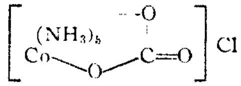
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Carbonato and Bicarbonato Pentammine Cobalti Ions[1]

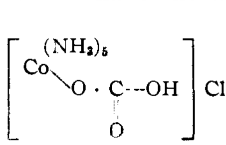
BY ARTHUR B. LAMB AND KAROL J. MYSELS[2]

Werner[3] forty years ago called attention to an apparent anomaly, from the point of view of his theories of molecular structure, presented by certain substances such, for instance, as the carbonato tetra- and pentammine cobalti chlorides, $[Co(NH_3)_4CO_3]Cl$ and $[Co(NH_3)_5CO_3]Cl$. In these substances, to retain cobalt's otherwise invariable coördination number of six, it was necessary to assume that the carbonato radical with its two valences occupies two coördination places in the former and only one in the latter.

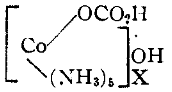
Werner explained this at first sight disturbing variability by asserting that when a radical is attached directly by one or more valences to the central atom of a complex, each valence emanates from a single atom and occupies a single coördination place. If there are two vacant coördination places available on the cobalt atom, a carbonato radical will attach itself directly to the cobalt atom by both its valences. If there is but a single space available, as in the pentammine, it will attach itself by only a single valence and thus occupy but one coördination place, the spare valence being attached to one of the ammonia groups and neutralizing one of the positive charges on the cobalt atom. Werner's formula for the carbonato pentammine cobalti chloride was therefore



This ammine reacts at once in solution with an added molecule of acid, for instance hydrochloric acid, to give bicarbonato pentammine cobalti chloride which would have the wholly orthodox formula

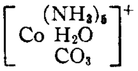


Later, Werner[4] became dissatisfied with this formulation. He had noted that all the carbonato pentammine salts then known contained a molecule of water which was not given off on drying at a higher temperature and which must, he reasoned, have some constitutional significance. Moreover, he had observed that these salts reacted strongly alkaline in aqueous solution. He therefore concluded that the carbonato pentammine ion was an intramolecular salt in which the carbonato radical was actually a bicarbonato radical attached to a basic hydroxyl group outside the pentammine complex, according to the following structural formula



Werner further pointed out that this structure corresponded to the betaine formulas then commonly written for glycine and other amino acids, and he therefore proposed that such intramolecular salts be called "betoxine salts."

Still later Matsuno,[5] also convinced of the presence of a molecule of water within the complexes of these and the analogous oxalato pentammine ions, proposed a coördination number of *eight* for the cobalt atom, the formula of the carbonato pentammine ion then becoming

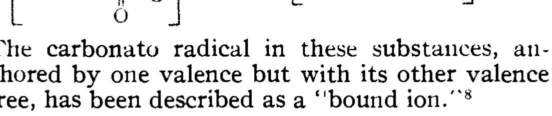


$$\left[\begin{array}{c}(NH_3)_5\\ Co\ H_2O\\ CO_3\end{array}\right]^+$$

Since the constituent groups in this complex ion could be assumed to occupy the corners of a cube rather than of a regular octahedron, Matsuno reasoned that it should be possible to resolve these substances into optically active isomers, and this he succeeded in doing to his satisfaction.

Duval,[6] however, was unable to accomplish any such resolution and, moreover, pointed out a serious discrepancy in Matsuno's analytical calculations. He also pointed out that there were a number of similar anomalous pentammines which did not, at least in the solid state, contain the molecule of water to which both Werner and Matsuno attached so much significance. Clearly there remains little, if any, convincing evidence supporting this cubic formula.

Werner's original formula has therefore been generally retained, but in later years it has been somewhat modified. Werner himself recognized that radicals not attached directly to the central atom are subject to electrolytic dissociation and the formula has been written[7] so as to make this evident, as follows



The carbonato radical in these substances, anchored by one valence but with its other valence free, has been described as a "bound ion."[8]

---

(1) Based on the Ph.D. thesis of K. J. Mysels, Harvard University, 1941.

(2) Present address: Leland Stanford University, California.

(3) Werner and Gosling, *Ber.*, **36**, 2378 (1903).

(4) Werner, *ibid.*, **40**, 4101 (1907).

(5) K. Matsuno, *J. Coll. of Sci. Univ. Tokyo*, **45**, Art. 8 (1925).

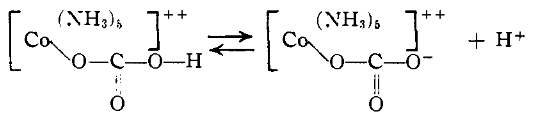
(6) C. Duval, *Compt. rend.*, **200**, 399-401 (1935).

(7) P. Job, "Traite de Chimie Mineral," Vol. X, Paris, 1933, p. 667, and G. T. Morgan and F. H. Burstal, "Inorganic Chemistry," Chemical Publishing Co., New York, N. Y., 1937, p. 224.

(8) Duff, *J. Chem. Soc.*, **123**, 560 (1923).

Interpreted in the light of current theories of valency it is evident that in this formula the carbonato group is attached to the cobalt atom through one oxygen atom by a covalent bond, the second oxygen atom, negatively charged, being attached to the positively charged complex ion by an electrovalent bond. When the ammine is dissolved in a medium of high dielectric constant, the negatively charged oxygen atom moves away from the complex probably as far as the covalent attachment of the other end of the carbonato radical permits.

No one appears to have pointed out that the carbonato pentammine ion when thus formulated is closely analogous to the dipolar ions, or zwitterions, which are now recognized to exist in relatively large amounts in solutions of the aliphatic amino acids. Thus the bicarbonato and carbonato pentammine ions in neutral and in acid solution, respectively, can be compared, for instance, with glycine, as follows

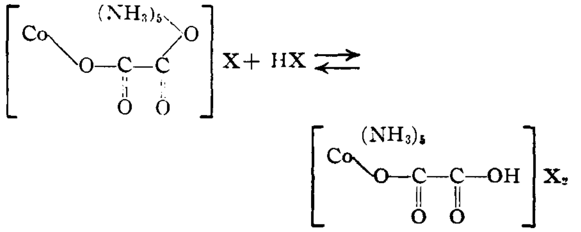


$$\left[\mathrm{Co}\overset{(\mathrm{NH_3})_5}{\diagdown}\mathrm{O{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}O{-}H}\right]^{++} \rightleftarrows \left[\mathrm{Co}\overset{(\mathrm{NH_3})_5}{\diagdown}\mathrm{O{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}O^-}\right]^{++} + \mathrm{H^+}$$

$$\mathrm{{}^+NH_3CH_2COOH} \rightleftarrows \mathrm{{}^+NH_3CH_2COO^-} + \mathrm{H^+}$$

It must be emphasized, however, that the carbonato pentammine ion differs from the dipolar glycine ion in one important respect; it carries a net charge, namely, an over-all excess of one positive charge. It should then be called a dipolar cation to distinguish it from an over-all neutral dipolar ion—which in turn might with advantage be called a dipolar *isoion*.[9]

Many other ammines exhibit apparently anomalous formulas similar to that of carbonato pentammine, *e. g.*, oxalato, sulfato, and sulfito pentammines, phosphato tetrammines, etc., and several of them have the same ability to add one molecule of acid as was shown above for the formulas of the bicarbonato pentammine ion. Werner did not extend the betoxine formula to these other anomalous salts but retained, as late as 1914,[10] his original interpretation, expressing the formation, for instance, of a "bi-oxalato" pentammine from an oxalato pentammine by the addition of acid, as follows



$$\left[\mathrm{Co}\overset{(\mathrm{NH_3})_5\diagdown}{\diagdown}\mathrm{O{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}\underset{\underset{\displaystyle O}{\|}}{C}\!\diagup\!\!>\!O}\right]\mathrm{X} + \mathrm{HX} \rightleftarrows \left[\mathrm{Co}\overset{(\mathrm{NH_3})_5}{\diagdown}\mathrm{O{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}OH}\right]\mathrm{X_2}$$

"Acid salt" formulas have sometimes[11] been written for these salts; for instance $[(NH_3)_5CoO_2CCO_2]X \cdot HX$, but there is little reason to expect these various salts to have structures different from that of the carbonato pentammines, and Morgan,[7] for instance, has classed them together. Any light thrown on the constitution of carbonato and bicarbonato pentammines should therefore clarify the structure of this whole class.

In the hope of deciding more definitely as to the structure of these apparently anomalous substances, we have attempted, first, to find out whether the molecule of water to which so much importance has been attached by prior investigations is indeed an essential constituent of the carbonato pentammine complex; and, second, to measure the acid dissociation constant of the bicarbonato pentammine ion and the dielectric increment of the carbonato pentammine ion.

