In order to estimate theoretically the magnitude of the Davydov splitting and the intensity enhancement for the direction parallel to the *c* axis, we carried out the calculation of the exciton–exciton type of interaction for the pyridine molecules in the crystal form. The actual calculation was made by the SCFMO method which was adopted by Tanaka and Tanaka[21] for the calculation of anthracene, long-range interaction (50 Å–∞) being taken into account following the approximate method developed by Rice, *et al.*[22] The result shows that the splitting is larger for the direction parallel to the *b* axis than for the direction parallel to the *c* axis. Further, in consistency with the theoretical consideration, the absorption band appears at lower frequencies for the former direction than for the latter. The calculated oscillator strengths depend strongly on the model used for the estimation of the intermolecular Coulomb integral.[23] This prevents us from discussing quantitatively the intensity change due to the exciton–exciton type of interaction. However, from the qualitative point of view, the calculation shows that the intensity of the *b*-parallel band considerably decreases as the result of exciton–exciton type of interaction and that this absorption has comparable intensity with the weak *c*-parallel band.[24] From the above discussion, we consider that the two bands at 4.84 eV ($c_{||}$) and 4.65 eV ($b_{||}$) may both be atrributed to the local excitation within pyridine.

Acknowledgment.—The authors wish to express their sincere thanks to Dr. Ichiro Hanazaki of the Institute of Physical and Chemical Research for his kind advice given them in doing the theoretical calculations.

---

[21] M. Tanaka and J. Tanaka, private communication.

[22] R. Silbey, J. Jortner, and S. A. Rice, *J. Chem. Phys.*, **42**, 1515 (1965).

[23] In the present calculation, interatomic Coulomb integrals for distances within 50 Å were estimated by use of two models. In one of them, the point charge approximation was adopted, and in the other, interatomic Coulomb integrals were represented by $e^2e^{-R/20}/R$ (R is the interatomic distance). In the latter, the screening effect of the other electrons was considered. The calculated oscillator strengths sometimes differ by the order of 10 by changing the model from one to the other. Moreover, it was found that the long-range interaction over 50 Å of interatomic distances gives great effect on the oscillator strengths. Taking the latter model and considering the long-range effect, the band under consideration turns out to have comparable intensities in the directions parallel to the *b* and *c* axes.

[24] As already mentioned above, as far as the plane of pyridine molecule tilts from the *yz* plane by only ~10°, the intensity of the *c*-parallel band is small.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF MINNESOTA, MINNEAPOLIS, MINNESOTA 55455

The Solvent Isotope Effect on the Dissociation of the Aquopentaamminecobalt(III) Ion[1]

BY ROGER C. SPLINTER,[2] SIMON J. HARRIS,[3] AND R. STUART TOBIAS

Received August 28, 1967

Potentiometric and spectrophotometric techniques were used to determine the equilibrium constants for three reactions: (1) $Co(NH_3)_5OH_2^{3+} + H_2O = Co(NH_3)_5OH^{2+} + H_3O^+$; (2) $Co(NH_3)_5OD_2^{3+} + D_2O = Co(NH_3)_5OD^{2+} + D_3O^+$; (3) $Co(ND_3)_5OD_2^{3+} + D_2O = Co(ND_3)_5OD^{2+} + D_3O^+$ at 25° in a medium with $[ClO_4^-] = 0.3000\ M$. Values of log $*K_1 = -6.22$, -6.75 (89% D_2O), and -6.70 (99% D_2O), respectively, were obtained. Each value of the equilibrium constant was refined by least squares. The partially exchanged species $Co(NH_3)_5OD_2^{3+}$ was studied using a flow system. Contrary to an earlier report, the aquopentaamminecobalt(III) ion exhibits a rather normal isotope effect, log $(K_H/K_D) = 0.48 \pm 0.01$ (error at the 99% confidence limit). A comparison of the dissociation constant of $Co(NH_3)_5OD_2^{3+}$ with that of $Co(ND_3)_5OD_2^{3+}$, log $K_1 = -6.81$ and -6.70 (valid for 100 mol % D_2O), respectively, indicates the size of any secondary isotope effect which arises from the exchange of the 15 ammine hydrogens.

Introduction

Both theory and measurement of acid dissociation constants in protium and deuterium oxides have indicated a correlation between the magnitude of the dissociation constant and the magnitude of the solvent isotope effect. This equilibrium isotope effect is conveniently described in terms of log (K_H/K_D) where K_H and K_D are the acid dissociation constants in H_2O and D_2O solution, respectively.[4] In general, this quantity increases as the acid strength decreases.

Early measurements suggested an approximately linear relation between log (K_H/K_D) and pK_H. The same conclusion was anticipated[4] on the basis of a very simple model; however, more recent studies[5,6] have shown that this result is not necessarily true if the acids are of different structural types.

One class of acid which has appeared to behave very

---

[1] Research sponsored by AFOSR(SRC)-OAR, USAF Grant No. AF-AFOSR-691-65 and -67; portions of this report are based on a dissertation submitted by R. C. S. to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the Ph.D. degree, 1967.

[2] Du Pont Fellow, 1964–1965.

[3] Research Fellow in Chemistry.

[4] See R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, Chapter 11, and R. W. Gurney, "Ionic Processes in Solution," McGraw-Hill Book Co., Inc., New York, N. Y., 1953, p 150, for discussions of this effect.

[5] R. P. Bell and A. T. Kuhn, *Trans. Faraday Soc.*, **59**, 1789 (1963).

[6] A. O. McDougall and F. H. Long, *J. Phys. Chem.*, **66**, 429 (1962).

irregularly is the aquo acid, that is, an acid where the proton is transferred from water molecules in the first coodination sphere of a metal ion. Huldis and Dodson reported that the first dissociation of the hexaaquoiron(III) ion ($p^*K_1 = 2.92$, 21°, $\mu = 0.55$) exhibited no measurable isotope effect[7] and a similar result was reported[8] for the first dissociation of the aquothallium(III) ion ($p^*K_1 = 1.16$, 25°, $\mu = 3.0$). Taube has reported[9] that the aquopentaamminecobalt(III) ion showed an unusually small isotope effect: $\log (K_H/K_D) = 0.18$, $p^*K_1 = 6.16$, 30°, $\mu \approx 0.25$.[10]

In contrast, measurements[11] on the aquo cation $(C_2H_5)_3Sn^+$ indicated a normal isotope effect: $\log (K_H/K_D) = 0.69$, $p^*K_1 = 6.81$, 25°, $\mu \approx 3.0$. The first dissociation of the hexaammineplatinum(IV) cation[12] also shows a rather typical isotope effect: $\log (K_H/K_D) = 0.62$, $pK_1 = 7.16$, 25°. Simple ammine complexes might be expected to show discrepancies analogous to those exhibited by aquo complexes.

