Ground State Splittings in the Iron Group, Particularly Cobaltous Ion. The Operation of Kramer's Rule

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permit the determination of the coordination number of the ion for water.

The exchange experiments with cobaltic ion are made difficult because this ion, particularly at high concentrations, oxidizes water fairly rapidly. Solutions of cobaltic perchlorate in perchloric acid were obtained by electrolytic oxidation of cobaltous perchlorate, and always contained cobaltous ion at concentrations about equal to that of cobaltic ion. The exchange experiments were conducted as described for Cr^{+++} with the difference that the various samples of water were obtained by successive distillations from a single sample of the solution in each experiment. Before the last water sample was taken, a portion of the solution was removed for analysis for Co^{+++} and then excess anhydrous hydrazine sulfate was added to the remainder of the solution to reduce the cobaltic ion to cobaltous ion. Separate experiments have shown that water is exchanged very rapidly between Co^{++}_{aq} and solvent; hence the isotopic composition of water in the final reduced sample corresponds to complete exchange. The data obtained in three experiments on the cobaltic ion exchange are presented in Table I.

TABLE I. Exchange of water between aqueous cobaltic ion and the solvent.

(Part A describes the composition and handling of the solution; Part B, the results of the isotopic analysis on the samples of water removed at the indicated intervals. Concentration is expressed as molality, time in minutes. N is the ratio $O^{18}/(O^{16} \pm O^{18})$ in water. Temperature, $O \pm 4°$.)

Part A			
Experiment No.	1	2	3
(Co^{+++})	0.510	0.430	0.406
(Total Co)	1.203	0.968	0.914
(H^+)	4.22	4.67	4.10
(ClO_4^-)	7.14	6.61	6.34
Expected decrease in $10^3 N$ for slow exchange[a]	0.24	0.26	0.20
Time elapsed between mixing and final analysis	—	19.0	47.5
% decomposition of Co^{+++} in this interval	—	1.9	4.4
Fraction of total water removed by distillation	0.52	0.20	0.14

Part B						
Experiment No. 1	Time	2.3	11.7	21.2	27.0	∞
	$10^3 N$	5.818	5.827	5.856	5.879	5.828
Experiment No. 2	Time	2.7	9.2	15.2	∞	∞
	$10^3 N$	6.313	6.327	6.330	6.356	6.370
Experiment No. 3	Time	2.2	14.4	30.1	43.3	∞
	$10^3 N$	6.114	6.103	6.114	6.084	6.138

[a] This represents the total change in $10^3 N$ expected if each Co^{+++} held back six molecules of water initially and then exchanged them during the course of the experiment.

The results show that the change in N, the isotopic composition, during each experiment is much smaller than that predicted on the basis of slow exchange of six water molecules per cobaltic ion. Indeed, the trend in N is in the opposite direction from that expected for slow exchange, and this trend has about the magnitude expected for that which would result from the fractionation of the water on repeated distillation (cf. the experiments with Co^{++}_{aq}). It may be concluded therefore that the exchange of water between aqueous cobaltic ion and the solvent is essentially complete under the conditions of our experiments by the time of the first sampling.

This result is surprising in view of the slow rates of substitution observed for Co(III) in all of the complex ions described for it. It is possible that the exchange of H_2O in this system does not proceed by direct substitution on Co^{+++}, but chooses an alternative path. If the electron exchange between aqueous cobaltous ion and cobaltic ion is rapid,[1] then Co^{++}_{aq} will be an efficient catalyst for the Co^{+++}_{aq}–H_2O exchange, since Co^{++}_{aq} does exchange coordinated water rapidly with the solvent. Further experiments are being made to measure the Co^{+++}_{aq}–H_2O exchange at much lower concentrations of Co^{++}_{aq}.

The observations on the exchange of H_2O between Co^{++}_{aq} and the solvent are presented in Table II.

TABLE II. Exchange of H_2O between Co_{aq}^{++} and solvent.

Experiment 1			
(Co^{++}) = 1.545 molal; (H^+) = 3.00 molal. Temperature 1°±1°.			
Time, min.	2.0	12.2	1600[a]
$10^3 N$	6.490	6.505	6.512

Experiment 2		
(Co^{++}) = 1.68 molal; (H^+) = 1.68 molal. Temperature 1°±1°.		
Time, min.	2.5	34
$10^3 N$	5.593	5.589

[a] The solution was allowed to warm up to room temperature in the interval between the end of the second distillation and the beginning of the third.