The Water Content of Carbonato Pentammine Cobalti Nitrate

Preparation of Carbonato Pentammine Cobalti Nitrate.—Of the several known salts of this series, the nitrate is the least soluble and is therefore the easiest to prepare. However, its purification by recrystallization is impractical because of the accompanying decomposition. It must therefore be obtained as pure as possible from the start. For this reason, after repeated

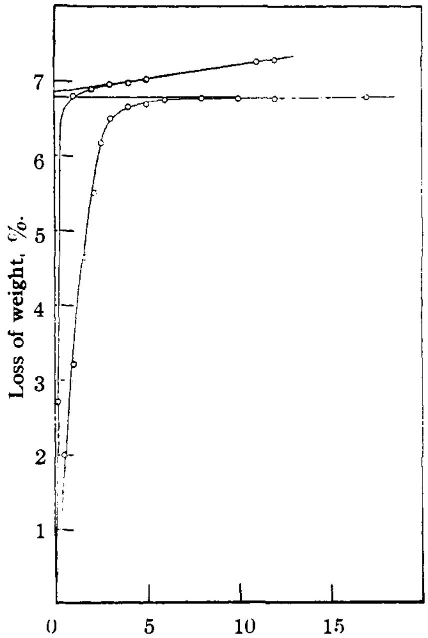


Fig. 1.—Loss of weight of carbonato pentammine cobalti nitrate in dry vacuum, upper curve at 60°, lower curve at 41°.

---

[9] It is certainly indicative of Werner's great insight that, as pointed out above, he recognized some similarity between these anomalous pentammines and the amino acids, although, as will appear from what follows below, the primary evidence on which he based his conclusions and the new formula to which he was led were almost certainly mistaken.

(10) Werner, *Ann.*, **406**, 213 (1914).

(11) Gmelin's "Handbuch," Syst. No. **58**, Part **B**, Berlin, 1930, pp. 190-201; Job, ref. 5, pp. 815-826.

trials, we adopted a modification of the Briggs[12] procedure as follows:

An aqueous solution containing 150 g. of cobalt nitrate hexahydrate in 175 cc. was poured into a mixture of 300 g. of pulverized, commercial ammonium carbonate in 750 cc. of concentrated (28%) aqueous ammonia, and air was bubbled through this solution at room temperature for forty-eight hours. The flask with its large crop of red crystals was then heated on a steam-bath to about 70°, until the crystals dissolved in the mother liquor. After filtration from the scanty, dark residue (cobalt oxide), the solution was allowed to crystallize at 0°. with frequent shaking to avoid supersaturation. The crystals were then washed ten times by suction with ice-cold water and twice each with 50% and 95% alcohol and finally with absolute alcohol. The thorough washing necessary to remove the large amount of soluble impurity initially present did not seriously impair the yield, since the carbonato pentammine nitrate is soluble in water at 0° only to the extent of 1.5%. The crystals were then air-dried overnight. The yield was 65 g.

This product was analyzed as follows: for cobalt by heating with sulfuric acid[13]; for ammonia by decomposition with stannous chloride and hydrochloric acid at the boiling point and distillation with a current of purified air followed by titration; for carbon dioxide, gravimetrically, after aquation of the ammine.

The resulting data are collected in the table:

$(Co(NH_3)_5CO_3)NO_3,\ H_2O$

	Percentage composition		
	Calculated		
Component	Pure	+0.3% H_2O	Found
Co	20.74	20.68	20.67
CO_2	15.49	15.44	15.43
NH_3	29.98	29.89	29.90
H_2O	6.34	6.64	6.80

Dehydration.—To avoid decomposition of the ammine the dehydration was carried out at low pressure and at the lowest feasible temperature, namely, at the boiling point of methylene chloride (41°) or of chloroform (60°) for long periods in an Abderhalden drying apparatus charged with phosphorus pentoxide and evacuated by means of a Hy-Vac oil pump. The curves in Fig. 1, showing the percentage weight loss at the two temperatures as a function of the time, demonstrate that although at 60° the dehydration is accompanied by some decomposition, at 41° dehydration is complete after nine days, yet no decomposition takes place in eight days of further heating.

The dehydrated crystals when exposed to the atmosphere of the room gained weight over a period of several days, indicating a slow re-hydration.

Werner and Gosling[3] noted that carbonato pentammine nitrate crystallizes from the original ammoniacal solution as unsymmetrical needles and from water as small rectangular plates with a mother-of-pearl luster. We can confirm this and can add that these "half moon" needles and the rectangular plates dehydrate similarly and give dehydrated crystals that retain the form, luster, transparency, and color of the original hydrated crystals.

Following the methods of Larsen and Berman[14] we have measured the refractive indices, by the immersion method, of the needles and the plates, each both hydrated and dehydrated. The needles and plates both belong to the orthorhombic system and present the same pleochroism and the same indices of refraction, namely, for the hydrates α (pink) = 1.555; β (yellow) = 1.673; γ (purple), for the needle form, = 1.72.

Thus the two forms are different habits of the same structure. On dehydration the structure and pleochroism remain the same; but, as would be expected, the refractive indices are slightly yet definitely lowered, α by 0.30; β by 0.013.

These dehydration and crystallographic measurements demonstrate that the findings of Werner[4] and later of Briggs[12] and Kraanig[15] that this water cannot be expelled without destruction of the ammine, are incorrect and were presumably due to the use of too high a temperature or pressure during drying. It follows from this that the contained water cannot have the constitutional significance ascribed to it by Werner and thus a main support of his "betoxine" formula is lost.

The Acid Dissociation Constant of Bicarbonato Pentammine Cobalti Ion

The degree of dissociation of the bicarbonato pentammine ion will be affected by the stability and hence the structure of the carbonato ion with which it is known to be in equilibrium.[3,16] Conversely a knowledge of its dissociation constant

$$\frac{(Co(NH_3)_5CO_3^+)(H^+)}{(Co(NH_3)_5HCO_3^{++})} = K$$

might give an intimation as to the most probable structural formula of the carbonato pentammine ion.

Thus, on the basis of Werner's "betoxine" formula, a very small value of K would be anticipated. According to this formula the hydroxyl radical is outside of the complex and its dissociation as a base would then be represented as

$$[Co(NH_3)_5HCO_3]^+OH \rightleftarrows [Co(NH_3)_5HCO_3]^{++} + OH^-$$

and its dissociation constant as a base would be

$$\frac{([Co(NH_3)_5HCO_3]^{++}) \times (OH^-)}{([Co(NH_3)_5HCO_3]^+OH)} = K_B$$

Werner describes this hydroxyl group as "strongly basic" and indeed it has been shown[17] that hydroxyl groups outside of cobaltiammine complexes are highly ionized. K_B must therefore be relatively large; it might reasonably be assumed to be larger, at least, than 1×10^{-4}.

We can now calculate what, on this assumption, the value of K would be. Thus, replacing in the above equation the concentration of hydroxyl ion by $K_{H_2O}(H^+)^{-1}$, inverting it and inserting numerical values we get

---

(12) Briggs, *J. Chem. Soc.*, **115**, 75 (1919).

(13) Lamb and Damon, THIS JOURNAL, **59**, 383 (1937).

(14) Larsen and Berman, "The Microscopic Determination of the Nonopaque Minerals," U. S. Department of the Interior, Geological Survey Bulletin, No. 848, p. 11.

(15) Kraanig, *Ann. chim.*, [10] **11**, 89 (1929).

(16) Lamb and Stevens, THIS JOURNAL, **61**, 3229 (1939).

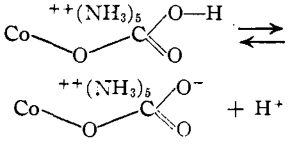
(17) Lamb and Yngve, *ibid.*, **43**, 2352 (1921).

$$\frac{([Co(NH_3)_5HCO_3]^{+}OH) \times (H^+)}{([Co(NH_3)_5HCO_3]^{++})} = \frac{K_{H_2O}}{K_B} = \frac{1 \times 10^{-14}}{>1 \times 10^{-4}} = <1 \times 10^{-10} = K$$

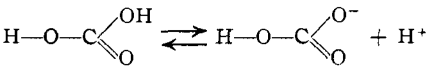
Or, in words, if the bicarbonato pentammine ion gave rise to carbonato pentammine ion having the assumed hydrated "betoxine" structure, the constant for its dissociation should be less than 1×10^{-10}.

The "acid-salt" formula $[(NH_3)_5CoCO_3]NO_3 \cdot HNO_3$, on the other hand, leads, of course, to the expectation of a dissociation constant of the same order as that of a strong acid, $K \geqq 10^1$.