A better understanding of the structure and solvation of aquo acids and the nature of their proton-transfer processes may be gained from a study of the apparent anomalies which they sometimes exhibit in the isotope effect.

It has been suggested[11] that a possible cause of small isotope effects with aquo and ammine complexes could be large secondary isotope effects. Not only is the ionizing proton changed to a deuteron in the study of an ion like $Fe(OH_2)_6^{3+}$ but 11 other hydrogens are also exchanged. The studies of the aquopentaamminecobalt(III) ion were conducted on the species $Co(NH_3)_5OH_2^{3+}$ and $Co(ND_3)_5OD_2^{3+}$ where 16 hydrogens other than the one ionizing are isotopically substituted. Since the charge on the acid is reduced in going to the conjugate base, the hydrogens should become less satisfactory donors in forming hydrogen bonds to the solvent molecules. This has been reported to lead to a strengthening of the N–H bonds within the first coordination sphere of ammine complexes.[13]

This change in bond character going from reactant to product could give rise to a secondary isotope effect which would either oppose or, conceivably, completely compensate for the primary effect. Indeed the reaction

$$Co(NH_3)_5OH_2^{3+} + Cl^- = Co(NH_3)_5Cl^{2+} + H_2O$$

where no primary effect is involved, has been reported[8] to exhibit an "inverse" isotope effect: $\log (K_H/K_D) = -0.167$. A significant secondary isotope effect has been observed[14] with formic and deuterioformic acids, DCO_2H, in H_2O. The exchange of the single hydrogen leads to a change in pK_H of 0.035 ± 0.002 unit.

In order to determine whether appreciable secondary isotope effects occur with aquo and ammine complexes, we have measured the equilibrium constants at 25° in a constant ionic medium with $[ClO_4^-] = 0.3000\ M$ for reactions 1–3 using precise spectrophotometric and potentiometric techniques.

$$Co(NH_3)_5OH_2^{3+} + H_2O = Co(NH_3)_5OH^{2+} + H_3O^+ \quad (1)$$

$$Co(NH_3)_5OD_2^{3+} + D_2O = Co(NH_3)_5OD^{2+} + D_3O^+ \quad (2)$$

$$Co(ND_3)_5OD_2^{3+} + D_2O = Co(ND_3)_5OD^{2+} + D_3O^+ \quad (3)$$

The aquopentaamminecobalt(III) cation is probably the most extensively studied aquo ion, and its equilibrium constant is of a convenient magnitude for precise determination.

Since effects such as those outlined above could occur in the formation of the transition state of a reaction involving aquo or ammine complex cations, large secondary *kinetic* isotope effects might also occur with these cations. For reactions proceeding by a conjugate-base mechanism, a knowledge of the equilibrium isotope effect is also necessary for an interpretation of the observed kinetic effect. The change of solvent from H_2O to D_2O affects both the magnitude of the equilibrium constant for the proton-transfer process as well as the rate constant of the slow step. Some of these aspects have been discussed by Pearson, *et al.*[12]

Experimental Section

Preparation of Solutions.—Aquopentaamminecobalt(III) perchlorate was prepared from carbonatopentaamminecobalt(III) nitrate which was synthesized by standard methods.[15] Carbonatopentaamminecobalt(III) nitrate (70 g) was dissolved in 4500 ml of water at room temperature. Perchloric acid (390 ml, 2 M) was added, and the solution at pH 2 was evaporated to 1100 ml, filtered, and cooled overnight in an ice bath. The crystals were separated by filtration, washed with 20 ml of ice water, recrystallized three times from 2 M $HClO_4$ and once from water, and finally air dried at 50° for 4 hr. The compound was analyzed for cobalt by destroying the complex with sodium hydroxide, reducing the oxide with sulfur dioxide, and titrating the cobalt (II) with EDTA.[16] The other analyses were carried out commercially.[17]

Anal. Calcd for $[Co(NH_3)_5OH_2](ClO_4)_3$: Co, 12.8; N, 15.2; H, 3.72; Cl, 23.1. Found: Co, 12.9; N, 15.6; H, 3.79; Cl, 23.2.

Anhydrous $NaClO_4$ and stock solutions of $DClO_4$ and NaOD were prepared as described earlier.[11] Solutions containing $Co(NH_3)_5OH_2^{3+}$ were prepared by adding weighed amounts of $[Co(NH_3)_5OH_2](ClO_4)_3$ to standard $HClO_4$ or $DClO_4$ and protium or deuterium oxide. The perchlorate ion concentration was adjusted to 0.3000 M by adding either anhydrous $NaClO_4$ to the deuterium-containing solutions or weighed portions of a standard solution of the salt in H_2O for the protium oxide solutions.

The near-infrared spectrum of solutions of the aquopentaamminecobalt(III) in D_2O was scanned, and the intensities of the band at 5988 cm^{-1} ($\nu_1 + \nu_3$(HDO)) and the band at 6452 cm^{-1} of the ammine complex were measured as a function of time. Exchange was found to be almost complete in 1.5 hr at the pH of the stock solution, and it was only necessary to let the solutions stand at 25° for 24 hr to ensure complete exchange.

All ammine hydrogens behave as if they were equivalent, and a pseudo-first-order rate constant for their exchange was calculated

---

[7] J. Huldis and R. W. Dodson, *J. Am. Chem. Soc.*, **78**, 94 (1956).

[8] T. E. Rogers and G. M. Waind, *Trans. Faraday Soc.*, **57**, 1360 (1961).

[9] H. Taube, *J. Am. Chem. Soc.*, **82**, 524 (1960).

[10] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," Thesis, Copenhagen, 1941; reprinted by P. Haase and Son, Copenhagen, 1957, p 280.

[11] R. S. Tobias and M. Yasuda, *J. Phys. Chem.*, **68**, 1820 (1964).

[12] R. G. Pearson, N. C. Stellwagen, and F. Basolo, *J. Am. Chem. Soc.*, **82**, 1077 (1960).

[13] See ref 11 for a discussion of the evidence for this.

[14] R. P. Bell and W. B. T. Miller, *Trans. Faraday Soc.*, **59**, 1147 (1963).

[15] A. B. Lamb and K. J. Mysels, *J. Am. Chem. Soc.*, **67**, 468 (1945); *Inorg. Syn.*, **4**, 171 (1953).

[16] F. J. Welcher, "The Analytical Uses of Ethylenediaminetetraacetic Acid," D. Van Nostrand Co., Inc., New York, N. Y., 1958, p 230.