The data necessary for computing precise isotope balances in Experiment 2 were obtained. The value of N_∞ calculated for random mixing in the liquid is 5.660×10^{-3}, which agrees with the observed values of N within about the fractionation factor for distillation. The value of N_0 calculated for initial holdback of $6H_2O$ for each Co^{++} is 6.469×10^{-3}. For Experiment 1, N_∞ calc. and N_0^6 are ca. 6.52×10^{-3} and 7.43×10^{-3} respectively. The experiments prove that the exchange is complete within the time of the first sampling.

The isotope analyses were made in the laboratory of Professor Harold C. Urey of the Institute for Nuclear Studies, The University of Chicago, with the generous assistance of Dr. Samuel Epstein.

[1] Hoshowsky, Holmes, and McCallum, Can. J. Research 27, No. 4, 258 (1949), using various separation procedures, have observed complete electron exchange in this system within the time of separation of the ions.

Erratum: Photolysis of Methyl Iodide
[J. Chem. Phys. 18, 194 (1950)]

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THE sentence on page 195 pertaining to the infra-red analytical method should read: "CH_4 absorption at 7.7μ, C_2H_6 at 6.8μ, C_2H_4 at 10.6μ and $C_2H_2^4$ at 13.7μ were used for the analysis."

Ground State Splittings in the Iron Group, Particularly Cobaltous Ion. The Operation of Kramer's Rule

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THE theoretical treatments of the susceptibility of paramagnetic salts, such as that of Schlapp and Penney[1] who have been quite successful with the rare earths and with many of the iron group salts, have met with little success in the interpretation of the data on those of cobalt. Bose,[2] in comparing his recent measurements on the principle susceptibilities of two double salts of cobaltous sulfate down to 80°K with the theory of Schlapp and Penney,[1] was able to choose between the two possibilities they suggested but was unable to get an over-all agreement between theory and experiment. Schlapp and Penney[1] had discarded as incorrect the hydrogen temperature data of Jackson,[3] which could not be made to fit the theory. Bose corrected Jackson's data for numerical errors, but was still unable to fit the theory to all of the low temperature data.

Recent measurements[4] on the magnetic susceptibility and heat capacity of powdered $CoSO_4 \cdot 7H_2O$ below 20°K suggest further difficulties with the theory and offer evidence of means for improving it. While the susceptibility of this salt is above the "spin-only" value even at 1°K, the deviations from Curie's law in this range are quite small. The intensity of magnetization in magnetic fields approximates that of an ideal paramagnetic material with $S = \frac{3}{2}$. Heat capacity data indicate that the over-all splitting of the four lowest levels is no more than 0.1 to 0.2 cm^{-1}.

In view of the present evidence, the theoretical treatment poses the following difficulties. First, it predicts an average susceptibility somewhat less than the "spin-only" value below 20°K, which is tantamount to the assumption of a splitting of the ground quartet much over 0.2 cm^{-1}. It predicts values which are too low near 20°K, but too high near room temperature. This evidence suggests that the theory has overestimated the effect of spin-orbit coupling in the splitting of the energy levels of the crystal and in increasing the magnetic susceptibility at higher temperatures.

For the average susceptibility we can obtain curves similar to those of Schlapp and Penney[1] by a very simple approximation. This involves considering a fourfold degenerate level with $L=0$ as the ground state and an upper fourfold level with $L=1$ and correspondingly higher J-values, without any interaction between the two. This scheme can be made to fit roughly the data of Bose,[2] and will improve the fit of data below 20°K, if the separation of the two levels is taken as 67 cm^{-1}. (The heat capacity data above 10°K indicate that a fourfold level could not be centered at any lesser distance above the ground state.) Somewhat better agreement could be obtained if these levels were split into two pairs with an appreciable spacing between.

This suggests that the lowest splitting assumed by Schlapp and Penney[1] (approx. 400 cm^{-1}) may be much too high, and the spin-orbit interaction consequently overestimated. It is possible that a revision of the theory taking direct account of a fourfold lowest level and lowering both splittings and spin-orbit interaction will provide a better explanation of the data. If the splitting is much below 400 cm^{-1}, as suggested, it should be possible to detect it from either absorption spectra or heat capacity measurements above 20°K.

An additional observation may be made by comparison of the helium temperature data for $CoSO_4 \cdot 7H_2O$[4], $NiSO_4 \cdot 7H_2O$,[5] and $FeSO_4 \cdot 7H_2O$.[6] The over-all ground state splittings for these three salts from heat capacity data are approximately 0.1 cm^{-1}, 5 cm^{-1}, and 20 cm^{-1}, respectively. Of the three Co^{++} is the only one which should show Kramer's degeneracy. The data suggest that the actual degeneracy in the crystalline field may be fourfold rather than the double degeneracy required by theory. The great difference in the ground state splitting raises the possibility that the orbital splittings may be much less for ions of even multiplicity than would be expected. It is important to note that most experimental and theoretical work on the iron-group salts has dealt with nearly ideal materials, where orbital splittings were taken so large that even major changes in them would not greatly affect the results.