On the basis of the dipolar cation formula the dissociation of the bicarbonate pentammine would be written

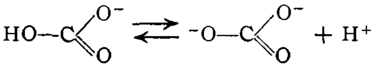


This suggests a value of K lying between the extremes of the above hypothesis. This dissociation can be compared with the first and second dissociations of carbonic acid



$K_1^{18} = 3 \times 10^{-4}$

and



$K_2 = 5.6 \times 10^{-11}$

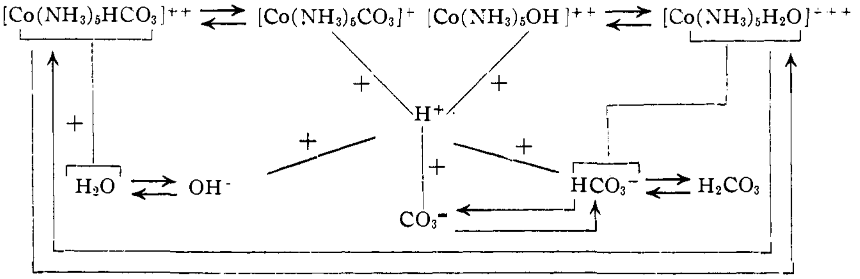
where, as can be seen, the replacement of a hydrogen atom of the carbonic acid molecule by a negative charge on one of the oxygen atoms decreases the dissociation constant by a factor of 5×10^{-6}.

The replacement of a hydrogen atom in carbonic acid by the $Co^{++}(NH_3)_5$ radical might be expected to have several effects. First, it would tend to decrease the ionization for statistical reasons. Second, the two positive charges on the cobalt atom would tend to increase the ionization, but third, the accumulation on or about the cobalt atom of the ten electrons donated by the coördinated ammonia molecules would have an opposite effect. On the whole, it would appear reasonable to expect a net decrease in the dissociation constant. In other words, a dissociation constant intermediate between that of the first and second dissociation constants of carbonic acid would be anticipated.

In view of these considerations it appeared worth while to undertake the measurement of the dissociation constant of the bicarbonato pentammine ion in order to distinguish if possible between the two formulas proposed for the carbonato pentammine ion. These measurements have now been made and values of the dissociation constant of the bicarbonato have been found which indicate the correctness of the dipolar cation formula.

Rapidity of Adjustment of the Equilibria.—The interdependent ionization and aquation equilibria which are involved in a solution containing carbonato and bicarbonato pentammine ions are shown in the following chart

CHART I



The ionization equilibria adjust themselves rapidly but the aquation and anation reactions progress relatively slowly. The question therefore arose as to whether these equilibria would adjust themselves rapidly enough to make accurate measurements with the hydrogen electrode feasible. The conductimetric measurements of Lamb and Stevens[16] had indicated that in 0.003 M solution at 0° the aquation of the bicarbonato pentammine required about twenty minutes and that of the carbonato a number of hours; at 25° only a few minutes and perhaps a half-hour, respectively, were required.

There was, however, contradictory evidence on this matter in the literature. Duff[19] had concluded from his conductivity measurements that aquation of carbonato pentammine nitrate took place *only* in contact with the platinized electrodes. Schwartz and Tede[20] found there was *no* change in the solution away from the light. To secure further evidence we have made additional conductimetric measurements of the rates of aquation.

Conductimetric Measurements.—In these measurements we used cells, bridges, oscillators, etc., as described by Jones and Bollinger.[21] All our measurements were made at a frequency of 2000 cycles per second. We found that while decomposition of these solutions does indeed take place in contact with the platinized electrodes, prolonged prior exposure of the electrodes to the ammine solutions decidedly lessens this effect, so that over the short

---

[18] One must take here the "true" first dissociation constant of carbonic acid which is greater than the apparent dissociation constant because of the large fraction of the carbonic acid present as unhydrated carbon dioxide. The most recent value of this constant is that of Roughton [THIS JOURNAL, **63**, 2933 (1941)] who found $K_1 = 2.5 \pm 0.3 \times 10^{-4}$ at 0°. Using the heats of ionization which he also determined, the true dissociation constant at 25° would be $3.0 \pm 0.3 \times 10^{-4}$.

(19) Duff, *J. Chem. Soc.*, **123**, 573 (1923).

(20) Schwartz and Tede, *Ber.*, **60**, 63 (1927).

(21) Jones and Bollinger, THIS JOURNAL, **50**, 1049 (1928).

period of our measurements, it was negligible.[22] We found no difference in velocity in experiments run in the dark and in diffuse daylight.

For measuring the rapidly changing solutions, we found it advantageous to adjust the bridge to a suitable setting and then note the instant when the telephone was silent.

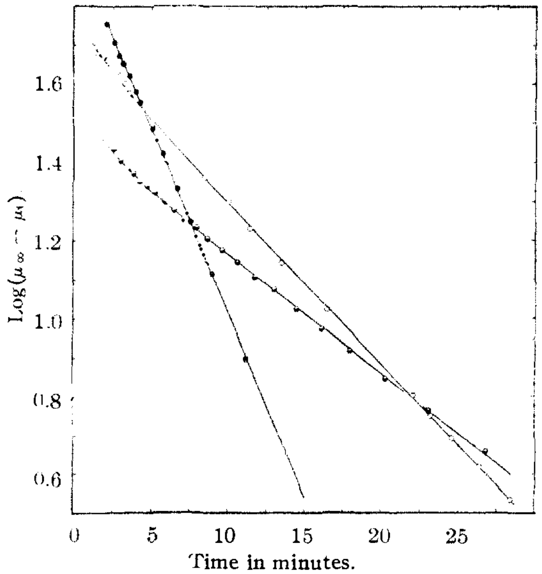


Fig. 2.—Change of the conductance of solutions of carbonato pentammine cobalti nitrate with time at 25°:

◐ 0.020 M 124.5 1/ohms
○ 0.004 M 149.6 1/ohms
● 0.001 M 184.4 1/ohms

Our experimental results for the carbonato pentammine at 25° are shown in Fig. 2, where the logarithms of the differences between the molar conductances at equilibrium and at the observed time are plotted against the time. It can be seen that, except for the first few minutes with the more concentrated solutions, the observed points, where accurately known, lie closely on straight lines whose slopes increase with the dilution. The slight initial divergences may be ascribed to the known negative heat of solution of the ammine. It therefore appears that the aquation follows a unimolecular or quasi-unimolecular course as previously found, and that the slopes represent the velocity constants. These constants thus obtained are collected in Table I.

Table I

Velocity of Aquation of Solutions of Carbonato Pentammine Cobalti Nitrate at 25°

Concentration, M	Initial mol. conductance, 1/ohms	$(k_1 + k_2)$, 1/min.
0.020	124.8	0.070
.004	149.6	.095
.001	184.4	.218

Similar results were obtained at 0° for two solutions of carbonato pentammine nitrate to which one-half and two-thirds of an equivalent of hydrochloric acid had been added. The original concentrations of the solutions were 0.01500 and 0.01284 M. They of course contained, respectively, one-half and two-thirds equivalent of bicarbonato pentammine ion whose velocity of aquation overshadowed that of the residual carbonato ions.

The results are shown graphically in Fig. 3, and here again it is clear that except during the first two minutes the observed points lie closely on straight lines whose slopes, 0.109 and 0.122, represent the velocity constants. The slight inflection at the start was doubtless due to some warming of the solutions during their preparation and introduction into the Dewar vessel filled with ice.

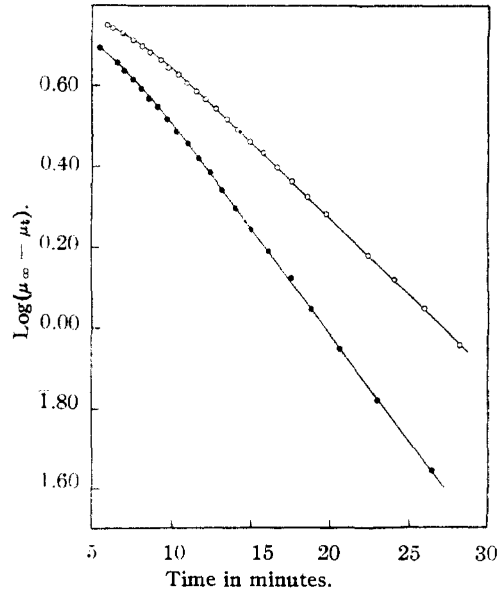


Fig. 3.—Change with time of the conductance of solutions of carbonato pentammine cobalti nitrate containing added hydrochloric acid at 0°: ○, with $^1/_2$ equivalent of HCl; ●, with $^2/_3$ equivalent of HCl.

