooled to 0° . A weighed quantity of ammine bromide sufficient to give a 0.004 *M* solution was then added to the silver oxide and triturated for one minute, and the solution rapidly filtered by suction into a 100-cc. delivery volumetric flask packed in ice. The

⁴ Ref. 2, pp. 49–54.

⁵ Jörgensen, *Z. anorg. Chem.*, **2**, 294 (1892); *J. prakt. Chem.*, [2] **31**, 62 (1885).

⁶ Christensen, *ibid.*, [2] **23**, 27 (1881).

mortar was then washed out several times, and the residue on the filter ten times, with ice-cold conductivity water. The solution was brought up to the mark with more of this water, thoroughly mixed, and poured into the dry cell immersed in an ice-bath. The solution was then rapidly stirred by a guarded movement of the dip-electrodes, since a too violent up and down movement was found to introduce a noticeable amount of carbon dioxide. All of these operations were conducted with the greatest possible dispatch. They usually required between six and ten minutes, counting as zero time the moment when the ammine bromide was added to the silver oxide. The temperature of the solution at this point was usually about $+1^{\circ}$ and several minutes longer was usually required for the temperature to reach substantially 0° when conductivity measurements were begun and continued at frequent intervals. Ice-cold 0.02 *M* hydrochloric acid was then added in 5-cc. portions (corresponding to one quarter of a molecule of acid per molecule of ammine); a minute was allowed for readjustment of the temperature, when stirring was resumed and conductivity measurements were again made.

The Water Correction.—Since the conductivity of ordinary carefully distilled water is chiefly due to the carbon dioxide present, and since this will neutralize two equivalents of hydroxyl ion in alkaline solution, thus replacing a rapid ion by a slow one ($\text{CO}_3^{=}$), the conductivity of a dilute solution of a base in such water will appear slightly too low. The correction for an isolated solution at 0° is equal to $8.3 \times 10^6 \times L_{\text{H}_2\text{O}}^2$, where $L_{\text{H}_2\text{O}}$ is the conductivity of the water; or taking⁷ $L_{\text{H}_2\text{O}} = 1 \times 10^{-6}$ mhos, the correction is -8.3×10^{-6} mhos. This has been applied to the specific conductivities up to but not beyond the point of neutralization (minimum conductivity).

Results.—The results of a single representative experiment, namely, that with aquo-pentammine cobaltic hydroxide, are given in full in tabular form (Table I) to illustrate the procedure. The experimental results as a whole are shown in graphical form in Fig. 1.

TABLE I
TITRATION OF AQUO-PENTAMMINE COBALTIC HYDROXIDE (0.004 *M*) WITH HYDROCHLORIC ACID (0.02 *M*)

Time, minutes	HCl added, equiv.	Temp., 0.0°		Molecular conductivity, 1/ohm
		Specific conductivity, 1/ohm		
		Observed	Corrected	
15	..	1034.2	1042.5	260.5
16	..	1032.5	1040.5	260.1
19	..	1025.0	1033.0	258.2
26	..	1016.6	1024.6	256.1
27	0.25
28	..	903.9	911.9	239.4
29	..	902.5	910.5	239.0
30	0.50
31	..	794.9	802.9	220.8
33	0.75
34	..	691.8	699.8	201.2
36	1.00
37	..	599.3	607.3	182.2

⁷ Ref. 1, p. 2354.