[17] Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

from the spectrophotometric data using the expression[18] $k = (2.303/t) \log [(A_\infty - A_0)/(A_\infty - A_t)]$. Here t is the time after mixing, A_∞ is the absorbance at infinite time, A_0 is the absorbance at zero time, and A_t is the absorbance at time t. The stock solutions prepared for the potentiometric measurements had pH 4.7 ± 0.2. Under these conditions at 25°, measurements of the disappearance of the 6452-cm^{-1} band with solutions having $[Co(NH_3)_5OH_2^{3+}] = 0.100$ and 0.010 M gave $k = 0.054 \pm 0.005$ min^{-1}. Measurements of the growth of the 5988-cm^{-1} band with solutions 0.050 and 0.005 M yielded a value of $k = 0.051 \pm 0.005$ min^{-1}. These correspond to a second-order rate constant of *ca.* 2×10^6 M^{-1} sec^{-1} similar to the value reported[19] for $Co(NH_3)_6^{3+}$ of 1.6×10^6 M^{-1} sec^{-1}.

Emf Measurements.—The general procedures, the cell, and the associated vibrating-reed electrometer circuitry have been described before.[20] The H_3O^+ and D_3O^+ concentrations of the solutions were measured at 25 ± 0.05° with the cell

$$\begin{array}{c|c|c||c||c|c} \mathrm{Ag} & \mathrm{AgCl} & \begin{array}{c} 10\ \mathrm{m}M\ \mathrm{Cl^-} \\ 290\ \mathrm{m}M \\ \mathrm{ClO_4^-} \\ 300\ \mathrm{m}M \\ \mathrm{Na^+} \end{array} & \begin{array}{c} 300\ \mathrm{m}M \\ \mathrm{NaClO_4} \end{array} & \begin{array}{l} H\ \mathrm{m}M\ \mathrm{H_3O^+}\ \mathrm{(D_3O)^+} \\ C_\mathrm{M}\ \mathrm{m}M\ \mathrm{Co(NH_3)_5OH^{3+}} \\ \quad \mathrm{(Co(ND_3)_5OD_2{}^{3+})} \\ 300-3C_\mathrm{M}-H\ \mathrm{m}M\ \mathrm{Na^+} \\ 300\ \mathrm{m}M\ \mathrm{ClO_4^-} \end{array} & \begin{array}{l} \text{Glass} \\ \text{elec-} \\ \text{trode} \end{array} \end{array}$$

The standard "Wilhelm" type of reference electrode was used.[21] For the measurements with the deuterium oxide solutions, the solutions were made up with D_2O throughout, and the glass electrode was stored in D_2O. Beckman Type 40498 electrodes were used. Although the suitability of the glass electrode for measurements in D_2O solutions has been challenged,[5] they appear to give reliable results.[6,11,22-26] The electrodes were calibrated as concentration probes in the constant ionic medium. The parameters $E°$ and k in the expression $E = E° + 59.152 \log [H^+] + k[H^+]$ were determined from titrations of excess $HClO_4$ *vs.* NaOH or $DClO_4$ *vs.* NaOD in the same solutions used to obtain the data on the dissociation of the ammine complex. In the 0.300 M perchlorate ionic medium, $k = -0.172$ mV/mM with protium oxide and -0.05 mV/mM with deuterium oxide. The smaller value for the junction potential term with D_2O is to be expected because of the lower mobility of the oxonium ion in the latter solvent. A few data also were collected with a fast titration technique as exchange was occurring. A solution of $Co(NH_3)_5OH_2^{3+}$ in H_2O was added to D_2O, and several data sets were obtained in a few minutes.

Flow Measurements.—In order to titrate the partially exchanged species $Co(NH_3)_5OD_2^{3+}$, a procedure was devised whereby concentrated solutions containing $Co(NH_3)_5OH^{3+}$ in H_2O could be diluted very rapidly with D_2O and subsequently titrated with NaOD. The apparatus diagrammed in Figure 1 was used to collect data within a fraction of 1 sec after titration of the ammine complex in D_2O at $\bar{n}$, the average number of protons transferred per aquopentaamminecobalt(III) ion, ≈0.5. The solvent reservoir was constructed either from Pyrex glass or, in some later experiments, from stainless steel. The motor-driven piston burets were Aminco-Koegel Menisco-matic burets, American Instrument Co., Silver Springs, Md. They were equipped with 32-ml titrant reservoirs. The mixing chamber was constructed from a solid block of Plexiglas with offset inlet jets for the two solutions. A Beckman 40310 electrode was used. The apparatus was housed in a room maintained at 25 ± 2°.

The concentrated acidic solution of the aquopentaamminecobalt(III) ion was injected into a stream of 99.5 mol % D_2O. This solution was then mixed with an NaOD solution. By varying the relative volumes of the D_2O solution and of NaOD, different degrees of neutralization were obtained. For example, 45 ml of D_2O was streamed with 5.130 ml of a solution 50.03 mM in $Co(NH_3)_5OH_2^{3+}$. During this time, 1.224 ml of 0.1035 M NaOD was added. The degree of neutralization, which within the experimental error is equal to $\bar{n}$, was then 0.494 at the mixing chamber. The complex was titrated with OD^- within 10 sec after it was streamed with D_2O. Each run was of 3-min duration, a sufficient period for the electrode to attain a constant potential.

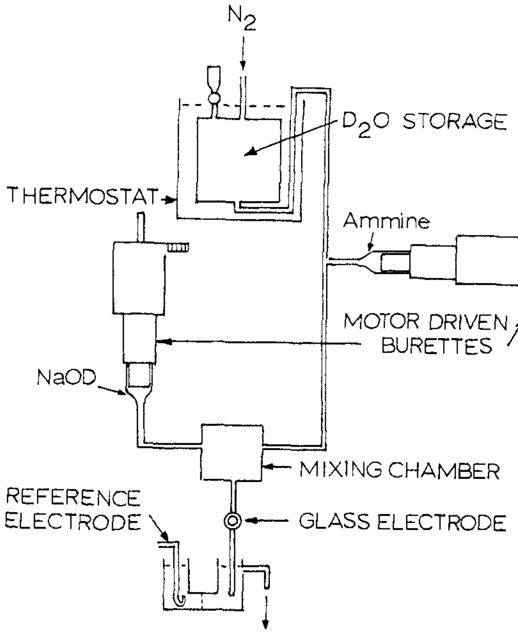

Figure 1.—Flow system for the titration of $Co(NH_3)_5OD_2^{3+}$ in D_2O.

Since the diluted amine complex solution was still slightly acidic, exchange was negligible during this period. The hydrogen isotopic composition of the final solution was calculated from the initial volumes of protium and deuterium oxide. It was 89 mol % deuterium.