These values for the velocity constant for 0° are shown also in Fig. 4, where corresponding values of Lamb and Stevens, as well as comparison values obtained from our potentiometric measurements to be described further below, are also included.

This further evidence leaves no doubt[23] as to the reality of the aquation and the substantial agreement of the velocity constants as determined at different times and by different methods.

It was therefore reasonable to expect that these equilibria would adjust themselves rapidly enough, at least at 25°, so that the use of a glass (hydrogen) electrode would be feasible for the measurement of equilibrium hydrogen-ion con-

---

[22] Cleaning the electrodes with hydrochloric acid not only restored the original activity but greatly increased it.

[23] It is probable that Duff[19] and Schwartz and Tede[20] took so long to prepare the solutions and to adjust their temperatures that the solutions were fully aquated when they were measured. What Duff looked upon as aquation (hydrolysis) was presumably decomposition catalyzed by freshly prepared or *freshly cleaned* platinum black.

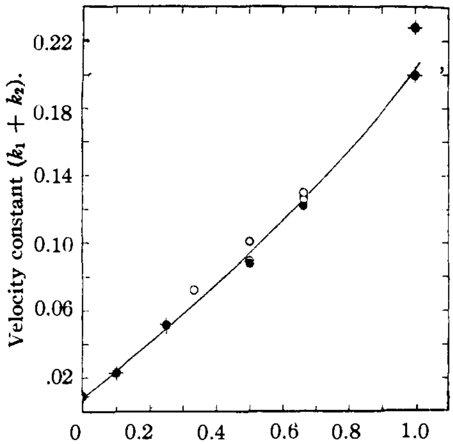


Fig. 4.—Velocity of aquation of carbonato and bicarbonato pentammine cobalti ions and their mixtures at 0°: ○, potentiometric determinations, ●, conductimetric determinations; -●-, conductimetric determinations, Lamb and Stevens.

centrations from which in turn the dissociation constants could be calculated. On the other hand, the rate of aquation is so rapid at this temperature that no accurate estimation of the initial *p*H would be possible.

Measurements of Hydrogen Ion Concentration at 25°.—For these measurements we used a thermostat, potentiometer and glass hydrogen electrode which have been previously described.[13] Special precautions were taken to avoid the absorption or evolution of carbon dioxide.

The procedure was as follows: A Pyrex glass separatory funnel of tall form and known capacity containing a short Pyrex glass rod to serve as stirrer was swept out with carbon dioxide-free air, stoppered, and placed in the thermostat for several hours. Into it the necessary quantity of acid was then rapidly introduced and distilled, carbon dioxide-free water added until the funnel was three-quarters full. Then the weighed ammine was introduced in a small test-tube which sank to the bottom and the funnel was filled with water and closed in such a way with the glass stopper that no air bubbles were entrapped. The solution was homogenized by energetic shaking and then left in the thermostat for one to three hours. Before the measurements were made the stem was filled with distilled, water and connected with the glass electrode by a short gum-rubber tube. The stopper and then the stopcock were opened. This allowed the lower part of the solution to flow into the glass electrode without any contact with air. Variation in the length of time the solutions stayed in the thermostat before the measurements (between one-fourth and twenty-four hours) had no effect.

TABLE II

Expt.	Concentration $Co(NH_3)_5CO_3^+$ M × 10^2	Concentration HCl M × 10^2	$b = \frac{HCl}{Co(NH_3)_5CO_3^+}$	*p*H
1	3.086	0	0	8.688
2	1.981	0	0	8.712
3	2.650	0.02865	0.0108	8.398
4	2.577	.02817	.0109	8.330
5	2.839	.06944	.0241	8.093
6	2.035	.05840	.0287	8.086
7	1.499	.1135	.0757	7.554
8	1.163	.2196	.1888	7.063
9	1.993	.5838	.283	6.820
10	1.699	.738	.434	6.579
11	1.006	.448	.445	6.567
12	1.295	.652	.503	6.488
13	0.807	.476	.590	6.378
14	1.436	.954	.665	6.282
15	1.348	.942	.698	6.233
16	1.130	.907	.802	6.122
17	Bicarbonato Pentammine Nitrate		1.000	5.936
18	0.346	.357	1.032	5.907
19	.666	.722	1.087	5.837
20	.738	.812	1.099	5.813
21	.518	.763	1.471	5.404
22	.510	.764	1.498	5.367

By successive operations of this kind, the data given in Table II and shown as a titration curve in Fig. 5 were obtained. Their accuracy is attested by the exactness with which the measured value for a sample of pure bicarbonato pentammine nitrate independently prepared and measured lies along the titration curve.

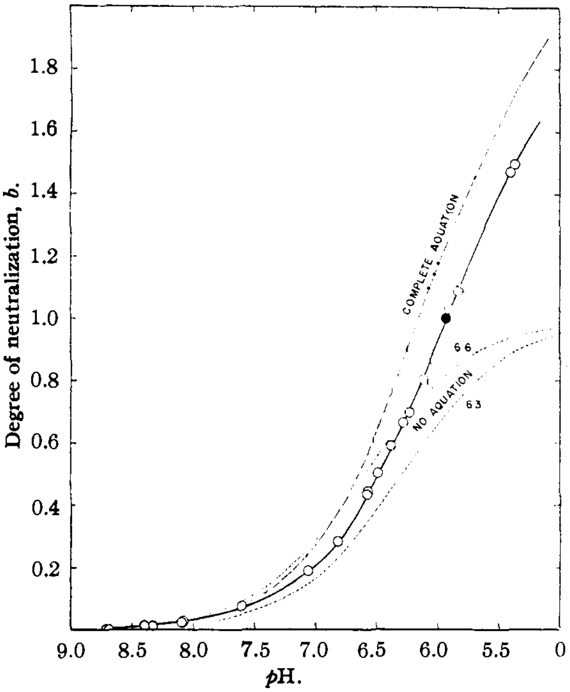


Fig. 5.—*p*H measurements in mixtures of carbonato pentammine cobalti nitrate with hydrochloric acid at 25°.

Calculation of the Dissociation Constant of Bicarbonato Pentammine Ion[24]

It can be seen from the above chart that the calculation of the dissociation constant of the bicarbonato pentammine ion from the measured values of the hydrogen ion concentration requires a knowledge of the six interdependent equilibria involved in this system. Assigning the following letters to the concentration of the reactants:

---

[24] The complete derivation of this equation is available as a Science Service Document 1821, A.D.I., 1719 N Street, Washington 6, D. C., remitting 50¢ for microfilm or 60¢ for photoprints.

$$\begin{array}{llll}
(\mathrm{Co(NH_3)_5CO_3})^+ & = d & \mathrm{CO_3H^-} & = m \\
(\mathrm{Co(NH_3)_5CO_3H})^{++} & = e & \mathrm{CO_2 + CO_3H_2} & = n \\
(\mathrm{Co(NH_3)_5H_2O})^{+++} & = f & \mathrm{H^+} & = H \\
(\mathrm{Co(NH_3)_5OH})^{++} & = g & \mathrm{OH^-} & = O \\
\mathrm{CO_3^=} & = l & &
\end{array}$$

we can define the various equilibrium constants as follows:

$$d \cdot H = K.e \qquad (1)$$
$$f \cdot m = C.e \qquad (2)$$
$$g \cdot H = P.f \qquad (3)$$
$$m \cdot H = R.n \qquad (4)$$
$$l \cdot H = Q.m \qquad (5)$$
$$H \cdot O = K_w \qquad (6)$$

The conservation of carbon gives

$$d + e + l + m + n = A \qquad (7)$$

where A is the concentration of the carbonato pentammine salt introduced. The conservation of cobalt gives

$$d + e + f + g = A \qquad (8)$$

The condition for electroneutrality is

$$2e + d + 3f = A + B + m + 2l + O - H - 2g \qquad (9)$$

where B is the concentration of strong acid added.

Since the constants for the equilibria in no. 3, no. 4, no. 5 and no. 6 are known,[25] and A, B, and H are measured quantities, there are ten unknown quantities with only nine equations to define them. The best that can be done, therefore, is to derive an equation containing the equilibrium constants for the dissociation and the aquation of the bicarbonato pentammine (K and C, respectively) expressed in terms of known or measured quantities.