TABLE I (Concluded)

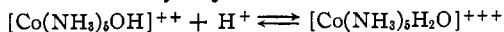
Time, minutes	HCl added, equiv.	Specific conductivity, 1/ohm		Molecular conductivity, 1/ohm
		Observed	Corrected	
39	1.25
40	..	514.6	522.6	163.3
41	..	512.5	520.5	162.6
42	1.50
43	..	437.5	445.5	144.8
45	1.75
46	..	380.7	388.7	131.2
47.5	1.80
48	..	378.4	386.4	131.4
48.5	1.85
49	..	379.8	387.8	132.8
49.5	1.90
50	..	389.1	389.1	134.2
50.5	1.95
51	..	399.2	399.2	138.7
51.5	2.00
52	..	407.9	407.9	142.8
55	2.25
56	..	452.1	452.1	163.9
58	2.50
59	..	487.1	487.1	182.6
65	2.75
66	..	526.0	526.0	203.8
72	3.00
89	..	574.3	574.3	229.7
90	3.25
93	..	705.7	705.7	291.1
102	3.50
103	..	840.8	840.8	357.3
105	3.75
106	..	961.0	961.0	420.4
108	4.00
109	..	1073.0	1073.0	482.8

As can be seen from the table, the initial conductivities show a slow progressive decrease even after the temperature has become constant. The decrease was more rapid when the solution was not stirred. This indicates a slow decomposition accelerated in the presence of the platinized electrodes. This is in agreement with earlier observations.⁸

The adjustment of the neutralization equilibrium was instantaneous so far as our measurements could disclose, although after the addition of the first portions of acid there was a slight progressive decrease which was evidently caused by the incomplete removal of the heat of neutralization. This instantaneous adjustment of the neutralization equilibrium is what

⁸ Ref. 1, p. 2354. Also Lamb and Larson, *THIS JOURNAL*, **42**, 2025 (1920); and others.

would be expected when free hydroxyl and hydrogen ions interact. It is of great interest that the adjustment should also be instantaneous when all the free hydroxyl ions have been removed and only the complexly bound hydroxyl groups are involved. This indicates either that the equilibrium between hydroxyl ion and water on the one hand and aquo ion and hydroxyl ion on the other is instantaneously adjusted, or that the equilibrium involving the direct combination of hydroxyl ion with hydrogen ion, as postulated by Werner,² is instantaneously adjusted.



An examination of Fig. 1 leads to the following deductions relative to the constitution of the several hydroxides.

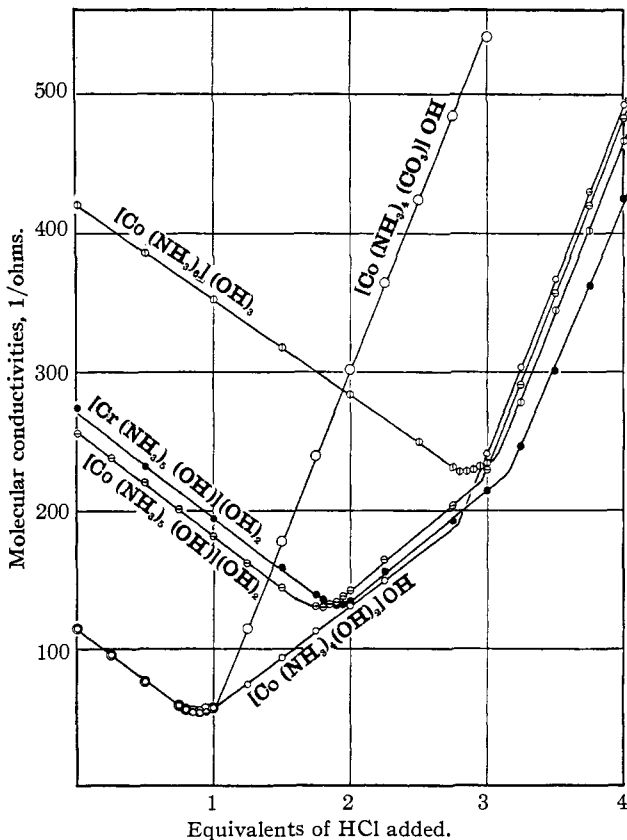


Fig. 1.—Titration of ammine bases by measurements of conductivity.

(a) Hexammine hydroxide, containing no complexly bound water, gives a curve with a uniform downward slope which reaches a minimum

at the point corresponding to an addition of three molecules of hydrochloric acid, and rises sharply thereafter. This is a normal curve such as would be expected for a highly ionized trivalent base.