Spectrophotometric Measurements.—Absorbance data were obtained at 25.00 ± 0.05° using a Cary Model 14 recording spectrophotometer equipped with a thermostated cell compartment. The solutions were matched against blanks containing 0.300 M $NaClO_4$ in either H_2O or 99.9 mol % D_2O, and 1-cm quartz cells were used throughout. All solutions containing deuterium were prepared under dry nitrogen gas to prevent isotopic dilution, and the solutions were filtered under the same gas prior to the absorbance measurements. The absorbance values were varied as a function of pH by mixing a solution of $[Co(NH_3)_5OH_2](ClO_4)_3$ with standard $HClO_4$ or NaOH and adjusting $[ClO_4^-]$ to 0.300 M. The D_2O solutions were prepared in a similar way. Molar absorptivities of $[Co(NH_3)_5OH_2](ClO_4)_3$ and $[Co(ND_3)_4OD_2](ClO_4)_3$ were obtained from measurements on solutions with pH 3. The values for $[Co(NH_3)_5OH](ClO_4)_2$ and $[Co(ND_3)_5OD](ClO_4)_2$ were obtained with solutions adjusted to pH 11. Experiments at pH 12.6 showed that the absorbance, particularly in the ultraviolet region, increased appreciably in the time needed for the measurements probably because of base hydrolysis of the complex. No such drift was observed at pH 11. The absorbance values for the acid and conjugate base represent the average of nine independent measurements each. The remaining absorbance values were measured in triplicate. Mass spectrometric determination of the isotopic distribution of the aquopentaamminecobalt(III) solutions indicated that they still contained more than 99 mol % deuterium.

Results

Calculation of the Equilibrium Constants from Emf Data.—The emf data were subjected to least-squares

---

[18] F. Basolo, J. W. Palmer, and R. G. Pearson, *J. Am. Chem. Soc.*, **82**, 1073 (1960).

[19] J. W. Palmer and F. Basolo, *J. Inorg. Nucl. Chem.*, **15**, 279 (1960).

[20] C. E. Freidline and R. S. Tobias, *Inorg. Chem.*, **5**, 354 (1966).

[21] W. Forsling, S. Hietanen, and L. G. Sillén, *Acta Chem. Scand.*, **6**, 901 (1952).

[22] V. Gold and B. M. Lowe, *J. Chem. Soc.*, *A*, 936 (1967).

[23] P. K. Glascoe, *J. Phys. Chem.*, **69**, 4416 (1965).

[24] D. Bunn, F. S. Dainton, and S. Dickworth, *Trans. Faraday Soc.*, **57**, 1131 (1961).

[25] N. C. Li, P. Lang, and R. Mathur, *J. Phys. Chem.*, **65**, 1074 (1961).

[26] K. Mikkelson and S. O. Nielsen, *ibid.*, **64**, 632 (1960).

refinements using[27] the FORTRAN-60 program GAUSS Z and the University of Minnesota CDC-1604 computer. This program minimizes the quantity $\Sigma_i w_i(\bar{n}_{i,\text{obsd}} - \bar{n}_{i,\text{calcd}})^2$ where w_i is a weighting factor.

The input data for this calculation are the total aquopentaammine concentration, the measured pH, and experimental $\bar{n}$ values. For reasons discussed earlier[20] equal weights were employed in the refinement. The pH (or pD) value at $\bar{n} = 0.5$ was used as the input value of the equilibrium constant. (The refined values are listed in Table III, and the observed and calculated $\bar{n}$ values from the last cycle of the least-squares refinement are given in Table IV.)

Calculation of the Equilibrium Constants from the Spectrophotometric Data.—A modification of the GAUSS method program described above was written in order to carry out a least-squares refinement of the spectrophotometric data. In this program, GAUSS AB, the quantity minimized is $\Sigma_i w_i(A_{i,\text{obsd}} - A_{i,\text{calcd}})^2$ where A is the solution absorbance.[28] The input data for these calculations are the independently measured absorptivities of the acid and conjugate base, the observed absorbance of the solution, and the pH of the solution. The pH values of these solutions were calculated using the equilibrium constants obtained from the standard emf measurements. Experimental determination of the pH of some of the solutions used in the spectrophotometric measurements, using the cell described above for standard emf measurements, gave values equal within the anticipated experimental error to those calculated. The values of the constants obtained from the emf measurements were used as input values for the least-squares refinement. In these calculations, w_i was set equal to unity, since an examination of the effect of errors in the ammine concentration, the value of $[H^+]$, the measured absorbance, and the two molar absorptivities indicated that the weights would not be greatly different for the different points. The molar absorptivities are listed in Table I for the different wavelengths studied. A comparison with data obtained by other workers using the same cation (though not necessarily the same anion) is given in Table II. The agreement is generally reasonable, although errors are difficult to estimate. The refined values of the equilibrium constants are given in Table III, and the observed and calculated absorbances from the last cycle of the least-squares refinement are listed in Table IV.

TABLE I

MOLAR ABSORPTIVITIES (cm^{-1} M^{-1}) AT DIFFERENT WAVELENGTHS

λ, Å	[Co-$(NH_3)_5OH_2$]-$(ClO_4)_3$	[Co-$(ND_3)_5OD_2$]-$(ClO_4)_3$	[Co-$(NH_3)_5OH$]-$(ClO_4)_2$	(Co-$(ND_3)_5OD$]-$(ClO_4)_2$
5500	20.3	18.2	38.7	36.2
5400	26.9	24.6	47.1	44.6
5300	33.65	31.35	55.3	53.2
5200	39.3	37.3	62.4	60.6
5100	43.7	42.1	66.6	66.0
5000	46.45	45.0	67.0	67.5
4900	47.3	46.2	63.4	64.5
4000	8.2	6.9	38.4	35.1
3900	10.3	8.7	51.6	48.9
3800	16.7	14.5	60.4	59.55
3700	26.65	23.7	63.1	63.35
3600	36.8	34.0	60.8	61.75

TABLE II

MOLAR ABSORPTIVITIES (cm^{-1} M^{-1}) AT SELECTED WAVELENGTHS

λ, Å	$Co(NH_3)_5OH_2^{3+}$	$Co(ND_3)_5OD_2^{3+}$	$Co(NH_3)_5OH^{2+}$	$Co(ND_3)_5OD^{2+}$
5500	20.3,[c] 21.0[a]	18.2,[c] 19.2[a]		
5000	46.45,[c] 47.0[a]	45.0,[c] 45.3[a]	67.0,[c] 66.8[a]	67.4,[c] 69.2[a]
5040[d]			67.2[c]	
5020[d]				67.6[c]
4910[d]	47.3,[c] 47.5[b]			
4890[d]		46.2,[c] 46.2[b]		
3700[d]			63.4[c]	
3680[d]				63.6[c]
3450[d]	44.3,[c] 44.8[b]			
3430[d]		43.2,[c] 43.2[b]		

[a] A. W. Adamson and F. Basolo, *Acta Chem. Scand.*, **9**, 1261 (1955). [b] Reference 9. [c] This work. [d] Band maxima.