This can be conveniently done by first introducing the auxiliary quantities D, M, E, a, b, defined by the following equations

$$D = (l + m + n)/m = (QR + HR + H^2)/HR \qquad (10)$$
$$M = (2H^3 + (P + R)H^2 - PQR)/HR(H + P) \qquad (11)$$
$$E = H^2 - BH - K_w \qquad (12)$$
$$a = (l + m + n)/A = mD/A \qquad (13)$$
$$b = B/A \qquad (14)$$

Now by elimination between the first eight equations and (13) we obtain

$$a^2 \frac{A}{D(H + P)} \frac{(K + H)}{C} + a - 1 = 0 \qquad (15)$$

This formula gives a relation between the degree of aquation, a, and the different constants.

Eliminating all the unknown concentrations and square roots we obtain

$$CH(H + P)(ED + MAH)(M(K + H) - HD) = D(AH^2 + (K + H)E)^2 \qquad (16)$$

This equation gives us the desired relation between C, K, and known values. It is linear in respect to C and quadratic for K. If one desires to obtain algebraically the K and C values, two such equations are necessary based on independent data and could be solved. This method is very complicated and suffers from the drawback that small experimental errors produce wide deviations.

If we have, however, approximate values for K and C, we can obtain from (16) the value of E and from it directly b. Furthermore, E is nearly equal to $-BH$. This equality is practically perfect for values of b greater than 0.1. Since for smaller values, when B decreases, not only does the difference between E and $-BH$ increase, but as the solution is only negligibly buffered, the importance of impurities also becomes disturbing. Thus limiting ourselves to solutions of b greater than 0.1 we can make this approximation without rejecting valuable data. By solving then (16) for b, we obtain

$$b = \frac{2(K + H)HDA - DCS + \sqrt{DCS - 2(K + H)HDA^2 - 4(K + H)^2DA(DAH^2 - CSM)}}{2AD(K + H)^2} \qquad (17)$$

where $S = (H + P)(N(K + H) - HD)$. This equation, in about thirty operations, will give a numerical answer from the substituted known or measured values.

Approximate Values of K and C.—These can be arrived at by comparing the observed titration curve with titration curves computed on each of two alternative, simplifying assumptions; first, that there is no aquation, and, second, that aquation is complete.

On the first assumption, the solution would merely contain carbonato and bicarbonato pentammines. Titration curves expressing b_0, the degree of neutralization for no aquation, as a function of the hydrogen-ion concentration can then be readily constructed, assuming a series of values of K. This has been done in Fig. 5 where a pair of these curves is shown for $pK = 6.3$ and 6.6.

On the second assumption, the solution would contain a mixture of aquo and hydroxo pentammine with H_2CO_3, HCO_3^-, and $CO_3^=$, where there will always be an equivalent quantity of free carbonic acid in its various forms and aquo and hydroxo pentammine. Thus we will be dealing with an equimolecular mixture of the two acids. Furthermore, in the pH range of our experiments the carbonic acid can be considered as univalent, without any appreciable error. Consequently we have an equimolar mixture of two univalent acids and the real degree of neutralization is the mean of the degrees of neutralization of the two acids,[26] and these can be obtained for any pH value since we know the dissociation constants of both. It will be more convenient, however, to calculate all our degrees of neutralization not on the whole mixture but on the cobalt present, which, in this case, means multiplying the result by two. Let us call this degree of neutralization b_i (for infinite aquation); Fig. 5 shows this curve also.

We can see that if we mix one of the above ideal

---

[25] No. 3, Lamb and Damon, unpublished data. No. 4 and no. 5, MacInnes, THIS JOURNAL, **55**, 2630 (1933). No. 6, Harned, *ibid.*, **47**, 937 (1925).

[26] Mysels, *J. Chem. Ed.*, **18**, 478 (1941).

solutions where no aquation has occurred with another ideal solution of the same hydrogen-ion concentration, where aquation is complete, and in such a ratio that the percentage of the aquated ammine will be the same as at equilibrium, we shall obtain a solution identical with our observed equilibrium solution. We can call this ratio the "degree of aquation" a of our solution and we see that a = (non-complex carbonic acid)/total carbonic acid = (aquated ammine)/total ammine. In other words, we can calculate the degree of neutralization of our solution b as equal to that of a mixture of the two ideal solutions mixed in the indicated proportion a. But we know that this is the weighted average of the two limiting degrees of neutralization, *i. e.*, we have

$$b = ab_i + (1 - a)b_0 \qquad (18)$$

or, in another form

$$a = b - b_0/(b_i - b_0) \qquad (19)$$

Thus the degree of neutralization of our actual solution has to lie between b_i and b_0. We know b_i and we can calculate various values of b_0 for different values of K, as shown done in Fig. 2. By comparing with the observed values of the degree of neutralization (b) we can immediately see that certain values of K give curves such that the observed values of b lie outside of the interval b_i to b_0. Thus the curve for pK 6.6 is excluded, while that for pK 6.3 or less is acceptable. This affords a first approximation to the true value of K.

A further approximation can be obtained by finding what value of K gives the most constant values for the other unknown quantity, the aquation constant C, which can be computed from the previously derived, rigorous equation (15) which is easily rearranged to

$$C = \frac{[\mathrm{Co(NH_3)_5OH}][\mathrm{CO_3H}]}{[\mathrm{Co(NH_3)_5CO_3H}]} = \frac{a^2A(K + H)}{D(1 - a)(H + P)} \qquad (20)$$

provided the value of a, the degree of aquation is known. This value can, however, be simply calculated from the above equation (19), since b is easily obtained from the known dissociation constant of the aquopentammine ion, and b_0 from the approximate value of K now available. Making these calculations for Expts. 8, 9, 17 and 22 in Table II it was found that the best constancy of C was obtained for pK 6.4, *i. e.*, $K = 4 \times 10^{-7}$, the value of C then being 8.5×10^{-4}.

Calculation of Degree of Neutralization.—Taking the above values of K and C arrived at by successive approximation, numerical values of b, the degrees of neutralization, can be calculated rigorously from known quantities and the observed values of pH by means of equation 17. These calculations have been made for a number of our experiments and the results are listed in Table III. The agreement is satisfactory and confirms the accuracy of our values of K and C.

TABLE III

COMPARISON OF EXPERIMENTAL AND CALCULATED DEGREES OF NEUTRALIZATION

Assuming: $K = 4 \times 10^{-7}$; $C = 8.5 \times 10^{-4}$; $J = 0.04$.

Expt.	pH	Degree of neutralization b_e Experimental	b_c Calculated	Ionic strength calculated
9	6.820	0.283	0.279	0.032
13	6.378	.590	.610	
15	6.233	.698	.725	
17	6.122	.802	.817	.035
21	5.813	1.100	1.107	
22	5.404	1.471	1.477	.023

Effect of Ionic Strength.—It must be realized, however, that the various constants utilized in the above calculations vary with the ionic strength of the solution, and the question arises as to whether the differences in the ionic strengths of our solutions might introduce significant errors in our calculations. The ionic strengths of most of the solutions in which our measurements were made were in the vicinity of 0.03. Assuming that our constants for K and C at 25° apply at this ionic strength and that they vary with the ionic strength according to the Debye-Hückel law, *i. e.*, $\log f = -0.5z^2\sqrt{J}$, we have calculated values of b at ionic strengths of 0.02 and 0.04 for all of our significant experiments. The results of this calculation are shown by the small circles in Fig. 6. It can be seen that the experimental values of b (the large circles) in every case lie *between* these calculated values. This confirms the correctness of our values of K and C.

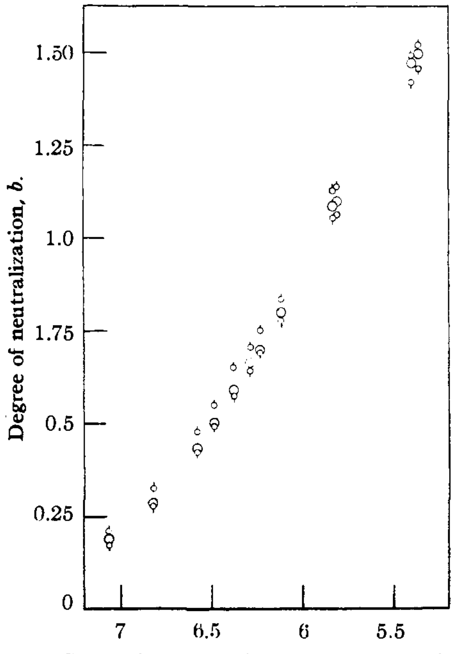


Fig. 6.—Comparison of calculated and experimental variation of degree of neutralization of carbonato pentammine cobalti nitrate and hydrochloric acid buffers with pH at 25°: ○, experimental values; ό, calculated for J = 0.04; ♀, calculated for J = 0.02.