(b) Pentammine hydroxide gives a curve which starts at a much lower point, indicating a much smaller concentration of hydroxyl ions. It slopes downward nearly parallel to the hexammine curve, but reaches a minimum after the addition of two molecules of acid.

Thereafter the curve rises moderately until another molecule of acid has been added, when it rises more steeply almost in superposition with the hexammine curve.

The part of the curve sloping downward evidently corresponds to the normal behavior shown by the hexammine curve; it records the replacement of fast hydroxyl ions by relatively slow chloride ions with a consequent decrease in conductivity. The next part of the curve, sloping moderately upward, is what would be expected if one un-ionized hydroxyl and one equivalent of added hydrogen ion were eliminated as water with the consequent introduction of a chloride ion into the solution and the conversion of the divalent into the trivalent ammine cation. The remainder of the curve, after the addition of the three molecules of acid, merely records the effect of adding relatively concentrated acid.

This curve, therefore, indicates that in pentammine cobaltic hydroxide one of the hydroxyl groups is complexly held, or but slightly ionized, while the other two are highly ionized at these concentrations.

(c) Tetrammine hydroxide gives a curve which shows the same phenomena as did the pentammine, but to a more pronounced degree. Here there is evidently a single, highly ionized hydroxyl group and two hydroxyl groups that are at most slightly ionized.

(d) Pentammine chromic hydroxide gives a curve corresponding very closely with that of the analogous pentammine cobaltic hydroxide.

(e) Carbonato-tetrammine hydroxide gives a curve that coincides almost exactly with the curve of the dihydroxo-tetrammine hydroxide down to the minimum of conductivity. This shows that it, too, has a single, highly ionized hydroxyl group, and that the two univalent cations have almost exactly the same mobilities. After the minimum, the carbonato curve diverges rapidly upward from the tetrammine curve, running nearly parallel to the curve for the addition of excess acid. It is evident that after the neutralization of the hydroxyl ion only a small fraction of the hydrogen ions combines with the carbonato radical during the time occupied by this measurement; otherwise, the rise in the conductivity would be much less rapid.

It is clear from these curves that in every instance where the base has been derived from an ammine having one or two water molecules in the complex, a corresponding number of hydroxyl groups are complexly

held⁹ or, in other words, the water molecules have been fully displaced by hydroxyl groups which are held firmly in the complex.

The correctness of this conclusion can be checked by a comparison of the conductivities indicated by the titration curves at the various minima and points of inflection with the directly measured conductivities of the substances there present. The data for such a comparison have been collected in Table II.

TABLE II
MOLAR CONDUCTIVITIES AT POINTS OF INFLECTION

Ammine hydroxide	Acid, moles added per mole	Chloride present	Concn. $\times 10^3$ molar	Directly measured	Conductivity molar l/ohms		Ref.
					Directly measured	From curves	
Hexa	3	Hexammine	2.5	Chloride	231	229	10
Penta	3	Pentammine	2.5	Nitrate	224	227	11
Tetra	3	Tetrammine	2.5	Bromide	221	220	12
Penta	2	Hydroxo-pentammine	2.857	Nitrate	135	132	11
Tetra	1	Dihydroxo-tetrammine	3.39	Dinitro chloride	56	54	10
Tetracar-bonato	1	Carbonato-tetrammine	3.39	Chloride	57	55	13

The agreement between the conductivities as read from the curves and those computed from independent measurements is good and confirms the conclusion that the water molecules in the complex have been completely replaced by firmly held hydroxo groups.¹⁴

Apparent Percentage Ionization.—With the hydroxo structure of these hydroxides thus clearly established, it is of interest to consider more fully the significance of the values of the apparent ionizations as calculated

⁹ It can be seen from the curves that the various minima are invariably displaced slightly to the left of the exact integral numbers of added molecules of acid. This is probably due to the above-mentioned slight decomposition of the free base into lower cobaltic or cobaltous amines and free ammonia. The neutralization of the ammonia in the presence of the residual stronger bases would cause an increase rather than a decrease in conductivity and a consequent premature rise in the curve.