TABLE III

REFINED VALUES OF THE EQUILIBRIUM CONSTANTS AND THEIR STANDARD ERRORS[a]

Method	Log K_H	Log K_D	Log (K_H/K_D)
Standard emf (K_D in 99 mol % D_2O)	−6.217 ±0.004 (242, ±0.022)	−6.702 ±0.002 (52, ±0.005)	0.485 ±0.005
Spectrophotometric (K_D in 99 mol % D_2O)	−6.216 ±0.002 (108, ±0.008)	−6.702 ±0.002 (96, ±0.01)	0.486 ±0.003
Fast titration (K_D in 89 mol % D_2O)	−6.184 ±0.003 (20, ±0.008)	−6.78 ±0.01 (23, ±0.01)	0.59 ±0.01
Flow system (K_D in 89 mol % D_2O)	−6.223 ±0.004 (4, ±0.004)	−6.748 ±0.001 (5, ±0.002)	0.525 ±0.004

[a] The number of experimental points used in calculating the constants and the standard error to the fit are given in parentheses.

Discussion

The results from the spectrophotometric and potentiometric measurements are not strictly independent of one another. The quantity $\bar{n}$ can be expressed in terms of the master variable $\alpha = {}^*K_1[H^+]^{-1}$, $\bar{n} = \alpha/(1 + \alpha)$. Similarly, the equilibrium concentration of the hydroxopentaamminecobalt(III) ion is given by $[M] = C_M(1 + \alpha)^{-1}$ where C_M is the total cobalt ammine concentration. Since the aquopentaamminecobalt(III) ion is a weak acid, $\bar{n}$ in the range of interest is essentially equal to the degree of neutralization of the complex and can be calculated from the solution stoichiometry. Experimental measurement of $[H^+]$ than permits the calculation of $^*K_1$. The absorbance of the solutions also can be expressed as a function of α, the path length l, the molar absorptivities of the aquo acid $\epsilon_{a\lambda}$ and of the conjugate base $\epsilon_{b\lambda}$, and the total cobalt ammine concentration C_M. Thus

$$A/l = \{\epsilon_{b\lambda}\alpha + \epsilon_{a\lambda}\}C_M/(1 + \alpha)$$

Measurement of the solution absorbance at different wavelengths and different stoichiometries gives only values of the master variable α. Once again, in order

---

(27) R. S. Tobias and M. Yasuda, *Inorg. Chem.*, **2**, 1307 (1963).

(28) Deck listings of all of the least-squares programs may be obtained by writing to R. S. T.

Table IV

Calculated and Observed $\bar{n}$ and Absorbance Values[a]