Measurements of Hydrogen-Ion Concentration at 0°.—In view of the conductimetric measurements described above, it did not appear feasible to try to measure the hydrogen-ion concentration in these solutions under equilibrium conditions at this temperature. Moreover, the dissociation constant of the aquopentammine ion required in our calculation has not been measured at 0°. Instead, it appeared promising to carry out a series of such measurements at successive intervals of time on freshly prepared solutions containing mixtures of the carbonato and bicarbonato ammines and from the results obtained to extrapolate to zero time, *i. e.*, to zero aquation.

However, attempts to employ the glass electrode for measurement of the hydrogen-ion concentration at 0° were at first unsuccessful owing to the high resistance of the glass membrane at this temperature and to its lowered external insulation resulting from the condensation of moisture on cold surfaces. These difficulties were overcome by the use of a sensitive electrometer-potentiometer and very thin membranes in the glass electrodes which we blew from Corning 015 glass with resistances as low as 2.8 megohms at 0° and 1 kilocycle.

The glass electrode and its assembly, used for measurements at this temperature, are shown in Fig. 7. The glass electrode (1), sealed to a very long, soft glass tube, was immersed in the solution to be studied contained in the large, Pyrex test-tube (2). This was connected by a salt-bridge (3) of small bore to a tube (4) containing a saturated solution of potassium chloride into which dipped a silver-silver chloride electrode. A reservoir containing a supply of this solution was attached to the upper part of (4). The bottom of (2) could be connected to outside suction through a second tube (5). Into the 0.1 *M* solution of hydrochloric acid contained in the glass electrode dipped another silver-silver chloride electrode sealed into a glass tube reaching well beyond the extension of the glass electrode.

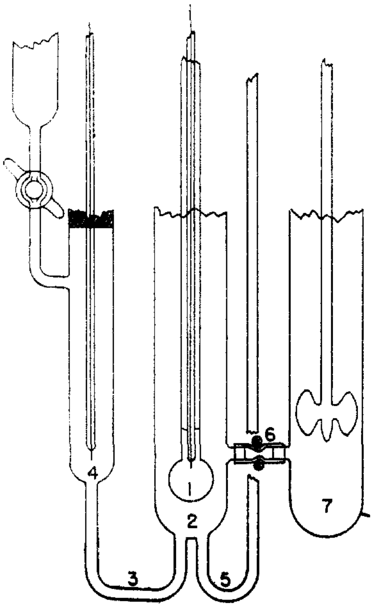


Fig. 7.—Apparatus for *p*H measurements at 0°.

Short side-tubes connected test-tube (2) through a rubber tube and pinchcock (6) to test-tube (7). This separate test-tube was provided in order that the solid carbonato pentammine could be rapidly dissolved in the acid by stirring without danger of breaking the very fragile glass electrode. The pinchcock could be opened from outside the ice-bath and controlled the access of the solution to the electrode. The salt-bridge (3) was flushed by opening the stopcock on the reservoir. The whole structure was fixed to a wooden board and immersed in ice and water in a large Dewar jug supported by a paraffined glass plate.

The concentric tubes supporting the glass and the silver-silver chloride electrodes extended sufficiently beyond the level of the ice-bath to remain at room temperature and to be dry and insulating at all times.

Procedure.—Before starting a measurement, the cell and all the solutions were cooled in ice. The electrodes were standardized with potassium acid phthalate and the leaks to the ground were checked and found negligible.

The apparatus was then flushed several times with ice-cold distilled water. The carbonato pentammine cobalti nitrate, previously ground in an agate mortar and exactly weighed in a thin glass ampule, was dropped into tube (7) and was followed by 25 cc. of distilled and boiled water which had been well pre-cooled. The ampule was crushed by the stirrer and agitation was continued for one minute; 25 cc. of acid of the concentration needed to yield the desired buffer was pre-cooled in a volumetric flask calibrated for delivery, and then poured into tube (7) with vigorous stirring over a period of about twenty seconds. The stop watch was started after half the acid had been added. The stirring was then continued for one minute and, after flushing the connecting passages, the main part of the solution was introduced into test-tube (2) and the measurements begun as soon as possible.

When reading the electrometer, it was necessary to take into account the relatively rapid shifting of its zero point. The potentiometer was approximately balanced, then the scale of the electrometer was adjusted to zero, and fifteen seconds before a reading was to be taken, the electrometer was connected. The deflection was read after the fifteen seconds had elapsed, which was sufficient time to permit the light spot to come to rest. The electrometer was then disconnected and the new zero point noted again after fifteen seconds. The difference between the two zero points was halved, and the reading corrrected by that amount. In this way, readings could be taken every thirty to forty seconds and the position of the light spot could be determined to within about half a millimeter, corresponding to one-tenth of a millivolt. Consequently the error of each reading should be less than about two-tenth's of a millivolt.

Aquation was reasonably rapid and within thirty minutes to an hour, equilibrium had been practically established. After another fifteen minutes, the solution was discarded, the apparatus again flushed with ice-cold distilled water, and the buffer re-introduced. The average of the readings of the potential of the glass electrode in the buffer was taken as corresponding to *p*H 4.

The reproducibility of measurements on the buffer was about ±1 millivolt, corresponding to ±0.02 *p*H. Discrepancies of this order could be attributed to small changes in the salt-bridge potential and to temperature fluctuations. However, it was ascertained that the temperature fluctuations in the solution in (2) did not exceed 0.3° during all the operations of a run.

The differences between the final potential and that observed at different intervals of time were plotted on a logarithmic graph as is shown for a typical run in Fig. 8. In this figure each experimental point is indicated by the middle point of a line whose length represents approximately the experimental uncertainty. It can be seen that these points lie closely on a straight line. By extrapolating this line to zero time the total change in potential and the initial potential were obtained. From these initial potentials, values for the dissociation constant of the bicarbonato pentammine were readily calculated. These values for all of the runs are collected in Table IV.

The extrapolation to zero time involves some

TABLE IV

POTENTIAL MEASUREMENTS IN SOLUTIONS OF CARBONATO AND BICARBONATO PENTAMMINE COBALTI NITRATE AT 0°

Ionic Strength = 0.01, except in the first experiment, where the ionic strength was 0.03.

Initial concentration mMl./l.			Fraction bi-	pH			$k_1 + k_2$,
Total	Carb.	Bicarb.	carb.	Initial	Final	pK	l./min.
12.84	4.28	8.56	2/3	6.69	6.81	7.11	0.126
4.28	1.427	2.853	2/3	6.69	6.83	7.13	.130
4.28	1.427	2.853	2/3	6.67	6.85	7.15	.128
5.00	2.50	2.50	1/2	6.90	7.07	7.07	.105
5.00	2.50	2.50	1/2	6.94	7.14	7.14	.091
6.00	4.00	2.00	1/3	7.21	7.40	7.10	.072

additional uncertainty beyond that inherent in the measurements. The carbonato pentammine nitrate is not easily soluble at 0° and it did not dissolve completely until the acid had been added. There may, therefore have been local excesses of acid which might have produced slightly erratic results. However, the acid was added relatively slowly and the interval of extrapolation never exceeded two minutes. Moreover, the proportion of acid added was varied widely in these experiments and, would have been expected to yield discordant results if the imperfect mixing had been of importance. In fact, however, the maximum variation from the average was only 0.05 pH and the deviations showed no trend. It would appear, therefore, that the average of all of our extrapolated results at 0°, namely, $pK = 7.12 \pm 0.05$ or $K = 7.6 \times 10^{-8} \pm 13\%$ can be accepted with a good deal of confidence.

This value at 0° can be compared roughly with our value obtained under equilibrium conditions at 25° by using Pitzer's[27] approximate formula for the change of the dissociation constant with the temperature. This gives $K = 1.4 \times 10^{-7}$ at 25°, which agrees as closely as could be expected with our measured value of 4×10^{-7} at this temperature.

These concordant values of the dissociation constant are very different from those indicated for the betoxine or the acid-salt formulas of the carbonato pentammine ion. They lie right in the range anticipated on the basis of the dipolar cation formula and are therefore indicative of its correctness.

Velocity of Aquation.—The closeness with which the experimental points fall on the straight line in the logarithmic plot (Fig. 8) indicates that the aquation does indeed follow a uni- or quasi-unimolecular course and the slope of this line gives the value of this velocity constant $(k_1 + k_2)$.[16] The values thus obtained are listed in Table IV and in Fig. 4 are shown along with the corresponding values obtained from conductimetric measurements both by Lamb and Stevens[16] and by ourselves as described in another connection. The agreement between the results, particularly in view of the different methods involved, is good and confirms the conclusion of Lamb and Stevens that the bicarbonato aquates much more rapidly than the carbonato.