¹⁰ Harkins, Hall and Roberts, *THIS JOURNAL*, **38**, 2656 (1916).

¹¹ King, *J. Chem. Soc.*, **127**, 2107 (1928).

¹² Werner and Miolati, *Z. physik. Chem.*, **12**, 42 (1893).

¹³ From measurements to be published later in another connection.

¹⁴ The firmness with which these hydroxyl groups are held can indeed be calculated in the case of the pentammine and the tetrammine bases from the very skilful and ingenious measurements of Brönsted and Volqvartz [*Z. physik. Chem.*, **134**, 133 (1928)] of the "acid dissociation" of aquo ions. Their constants for this dissociation divided into the dissociation constant of water should give the dissociation constants of the hydroxo bases:

$$K_{B_1} = \frac{C_{OH^-} \times C_{[Co(NH_3)_5H_2O]^{+++}}}{C_{[Co(NH_3)_5OH]^{++}} \times C_{H_2O}} \quad \text{and} \quad K_{B_2} = \frac{C_{OH^-} \times C_{[Co(NH_3)_4(H_2O)_2]^{+++}}}{C_{[Co(NH_3)_4(H_2O)OH]^{++}} \times C_{H_2O}}$$

These are respectively 1×10^{-10} and 3×10^{-11} for the pentammine and tetrammine ions.

on the basis of this structure by Lamb and Yngve from their measurements. For this purpose we have recomputed the values of Lamb and Yngve, using more recent data for the mobilities of certain of the ions than were available at that time. The results are collected in Table III.

TABLE III
APPARENT IONIZATIONS OF THE COBALTAMMINE BASES
Temperature, 0°. Concn. = 0.001336 *M*

Ammine hydroxides	μ_{cations}^0 (1/ohm)	μ^0 1/ohm	μ (observed) 1/ohm	α , %
[Co(NH ₃) ₆](OH) ₃	167	521	431.1	83
[Co(en) ₃](OH) ₃	115	469	375.4	80
[Co(NH ₃) ₅ OH](OH) ₂	78	314	261.8	83
[Cr(NH ₃) ₅ OH](OH) ₂	78	314	275.6	[88]
[Co(NH ₃) ₄ (OH) ₂](OH)	18	136	115.0	84
[Co(en) ₂ (OH) ₂](OH)	18	136	117	86
[Co(NH ₃) ₄ CO ₃](OH)	19	137	119	87
1,2[Co(NH ₃) ₄ (NO ₂) ₂](OH)	18.1	136.1	100	74
1,6[Co(NH ₃) ₄ (NO ₂) ₂](OH)	17.9	135.9	117	86
[Co(NH ₃) ₅ (H ₂ O)(NO ₂) ₂](OH)				
\rightleftharpoons [Co(NH ₃) ₅ (NO ₂) ₂ (OH)]	18	136	50	37

The mobilities of the various ammine ions have been computed as follows: that of the hexammine from its chloride and nitrate;¹⁵ that of the triethylenediamine from the data of Werner and Herty¹⁶ on the chloride at 25°, converting to international ohms and using the factor 1.8 derived from their other measurements to convert to 0°; that of the hydroxo-pentammine from the data of King¹¹ on the hydroxo nitrate by first computing *n* (= 1.5) in the Storch-Bancroft equation and then plotting $(C\mu)^{n-1}$ against $1/\mu$; the carbonato-tetrammine from the data of Werner and Miolati¹⁷ on the nitrate at 25° by extrapolation, taking *n* = 1.33 and then converting to ohms and to 0° by the above-mentioned factor; that of the dinitro-tetrammines from the chlorides and nitrates;¹⁸ that of the chromic hydroxo-pentammine on the well-supported assumption that it would be the same as that of the corresponding cobalt ammine; that of the dihydroxo-tetrammine and the dinitro-aquo-tetrammine on the assumption that they would be the same as that of the dinitro-tetrammines.