MCONC	-LOG H	NOBS	NCAL
PROTIUM OXIDE			
8.246	3.014	-.010	.001
8.233	3.104	-.010	.001
8.219	3.207	-.008	.001
8.206	3.328	-.004	.001
8.192	3.517	-.002	.002
8.179	3.831	.001	.004
8.166	4.261	.006	.011
8.152	4.699	.028	.029
8.139	4.929	.050	.049
8.126	5.114	.072	.073
8.113	5.240	.094	.095
8.100	5.339	.116	.117
8.086	5.417	.138	.137
8.073	5.494	.160	.159
8.047	5.622	.205	.202
8.022	5.745	.249	.252
7.996	5.827	.300	.289
7.971	5.917	.338	.334
7.945	6.005	.382	.380
7.920	6.064	.426	.413
7.895	6.144	.471	.458
7.870	6.218	.515	.500
7.846	6.297	.559	.546
7.821	6.379	.603	.592
7.797	6.454	.648	.633
7.773	6.541	.692	.678
7.748	6.632	.736	.722
7.725	6.734	.781	.767
7.701	6.846	.825	.810
7.689	6.909	.847	.831
7.677	6.976	.869	.851
7.665	7.050	.892	.872
7.654	7.143	.914	.894
7.642	7.243	.936	.914
7.630	7.376	.958	.935
7.619	7.523	.980	.953
7.607	7.772	1.000	.973
7.596	8.296	1.000	.992
7.584	8.938	1.000	.998
7.572	9.410	1.001	.999
7.561	9.711	1.001	1.000
7.550	9.966	1.001	1.000
7.538	10.159	1.001	1.000
7.527	10.282	1.002	1.000
7.516	10.402	1.002	1.000
7.504	10.492	1.002	1.000
8.630	2.206	-.000	.000
8.593	2.240	.000	.000
8.520	2.324	.000	.000
8.448	2.420	.000	.000
8.413	2.481	.001	.000
8.179	3.645	.013	.003
8.166	4.083	.018	.007
8.152	4.563	.033	.022
8.146	4.739	.043	.032
8.139	4.860	.054	.042
8.132	4.953	.064	.052
8.119	5.113	.086	.073
8.106	5.241	.107	.096
8.086	5.392	.141	.130
8.060	5.549	.185	.177
8.035	5.670	.229	.221
8.009	5.783	.273	.269
7.983	5.872	.318	.311
7.958	5.963	.362	.358
7.933	6.041	.406	.400
7.914	6.105	.440	.436
7.901	6.143	.462	.457
7.895	6.164	.473	.469
7.889	6.183	.484	.480
7.883	6.202	.495	.491
7.870	6.243	.517	.515
7.858	6.283	.539	.538
7.846	6.313	.561	.555
7.833	6.361	.584	.582
7.821	6.403	.606	.605
7.809	6.439	.628	.625
7.791	6.502	.661	.658
7.760	6.614	.717	.714
7.731	6.740	.772	.769
7.701	6.875	.827	.820
7.671	7.061	.883	.875
7.642	7.302	.938	.924
7.625	7.517	.971	.952
7.607	7.950	1.004	.982
8.207	3.461	-.017	.002
8.194	3.742	-.015	.003
8.181	4.200	-.007	.010
8.167	4.639	.011	.026
8.154	4.905	.030	.046
8.141	5.104	.052	.072
8.127	5.216	.074	.091
8.114	5.322	.096	.113
8.101	5.413	.118	.136
8.088	5.492	.141	.158
8.075	5.561	.162	.181
8.049	5.682	.207	.226
8.023	5.786	.251	.270
7.998	5.880	.296	.315
7.972	5.964	.340	.358
7.947	6.046	.384	.403
7.922	6.126	.428	.447
7.897	6.203	.473	.492
7.872	6.279	.517	.535
7.847	6.348	.561	.575
7.823	6.429	.606	.620
7.798	6.517	.650	.666
7.774	6.603	.694	.709
7.750	6.705	.739	.755
7.726	6.819	.783	.800
7.702	6.944	.827	.842
7.690	7.005	.849	.860
7.679	7.086	.872	.881
7.667	7.183	.894	.902
7.655	7.290	.916	.922
7.644	7.450	.938	.945
7.632	7.634	.960	.963
7.620	8.033	.982	.985
7.609	8.637	1.004	.996
4.632	3.055	-.035	.001
4.624	3.179	-.038	.001
4.615	3.338	-.037	.001
4.607	3.585	-.036	.002
4.600	4.119	-.027	.008
4.590	4.775	.006	.035
4.579	5.129	.042	.075
4.570	5.344	.086	.118
4.562	5.508	.130	.163
4.554	5.625	.174	.204
4.545	5.736	.218	.248
4.537	5.837	.263	.294
4.529	5.924	.307	.338
4.521	6.005	.351	.380
4.513	6.076	.396	.420
4.505	6.168	.440	.472
4.496	6.240	.484	.513
4.488	6.324	.529	.561
4.480	6.400	.573	.604
4.472	6.482	.617	.648
4.464	6.569	.662	.692
4.456	6.662	.706	.736
4.448	6.774	.750	.783
4.440	6.895	.795	.826
4.433	7.036	.839	.868
4.425	7.224	.884	.910
4.417	7.518	.928	.952
4.412	8.148	.971	.988
4.404	9.425	1.015	.999
4.682	2.641	-.025	.000
4.596	3.491	-.003	.002
4.587	3.876	.027	.005
4.579	4.594	.008	.023
4.570	5.043	.068	.063
4.562	5.291	.112	.106
4.554	5.459	.156	.149
4.545	5.602	.200	.195
4.536	5.726	.249	.244
4.529	5.818	.289	.285
4.521	5.906	.334	.328
4.513	6.010	.378	.383
4.505	6.074	.423	.418
4.496	6.151	.467	.462
4.488	6.224	.512	.504
4.480	6.299	.557	.547
4.472	6.376	.601	.590
4.464	6.452	.646	.632
4.456	6.536	.690	.676
4.448	6.620	.735	.717
4.440	6.717	.779	.760
4.433	6.824	.824	.802
4.425	6.942	.868	.842
4.417	7.089	.913	.882
4.409	7.289	.958	.922
4.401	7.619	1.002	.962
4.394	8.502	1.046	.995
5.000	4.268	.010	.011
4.990	4.985	.042	.055
4.980	5.271	.088	.102
4.970	5.447	.133	.145
4.960	5.593	.178	.192
4.950	5.709	.222	.237
4.941	5.816	.267	.284
4.931	5.898	.312	.324
4.921	5.991	.356	.373
4.912	6.071	.401	.417
4.902	6.150	.446	.461
4.892	6.225	.490	.505
4.883	6.302	.535	.549
4.873	6.376	.579	.591
4.864	6.457	.624	.635
4.854	6.536	.668	.676
4.845	6.625	.713	.719
4.836	6.723	.757	.762
4.826	6.825	.802	.802
4.817	6.949	.847	.843
4.798	7.290	.936	.922
4.789	7.603	.980	.961
5.000	4.300	.010	.012
4.990	4.939	.042	.050
4.980	5.234	.088	.094
4.970	5.428	.133	.140
4.960	5.576	.178	.186
4.950	5.696	.222	.232
4.941	5.802	.267	.278
4.931	5.894	.312	.322
4.921	5.983	.356	.369
4.912	6.066	.401	.414
4.902	6.139	.446	.455
4.892	6.216	.490	.499
4.883	6.292	.535	.543
4.873	6.369	.579	.587
4.864	6.447	.624	.629
4.854	6.528	.668	.672
4.845	6.621	.713	.717
4.836	6.711	.757	.757
4.826	6.820	.802	.800
4.817	6.936	.847	.840
4.808	7.087	.891	.881
4.798	7.297	.936	.923
.998	4.662	.022	.027
.996	5.018	.035	.059
.994	5.249	.084	.097
.992	5.426	.130	.139
.990	5.562	.176	.181
.988	5.673	.221	.222
.986	5.768	.266	.262
.984	5.861	.311	.306
.982	5.943	.356	.347
.980	6.022	.401	.390
.978	6.093	.446	.429
.976	6.159	.490	.467
.975	6.230	.535	.507
.973	6.300	.580	.548
.971	6.372	.625	.588
.969	6.444	.670	.627
.967	6.514	.714	.664
.965	6.583	.759	.699
.963	6.657	.804	.734
.961	6.741	.848	.770
.960	6.837	.893	.807
.958	6.941	.938	.841
.956	7.073	.982	.878
DEUTERIUM OXIDE			
11.026	4.770	.001	.012
10.982	5.376	.038	.045
10.938	5.653	.075	.082
10.895	5.831	.113	.119
10.875	5.900	.131	.136
10.852	5.965	.150	.155
10.831	6.024	.169	.174
10.810	6.080	.188	.193
10.789	6.129	.207	.211
10.768	6.175	.225	.229
10.747	6.219	.244	.248
10.726	6.263	.263	.267
10.705	6.300	.282	.284
10.684	6.341	.300	.304
10.663	6.379	.319	.323
10.643	6.417	.338	.342
10.622	6.450	.357	.359
10.602	6.483	.376	.377
10.582	6.518	.394	.396
10.561	6.551	.413	.414
10.541	6.573	.432	.427
10.521	6.615	.451	.450
10.501	6.647	.469	.469
10.481	6.680	.488	.488
10.461	6.713	.507	.506
10.441	6.746	.526	.525
10.422	6.777	.544	.544
10.402	6.809	.563	.562
10.382	6.843	.582	.581
10.363	6.875	.601	.599
10.343	6.911	.620	.618
10.324	6.945	.638	.637
10.305	6.982	.657	.656
10.285	7.018	.676	.675
10.264	7.057	.695	.694
10.247	7.093	.713	.711
10.228	7.134	.736	.730
10.209	7.174	.751	.748
10.190	7.219	.770	.767
10.172	7.267	.788	.786
10.153	7.316	.807	.805
10.134	7.368	.826	.823
10.116	7.428	.845	.842
10.097	7.491	.864	.860
10.079	7.561	.882	.879
10.057	7.658	.905	.900
10.042	7.739	.920	.916
10.024	7.844	.939	.933
10.005	7.987	.958	.951
9.987	8.191	.976	.969
9.969	8.534	.995	.985
9.951	9.344	1.014	.998
FAST TITRATION H20			
9.615	6.081	.446	.441
9.615	6.099	.446	.451
9.597	6.126	.468	.466
9.597	6.140	.468	.474
9.579	6.173	.490	.493
9.557	6.218	.517	.519
9.557	6.232	.517	.527
9.537	6.262	.541	.545
9.537	6.277	.541	.553
9.517	6.307	.566	.570
9.517	6.319	.566	.577
9.588	6.127	.479	.467
9.588	6.131	.479	.469
9.571	6.169	.499	.491
9.571	6.175	.499	.495
9.542	6.225	.535	.523
9.542	6.239	.535	.531
9.520	6.279	.561	.554
9.520	6.279	.561	.554
9.579	6.185	.490	.500
FAST TITRATION D20			
1.985	6.645	.414	.424
1.980	6.820	.518	.524
1.978	6.933	.600	.588
1.974	7.171	.704	.712
1.970	7.410	.807	.811
1.986	6.562	.393	.378
1.980	6.738	.518	.477
1.978	6.850	.600	.541
1.974	7.106	.704	.681
1.985	6.562	.409	.379
1.980	6.740	.518	.478
1.978	6.849	.600	.541
1.974	7.105	.704	.680
1.985	6.679	.393	.443
1.980	6.854	.518	.544
1.978	6.967	.600	.607
1.974	7.205	.704	.728
1.970	7.444	.807	.823
1.986	6.679	.393	.444
1.982	6.855	.497	.544
1.979	6.969	.579	.608
1.974	7.207	.703	.729
1.970	7.446	.807	.823
FLOW SYSTEM H20			
49.980	6.224	.495	.501
50.010	6.221	.499	.499
49.990	6.218	.500	.497
49.980	6.207	.494	.491
FLOW SYSTEM D20			
49.970	6.727	.470	.488
49.980	6.734	.494	.492
50.010	6.729	.489	.489
49.980	6.738	.494	.495
49.990	6.740	.493	.496