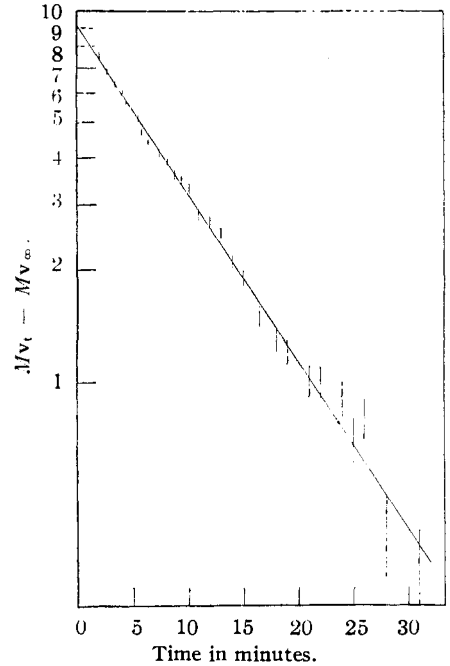


Fig. 8.—Variation of pH of a solution ofcarbonato pentammine cobalti nitrate (0.005 M) and hydrochloric acid (0.0025 M) with time.

The dissociation constant of the bicarbonato pentammine which we have obtained, $K = 7.6 \times 10^{-8}$ at 0°, is considerably greater than the value of about 4×10^{-10} which Lamb and Stevens showed would be required if the observed rate of aquation of the carbonato pentammine were due *wholly* to the aquation of the bicarbonato in equilibrium with it. On the basis of our value of K, the concentration of bicarbonato pentammine ion in 0.004 M aqueous solutions of the pure carbonato would be 2.3×10^{-5} M, which, using the empirical relation found by Lamb and Stevens, would give an apparent velocity constant for the aquation of the carbonato of 0.0012 as compared with the observed value of 0.0092. In other words, the aquation of the bicarbonato would account for only about one-eighth of the actually observed rate of aquation of the carbonato pentammine. The carbonato would thus appear to undergo direct aquation, although its velocity constant of aquation is only about one-thirtieth of that of the bicarbonato. It must be pointed out, however, that these inferences rest entirely on a single measurement of the rate of aquation of the pure carbonato pentammine ion in water at 0°, and this unbuffered solution would be very sensitive to slight acidic impurities. The presence in the water of carbonic acid at a concentration of 1×10^{-5} M would fully account for the observed higher rate of aquation as compared with the rate

---

(27) Pitzer, This Journal, **59**, 2370 (1937).

calculation from our value of the dissociation constant of the bicarbonato. The question as to the rate of the direct aquation of the carbonato ammine itself must therefore be considered as still open.

Dielectric Increment

Since, as has been shown above, the magnitude of the dissociation constant of the bicarbonato pentammine points strongly to the dipolar cationic structure of the carbonato pentammines, we have with Dr. J. L. Oncley's kind coöperation, investigated the dielectric increment of solutions of this ammine and several related ammines. Information on this score is desirable since it is known that solutions of ordinary, uncharged dipolar ions (isoions) exhibit relatively large dielectric increments,[28,29] although it is probable that in the case of charged dipolar ions, as contrasted with uncharged molecules and isoions, the dielectric increment can only be expected to give an approximate measure of the dissymmetry, unless more is known about the shapes of the ions.

It is not feasible to carry out dielectric measurements on aqueous solutions of these ammines, because if they are dilute enough to be sufficiently poor conductors, the contribution of the ions to the dielectric constant is relatively very small; while if they are concentrated, the conductance is so high that accurate measurements of the dielectric constant are precluded. It was necessary, therefore, to find a more favorable solvent, preferably one of small dielectric constant and of considerable viscosity, and to operate at low temperatures. Glycol (commercial) at 0° was found to be the most suitable solvent.

Preparation of Ammines.—Hydroxo pentammine cobalti chloride was prepared according to Werner's directions.[4] The salt, in the form of a crystalline powder, precipitated from the strongly ammoniacal solution, and analysis gave 23.68% Co and 34.39% NH_3, as compared with 23.57% and 34.06%, respectively, calculated for the monohydrated salt. It was readily soluble in glycol while the corresponding nitrate was insoluble.

Oxalato pentammine cobalti bromide, $Co(NH_3)_5C_2O_4Br\cdot 2H_2O$.—This new hydrate was prepared according to Jørgensen's[30] directions. Starting with 20.8 g. of the oxalato acid bromide, we obtained 16 g. of the neutral bromide. The former was not soluble in glycol while the latter was relatively very soluble. The appearance under the microscope of the fluffy crystals of the neutral bromide was, however, that of long prisms rather than that of the branched needles which Jørgensen describes. Moreover, analysis of our product gave 16.92% Co and 24.43% NH_3, which agrees closely with the 16.93% and 24.47% calculated for the neutral salt with two molecules of water of crystallization, rather than with the 17.38% and 25.11% calculated for Jørgensen's salt with $1^1/_2$ molecules of water.

Carbonato tetrammine cobalti nitrate was prepared according to Jørgensen[31] from cobaltous nitrate by oxidation with air, and recrystallization from water at room temperature.

Procedure.—To prepare the solutions for measurement, the pre-cooled glycol was poured into a centrifuge bottle, the finely ground salt added and the bottle promptly closed, energetically shaken for about five minutes and centrifuged to settle the undissolved powder. The clear solution was rapidly decanted into a glass-stoppered graduate in which it was agitated and if necessary diluted with some glycol, so as to obtain the desired conductivity. From the graduate it was delivered in part into weighing bottles for determination of the concentration. A similar procedure was used for preparing solutions of lithium chloride except that centrifugation was not necessary.

All these operations were conducted in a cold room, held at about 4° to avoid any possible decomposition or displacement of the acido groups by glycol analogous to aquation. The conductance of the solutions at 0° remained constant over several hours.

The cell[32] was of the type already described.[33] The measurements were kindly made by Dr. Oncley on his bridge essentially according to the procedure previously described.[33,34]

Each value of the dielectric increment was obtained by extrapolating to infinite frequency values obtained between 32 and 1000 kilocycles. Each value was the difference of measurements of two solutions having similar conductivities and prepared with the same glycol, one solution containing the ammine and the other the lithium chloride. The results at the higher frequencies are shown in Fig. 9 together with the straight lines used for their extrapolation.

Results.—The data resulting from these measurements are shown in Table V, which gives the concentration, the measured differences of capacitance of the cell, and the molecular dielectric increments of the solutes. As these last are small differences between two large quantities, they are probably accurate to only about 10%.

TABLE V

DIELECTRIC CONSTANT MEASUREMENTS OF COBALTAMMINE SOLUTIONS AT 0°

Ammine	Concn., mM.	Spec. cond., mhos × 10⁵	Capac., μμF	Dielectric increment		Molec. polarization/liter	Apparent separation charges, Å.
				Specif.	Molec.		
Carbonato pent-	35.3	6.8	10.5	3.0	85	12.7	5.4
ammine nitrate	31.5	5.3	13.0	2.5	79	11.6	5.1
Carbonato pent-	17.9	3.5	8.7	1.7	93	13.8	5.6
ammine nitrate	10.8	2.2	6.0	1.15	112	16.7	6.1
Average	..	...	..	..	92	13.7	5.5
Carbonato tetrammine nitrate	26.9	4.6	6.5	1.25	46	6.8	3.9
Oxalato pentammine bromide	48.3	6.8	26.5	5.1	105	15.6	5.9
Hydroxo pentammine chloride	20.0	6.6	9.6	1.85	92	13.7	5.6

It can be seen from this table that the values of the molecular dielectric increment of the carbon-

---

(28) Wyman, *J. Chem. Rev.*, **19**, 213 (1936).

(29) Oncley, THIS JOURNAL, **60**, 1115 (1938).

(30) Jørgensen, *Z. anorg. Chem.*, **11**, 416 (1896).

(31) Jørgensen, *ibid.*, **2**, 281 (1892).

(32) Except in the first experiment, where a cell with plane electrodes of platinized platinum 10 sq. cm. in area and 0.2 cm. apart was used.

(33) Ferry and Oncley, THIS JOURNAL, **63**, 272 (1941).

(34) Oncley, *ibid.*, **60**, 1115 (1938).