The apparent percentage ionization of all of these bases, except the last one shown in this table, is strikingly high. Thus the ionization of the univalent bases is only a little less than that of the alkali bases, while that of the trivalent bases is about the same as that of a *salt* of the same type, lanthanum chloride, at the same concentration. This high apparent

¹⁵ Ref. 1, p. 2360.

¹⁶ Werner and Herty, *Z. physik. Chem.*, **38**, 337 (1901).

¹⁷ Werner and Miolati, *ibid.*, **21**, 234 (1896).

¹⁸ Ref. 1, p. 2362.

ionization doubtless indicates, on the basis of present views as to electrolytic solutions, a substantially complete true ionization.

A still more striking feature of these values is their marked similarity irrespective of the nature of the central atom, or of the number or nature of the groups surrounding this atom; and perhaps most surprising of all, irrespective of the number of electric charges on the cation.

Plausible explanations can be advanced for most of the above observations.

(1) The slight ionization of the hydroxyl groups inside the complex and the high apparent and the presumably complete actual ionization of the hydroxyl groups outside the complex may be explained as follows. Water molecules in these quite stable complex substances, though held with considerable firmness to the central atom by coördinate links, are much more readily displaced from the complex by various acido groups than are ammonia, diethyleneamine and various other molecules. It is not surprising, therefore, that they can be quite completely displaced by hydroxyl ions. These become attached by strong non-polar links and are but slightly ionized. When, however, all six coördinate positions are occupied by firmly held ammonia molecules or the like, or by firmly held acido groups, the hydroxyl ion cannot penetrate this protective shell, cannot form a non-polar link and, being held at some distance from the central atom, is almost completely ionized.

(2) The similarity in the ionization of the bases may be due to the similarity of the general exterior architecture of the cations of these bases, since they all have six exterior groups held by non-polar valences (six electron pairs) around small central atoms whose outer electron shells are presumably also quite similar.¹⁹

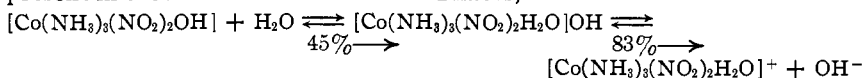
(3) The absence of any marked effect on the ionization of the differences in the number of electric charges on the cation might be due to the "chemical effect" of the acido groups as compared with that of the ammonia molecule. This effect, on the basis of ordinary experience in organic chemistry, would tend to decrease the ionization of the base when the accompanying valence change tended to increase it. However, the lack, as above mentioned, of any apparent difference between the effect of dinitro, dihydroxo and carbonato groups on the ionization when there are no changes in valence argues against this explanation. Another possibility is that the shell of coördinated groups so alters the electrostatic field about the central atom that the simple valence-squared function of the Debye-Hückel equation no longer obtains.

¹⁹ P. Ray, Nineteenth Indian Science Congress, Bangalore, 1932, Section of Chemistry, President's Address, p. 33. It should also be noticed that the most marked contrast among the percentage ionizations shown in our Table III is between the two stereoisomeric dinitro-tetrammines.

One further and significant conclusion may be drawn from Table III. The last hydroxide there listed exhibits a conductivity corresponding to a 37% ionization. Yet according to the above generalization that hydroxyl ions replace water molecules in the complex ion completely, the aquo-dinitro-triammine hydroxide should be converted completely into hydroxo-dinitro-triammine, and since this does not ionize, its solution should exhibit zero conductivity. It is clear that in this case hydroxyl ions do not replace water molecules in the complex at all completely.

Certain hydroxo salts also afford exceptions, although less marked ones, to this generalization, for it has been long known that their solutions exhibit marked alkalinity; hydroxo-aquo-tetrammine cobaltic chloride,²⁰ for instance, is a case in point.