-LOG H	AOBS	ACAL
*** MCONC = 10.00 ***		
PROTIUM OXIDE		
LAMBDA = 5500 A		
5.466	.234	.231
5.722	.248	.248
5.948	.266	.267
6.118	.286	.285
6.305	.301	.304
6.498	.324	.324
6.640	.337	.337
6.820	.351	.350
6.984	.362	.360
LAMBDA = 5400 A		
5.466	.301	.299
5.722	.318	.318
5.948	.342	.340
6.118	.361	.359
6.305	.377	.380
6.498	.401	.402
6.640	.417	.416
6.820	.431	.431
6.984	.443	.442
LAMBDA = 5300 A		
5.466	.370	.369
5.722	.390	.389
5.948	.413	.412
6.118	.433	.433
6.305	.453	.456
6.498	.478	.479
6.640	.495	.494
6.820	.513	.510
6.984	.525	.521
LAMBDA = 5200 A		
5.466	.428	.428
5.722	.449	.449
5.948	.476	.474
6.118	.494	.496
6.305	.517	.520
6.498	.542	.545
6.640	.562	.561
6.820	.579	.578
6.984	.593	.590
LAMBDA = 5100 A		
5.466	.473	.472
5.722	.493	.493
5.948	.520	.517
6.118	.541	.539
6.305	.563	.563
6.498	.585	.587
6.640	.605	.603
6.820	.621	.620
6.984	.633	.633
LAMBDA = 5000 A		
5.466	.497	.497
5.722	.516	.516
5.948	.541	.538
6.118	.558	.557
6.305	.581	.579
6.498	.599	.600
6.640	.615	.614
6.820	.630	.629
6.984	.642	.640
LAMBDA = 4900 A		
5.466	.499	.497
5.722	.514	.512
5.948	.533	.529
6.118	.548	.544
6.305	.566	.562
6.498	.578	.579
6.640	.593	.590
6.820	.604	.602
6.984	.612	.611
LAMBDA = 4000 A		
5.466	.128	.128
5.722	.159	.155
5.948	.188	.188
6.118	.217	.216
6.305	.247	.248
6.498	.277	.280
6.640	.300	.301
6.820	.322	.324
6.984	.343	.340
LAMBDA = 3900 A		
5.466	.167	.165
5.722	.210	.203
5.948	.247	.248
6.118	.287	.286
6.305	.326	.331
6.498	.369	.374
6.640	.402	.403
6.820	.432	.434
6.984	.458	.456
LAMBDA = 3800 A		
5.466	.237	.233
5.722	.280	.273
5.948	.317	.320
6.118	.361	.361
6.305	.405	.408
6.498	.449	.454
6.640	.483	.484
6.820	.516	.517
6.984	.543	.540
LAMBDA = 3700 A		
5.466	.323	.322
5.722	.361	.355
5.948	.390	.394
6.118	.428	.428
6.305	.462	.467
6.498	.501	.506
6.640	.532	.531
6.820	.558	.558
6.984	.579	.578
LAMBDA = 3600 A		
5.466	.405	.404
5.722	.432	.426
5.948	.450	.452
6.118	.477	.475
6.305	.496	.500
6.498	.523	.526
6.640	.542	.542
6.820	.561	.560
6.984	.574	.573
DEUTERIUM OXIDE		
LAMBDA = 5500 A		
5.991	.210	.211
6.225	.227	.227
6.489	.248	.250
6.567	.254	.258
6.658	.270	.267
6.788	.283	.281
6.975	.297	.299
7.140	.314	.314
LAMBDA = 5400 A		
5.991	.280	.279
6.225	.297	.296
6.489	.319	.322
6.567	.333	.331
6.658	.346	.341
6.788	.360	.356
6.975	.373	.376
7.140	.394	.393
LAMBDA = 5300 A		
5.991	.349	.349
6.225	.368	.368
6.489	.393	.397
6.567	.405	.406
6.658	.421	.417
6.788	.435	.434
6.975	.452	.456
7.140	.475	.474
LAMBDA = 5200 A		
5.991	.413	.411
6.225	.432	.431
6.489	.463	.462
6.567	.475	.472
6.658	.489	.484
6.788	.504	.501
6.975	.524	.525
7.140	.545	.544
LAMBDA = 5100 A		
5.991	.462	.460
6.225	.481	.481
6.489	.509	.512
6.567	.524	.522
6.658	.538	.534
6.788	.554	.552
6.975	.575	.577
7.140	.597	.596
LAMBDA = 5000 A		
5.991	.488	.487
6.225	.505	.506
6.489	.532	.535
6.567	.546	.545
6.658	.560	.557
6.788	.575	.574
6.975	.598	.597
7.140	.614	.615
LAMBDA = 4900 A		
5.991	.492	.492
6.225	.508	.508
6.489	.530	.532
6.567	.538	.539
6.658	.554	.549
6.788	.564	.563
6.975	.583	.581
7.140	.599	.596
LAMBDA = 4000 A		
5.991	.119	.115
6.225	.139	.140
6.489	.171	.176
6.567	.190	.188
6.658	.204	.203
6.788	.223	.224
6.975	.250	.253
7.140	.275	.276
LAMBDA = 3900 A		
5.991	.158	.153
6.225	.188	.188
6.489	.236	.240
6.567	.263	.257
6.658	.285	.278
6.788	.309	.308
6.975	.348	.349
7.140	.380	.382
LAMBDA = 3800 A		
5.991	.224	.218
6.225	.258	.258
6.489	.311	.316
6.567	.342	.336
6.658	.360	.359
6.788	.391	.393
6.975	.438	.439
7.140	.473	.475
LAMBDA = 3700 A		
5.991	.306	.302
6.225	.336	.336
6.489	.380	.388
6.567	.409	.405
6.658	.427	.425
6.788	.450	.455
6.975	.498	.496
7.140	.525	.528
LAMBDA = 3600 A		
5.991	.385	.385
6.225	.404	.409
6.489	.434	.445
6.567	.456	.457
6.658	.465	.472
6.788	.486	.493
6.975	.520	.521
7.140	.540	.543