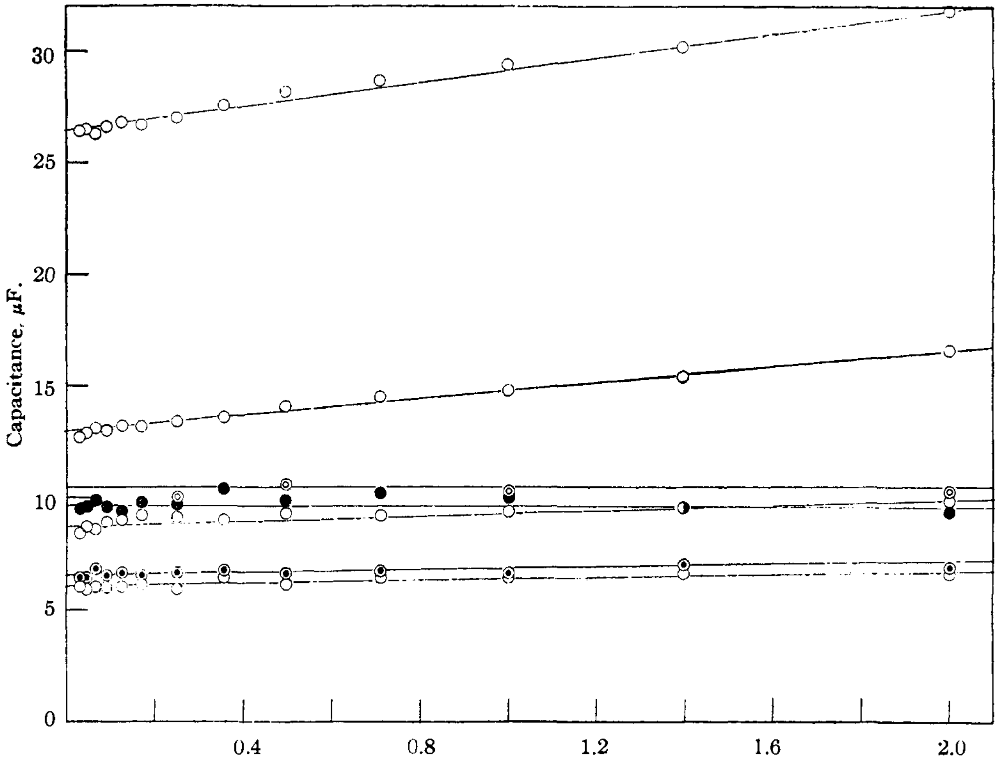


Fig. 9.—Variation with frequency of the difference between the measured capacities of solutions of ammines and of lithium chloride.

ato pentammine seem to increase with the dilution. However, the accuracy of measurement at low concentrations is so small that we cannot be sure that this increase is real. We have therefore taken the average, 92, as characteristic of this ammine.

This value of 92 for the carbonato and the 105 for the similarly constituted oxalato pentammine are decidedly larger than the 46 for the carbonato tetrammine. The carbonato tetrammine would not be expected to have a dipolar cationic structure as the carbonato group occupies two coördinate places, or, in other words, is attached to the cobalt atom by two bonds, both of which are covalent. The relative magnitudes of the dielectric increments are therefore just what would be expected on the assumption of a dipolar cationic structure for the carbonato and oxalato pentammines.

The dielectric increment of the hydroxo pentammine is reported for the sake of the record. It is unexpectedly large although the hydroxo pentammine like the carbonato tetrammine is undoubtedly normally constituted. No great degree of dissymmetry would therefore be expected from the formula of the unsolvated ion. However the difference in lyophilic character of the hydroxo and carbonato groups and the different charges of the complexes prevent a direct comparison of these ammines.

It would therefore appear reasonable to conclude that while the results of these dielectric measurements do not of themselves demonstrate the dipolar cation structure of the carbonato and oxalato pentammines, they are confirmatory of it.

Summary

1. Evidence is presented showing the lack of structural significance of the water content of crystals of carbonato pentammine cobalti nitrate, and the chief support of the "betoxine" structure of this and analogous ammines is thus eliminated.

2. A dipolar cationic structure is ascribed to the carbonato pentammine cobalti ion and to analogous ammines, and evidence in support of this structure is presented, based on:

(a) The dissociation constant of the bicarbonato pentammine cobalti ion as calculated from measurements made with the glass electrode in solutions containing mixtures of the bicarbonato and carbonato pentammine ions and their aquation product in equilibrium at 25°, and on similar unaquated mixtures at 0°.

(b) The large dielectric increments found for the carbonato and oxalato pentammine cobalti ions as compared with that found for the carbonato tetrammine cobalti iôn.

3. The velocity constant for the aquation of the bicarbonato pentammine cobalti ion has been

measured at 0 and 25° by a new procedure, confirming prior findings. The equilibrium constant for the aquation of this ion at 25° has also been determined.

4. The carbonato pentammine cobalti ion appears to undergo a very slow but still perceptible direct aquation.

Cambridge, Mass. Received September 26, 1944

[Contribution from the Sterling Chemistry Laboratory, Yale University]

The Volume of Mixing and the Thermodynamic Functions of Binary Mixtures. II. Benzene-Cyclohexane[1]

By Scott E. Wood and Alfred E. Austin[2]

The changes of the thermodynamic functions on mixing at constant pressure have been determined for mixtures of benzene and cyclohexane.[3] It is of interest in the theory of solutions to determine the changes of these functions on mixing at constant volume. In this paper the relation between the density and the composition of mixtures of benzene and cyclohexane at 30° and the specific volumes of the solutions from 15 to 75° have been measured. From these the changes of the volume on mixing at constant pressure and the changes of the thermodynamic functions on mixing at constant volume have been calculated.

The apparatus and procedure were identical to that described in the first paper of this series.[4] It was found that more consistent results in the measurement of the coefficient of expansion could be obtained if the walls of the capillary tip are quite thick. This prevents too rapid cooling while exchanging the mercury cups. The tip of the better dilatometer used in this work had an outside diameter of 5 mm. with a 0.1 mm. bore.

Purification of Materials.—Synthetic thiophene-free benzene was fractionally frozen twice, discarding approximately one-fifth of the starting material each time. It was then fractionally distilled in a 3-m. column,[4] six low-boiling and four high-boiling fractions being removed. The product was still not pure as determined by the density and consequently was frozen three more times, removing one-tenth of the liquid each time. The benzene was again distilled removing one low-boiling and one high-boiling fraction. The density of the final product at 30.00 ± 0.01° was 0.86833 g. per cc. in comparison with 0.86836 given by Scatchard, Wood and Mochel[3] and 0.86839 determined by Wood and Brusie.[1]

A technical grade of cyclohexane was nitrated with a mixture of five parts of concentrated nitric acid and nine parts of concentrated sulfuric acid for six hours at 5 to 10°. The two layers were separated and the cyclohexane was successively washed with water, dilute sodium hydroxide, and water. It was dried over Hydralo for forty-eight hours. It was then fractionally distilled, six low-boiling and three high-boiling fractions being removed. The density of the product at 30.00 ± 0.01° was 0.76910 g. per cc. in comparison with 0.76914 given by Scatchard, Wood and Mochel.[3]

Density-Composition Curve at 30°.—Since the composition of the solutions used in the dilatometer could not be determined directly, it was necessary to establish a density-composition curve. The temperature used was 30.00 ± 0.01°. Determinations of the density of the solutions were made at approximately each eighth mole fraction. Duplicate measurements, in which the order of weighing the components was reversed, were made at each composition. The observed weights were corrected for the displacement of air by both the liquid and vapor and for the weight of each component in the vapor after mixing, assuming equilibrium to be obtained. The vapor pressure data were used for these calculations.[3]

Since the density-composition measurements were made with the liquids saturated with air and the coefficient of expansion data were determined with solutions free from air, a further correction was applied. The difference between the density observed in the dilatometer and that in the pycnometer at 30° was 0.00012 g. per cc. for benzene and −0.00002 g. per cc. for cyclohexane. The corrections necessary for the solutions were assumed to be additive in the volume fraction although the difference between using the volume fraction and mole fraction is negligible.

The mole fractions of the solutions used in the dilatometer were determined from the density at 30° by means of the equations

$$d = \frac{d_2 + (d_1 - d_2)z_1}{1 + V^M/V^0} \qquad (1)$$

$$100V^M/V^0 = z_1z_2(3.0129 - 0.7590z_1) \qquad (2)$$

V is the molal volume of the mixture, V^0 that of the unmixed components, and $V^M = V - V^0$, z_1 is the volume fraction of benzene; d_1 and d_2 are the corresponding densities of the two components. The mole fraction of benzene in the solutions, the density corrected for air, the difference of the observed density and that calculated from equations 1 and 2, and 100 V^M/V^0 calculated from

---

[1] This contribution contains material taken from a thesis by Alfred E. Austin presented to the Graduate School, Yale University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Present address: Corning Glass Works, Corning, New York.

[3] G. Scatchard, S. E. Wood and J. M. Mochel, *J. Phys. Chem.*, **43**, 119 (1939).

[4] S. E. Wood and J. P. Brusie, This Journal, **65**, 1891 (1943).