Expressed in terms of the above explanation, either the water molecule in aquo-dinitro-triammine hydroxide is more firmly held, or is replaced with greater difficulty by negatively charged hydroxyl ions, than are the water molecules in the other complex ions that we have studied, so that only a partial replacement occurs. Assuming that the aquo base once formed would show about the same apparent ionization as the other bases (83%), it would follow that about $(0.37/0.83) \times 100$ or 45% of the compound is present in the solution in that form. That is,²¹

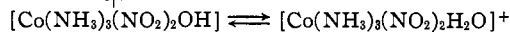
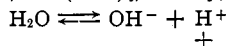


Irrespective of any mechanism one can, however, say that this base is a much stronger one than other exclusively hydroxo bases, its dissociation constant being of the order of 10^{-5} as contrasted with 10^{-10} for the hydroxopentammine ion.

This restriction of our generalization, however, clarifies rather than darkens the interpretation of these phenomena. It is evident that the hydroxyl ion reacts with these aquo cations quite as do other anions. It is known that many anions will replace water molecules in such complex ions reversibly. Some anions do so extensively, others but slightly; some rapidly, others slowly.²² The hydroxyl ion is thus not unique in its behavior. It is perhaps outstanding as compared with other anions in that it displaces the complexly held water molecules in the aquo ions *both* extensively and *very* rapidly.

²⁰ Werner, *Ber.*, **40**, 4133 (1907).

²¹ The mechanism of this equilibrium could be either the direct aqutation here shown or the mechanism postulated by Werner [*Ber.*, **40**, 4133 (1907)] and Brönsted [*Rec. trav. chim.*, **42**, 718 (1923)], namely,



²² Lamb and Marden, *THIS JOURNAL*, **33**, 1873 (1911); Pers, *Compt. rend.*, **153**, 673 (1911); Lamb and Fairhall, *THIS JOURNAL*, **45**, 378 (1923).

Summary

1. It has been shown by conductimetric titration of several nominally trivalent ammine bases prepared from aquo ammine bromides that the complexly held water molecules have in these instances been completely displaced by an equivalent number of the hydroxyl ions. The adjustment of these displacement equilibria is rapid and the hydroxo groups formed are firmly held.

2. The apparent ionizations of the hydroxyl groups remaining outside of the complex are high and are nearly identical in each of these cases, irrespective of the nature of the central atom, the coordinated groups and the valence of the cation.

3. The replacement of the complexly held water molecules is not, however, universally complete. Stated otherwise, the hydroxo group may in certain cases be largely replaced by a water molecule and thereafter ionized.

4. This interaction between these aquo ions and hydroxyl ions is comparable to that between aquo ions and anions in general, although the replacement of water molecules by the hydroxyl group is relatively extensive and the attainment of equilibrium is unusually rapid.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY,
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THERMODYNAMIC PROPERTIES OF FUSED SALT SOLUTIONS. V. LEAD BROMIDE IN SILVER BROMIDE

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The investigation described in this paper represents a continuation of a series of studies on the thermodynamics of fused salt solutions begun by Hildebrand and Ruhle.¹ The system lead bromide in silver bromide was chosen because the melting points of their solutions permitted a study extending over the entire range of their composition. Thus it was believed that the activities of both the solvent and solute could be determined.

Experimental Part

The lead bromide was prepared by precipitation from a solution of lead acetate with excess hydrobromic acid. The precipitate was repeatedly washed by decantation with a 3% solution of hydrobromic acid and finally dried at 150° for several days. Silver bromide was similarly prepared by precipitation from a silver nitrate solution. The bromine and hydrogen bromide were prepared as previously described in the lithium bromide-silver bromide study.²

¹ Hildebrand and Ruhle, *THIS JOURNAL*, **49**, 722 (1927).

² Salstrom and Hildebrand, *ibid.*, **52**, 4650 (1930).