[a] All aquopentaamminecobalt(III) concentrations in millimoles per liter.

to calculate $^*K_1$, values of $[H^+]$ must be obtained experimentally. Consequently, there is one type of error in the value of log $^*K_1$ which would go undetected in this work. If *all* values of the solution pH were in error by a constant amount, *e.g.*, if they were all 0.1 unit too large, the p$^*K_1$ value calculated by both the potentiometric and the spectrophotometric methods would then be 0.1 unit too large. This follows from the relation $\log \alpha = \mathrm{pH} - \mathrm{p}^*K_1$.

While small errors might be made in the determination of the cell $E°$ giving a constant error in log $[H^+]$, these should be randomized by the different sets of data. Errors in the pH data other than one which is constant throughout would give systematic deviations between the calculated and observed $\bar{n}$ and A data, and an examination of the data in Table IV indicates that these are absent.

The agreement obtained between the standard potentiometric data and the spectrophotometric data is excellent: $\log K_H = -6.217 \pm 0.010$ and -6.216 ± 0.005; $\log K_D = -6.702 \pm 0.005$ and -6.702 ± 0.005, respectively. In this discussion the errors are those at the 99% confidence level.[29] The values for H_2O are in good agreement with those of earlier workers: $\log {}^*K_H = -6.16$, 0.25 M NH_4NO_3, 30°;[10] -6.55, 1 M $NaNO_3$, 25°.[30] The most likely source of error in

---

(29) Tables of the "t" test of significance were used: see, for example, R. A. Fisher, "Statistical Methods for Research Workers," Hafner Publishing Co., New York, N. Y., 1954, p 174.

(30) G. E. Shaffer, quoted by L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964.

the earlier spectrophotometric measurements lies in the molar absorbtivity of the conjugate base since this species is slowly hydrolyzed in strongly basic solution.

The rate of exchange of the ammine hydrogen in similar complexes has been observed to vary inversely with the hydrogen ion concentration,[18,19] and Taube has suggested that this is probably the case with the aquopentaamminecobalt(III) ion.[9] Assuming this inverse first-order dependence obtains, the order of magnitude of the half-life for exchange of the ammine hydrogens of $Co(NH_3)_5OH_2^{3+}$ in D_2O at $\bar{n} \approx 0.5$ and pD ~6.7 is *ca.* 8 sec.

With the flow system, no appreciable ammine hydrogen exchange will have occurred at the time the $[H^+]$ is determined, but the exchange of the aquo protons is so rapid that these will have essentially the same composition as the solvent. The small number of points collected is a consequence of the large volumes of D_2O which were consumed in the 3-min flow measurements. Because of the high rate of exchange, the data in the fast titrations span the entire period during which exchange was taking place.

Values of the dissociation constant in H_2O were determined by the fast titration and flow techniques to assess the systematic errors inherent in these measurements. As can be seen from the results listed in Table III, the value from the flow measurements is in very good agreement with those from the standard emf and spectrophotometric procedures. The agreement of the fast titration value is poorer, probably a consequence of the short times allowed for the glass electrode to attain equilibrium.

Using a linear extrapolation, the value of log K_D for 100 mol % D_2O is -6.81 from both the flow and rapid titration measurements. Considering the errors in the rapid titrations, the agreement is probably fortuitous. This gives log $(K_H/K_D) = 0.59$ compared to 0.48 from the standard emf and spectrophotometric measurements. The former value involves the equilibrium constants for reactions 2 and 3, while the latter depends on the values for reactions 1 and 3. While the ratio of the dissociation constants of the complexes with the same isotopic composition as the solvent is considerably larger than reported by Taube, these data also indicate a small secondary isotope effect of *ca.* 0.11 log unit in the quantity log (K_H/K_D).

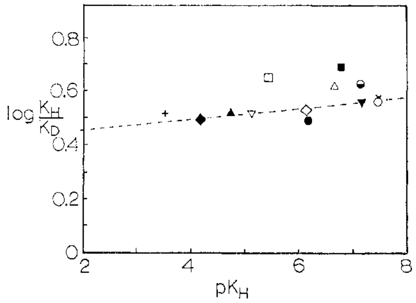

Figure 2.—The equilibrium isotope effect on the dissociation of several different acids: ◆, benzoic acid; △, acetic acid; ▽, 2,5-dinitrophenol; △, 3,5-dinitrophenol; ◇, brom thymol blue; ●, $Co(NH_3)_5OH_2^{3+}$; ▼, $H_2PO_4^-$; ×, *o*-nitrophenol; ○, *p*-nitrophenol; ■, $(C_2H_5)_3Sn^+$; □, $(CH_3)_2SnOH^+$; ◒, $Pt(NH_3)_6^{4+}$.

In summary, the decrease in the dissociation constant in going from $Co(NH_3)_5OH_2^{3+}$ in H_2O to $Co(ND_3)_5OD_2^{3+}$ in D_2O is relatively typical for an acid of this strength. Figure 2 illustrates data for isotope effects on the dissociation of several acids of different structural types. Any secondary effect caused by exchange of the ammine hydrogens must be small. There has been considerable confusion in the literature concerning the magnitude of isotope effects. Relatively small errors in the values of log K_H and log K_D can lead to values of log (K_H/K_D) which apparently are anomalous. It seems unlikely that the simple aquoiron(III) and aquothallium(III) ions have the same dissociation constants in H_2O and in D_2O as reported. In these cases, the acids are rather strong, so that the isotope effect is probably relatively small. In addition, because the values of K_H are greater than 10^{-3}, they are very difficult to determine accurately. While the small secondary effects observed with the reactions of the aquopentaamminecobalt(III) ion could be explained in terms of changes in the N–H bonds in going from the reactant to product, the data on the vibrational frequencies of these bonds are all derived from infrared studies on solid complexes. It is possible that Raman spectra will permit a direct comparison of the vibrations of $Co(NH_3)_5OH_2^{3+}$ and $Co(NH_3)_5OH^{2+}$ or of $Co(NH_3)_5OH_2^{3+}$ and $Co(NH_3)_5Cl^{2+}$ in aqueous solution.