The suggestions above are being examined more thoroughly and a more detailed treatment is in preparation.

[1] Schlapp and Penney, Phys. Rev. 42, 667 (1932).
[2] Bose, Ind. J. Phys. 22, 276 (1948).
[3] Jackson, Phil. Trans. Roy. Soc. (London) A224, 1 (1924).
[4] Fritz and Giauque, J. Am. Chem. Soc. 71, 2168 (1949).
[5] Stout and Giauque, J. Am. Chem. Soc. 63, 714 (1941).
[6] Lyon and Giauque, J. Am. Chem. Soc. 71, 1647 (1949).

The Structure of the Carboxyl Group

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THE data currently available on the geometrical structure of the carboxyl group show a marked inconsistency between the various methods of study; this is seen in the divergent values of the C—O "single" bond length.

With α as the angle between r_1 and r_2 whose values are in A units we have:

Model	$r_1(C=O)$	$r_2(C-O)$	$\alpha°$
x-ray	1.24±0.04	1.30±0.04	125±2
e.d.	1.24±0.04	1.38±0.04	125±5
V.Z.W.	1.225	1.41	125
o.t.	1.27±0.01	1.34±0.01	126±1

The large uncertainties in r_1 and r_2 from the x-ray[1] and electron diffraction[2] data provide a fair summary of the results of many different authors for some fourteen acids. It must be remembered that while the e.d. data refer to the gaseous state, the x-ray results apply to the crystalline solid where, in some instances (e.g., oxalic acid dihydrate) special circumstances may give rise to somewhat "abnormal" values. The figure ±0.04A is about twice the uncertainty claimed in most individual estimates.

The third set shows the parameters arrived at by Van Zandt Williams from the rotational constants for formic acid[3] and its three deuterated derivatives (H·COOH, H·COOD, D·COOH, D·COOD). This interpertation of a considerable amount of quantitative spectroscopic data approximates to the e.d. values but is clearly incompatible with the large body of x-ray results.

The first feature of our reassessment of this data is the possible elimination of this important discrepancy. The fourth set of parameters, chosen as the result of a systematic trial, has been shown to be consistent with all the rotational fine structure constants for formic acid molecules to within the experimental accuracy. It is the only such set of parameters which approaches agreement with both x-ray and e.d. data.

The formate ion has $r(C=O) = 1.27 \pm 0.02$.[4] Treating its vibrations as that of a symmetrical triatomic molecule ($m = 13.018$) by the general methods of Torkington[5,6] with the assignment $\nu_1 = 1374$ cm^{-1}, $\nu_2 = 760$ cm^{-1}, $\nu_3 = 1678$ cm^{-1}, leads to principal force constants (units×10^5 dynes/cm) in the ranges,

$$f(C=O) = 10.4 \pm 1.0 : f\left(C \begin{smallmatrix} O \\ \\ O \end{smallmatrix}\right) = 1.3 \pm 0.1.$$

A similar three-particle system treatment of the formic acid molecule with $\nu_1 = 1105$ cm^{-1}, $\nu_2 = 667$ cm^{-1}, $\nu_3 = 1770$ cm^{-1}, provides the following as probably the most significant set of valence force constants.*

$$f(C=O) = 14.0 : f(C-O) = 5.00 : f\left(C \begin{smallmatrix} O \\ \\ OH \end{smallmatrix}\right) = 0.88.$$

$$f_{12}(\Delta r_1 \Delta r_2) = 1.8 : f_{13}(\Delta r_1 \Delta \alpha) = 0.6 : f_{23}(\Delta r_2 \Delta \alpha) = 0.6.$$

When a four-particle system treatment is carried out a significant change to 6.4 occurs in the value of $f(C-O)$.

A full account of the present results and of a more extended treatment of the vibrational problem, including the assignment of the fundamental vibrations of formic acid and its deuterated derivatives is in course of preparation.

[1] Wheland, The Theory of Resonance and Its Applications to Organic Chemistry (John Wiley and Sons, Inc., New York, 1947), appendix. Robertson et al., J. Chem. Soc. (London) 142 (1947); ibid., 980, 987, 993, 1001 (1949).
[2] L. O. Brockway, Rev. Mod. Phys. 8, 231 (1936); J. Karle and L. O. Brockway, J. Am. Chem. Soc. 66, 574 (1944).
[3] Van Zandt Williams, J. Chem. Phys. 15, 232 (1947); S. H. Bauer and R. M. Badger, ibid. 5, 852 (1937); H. W. Thompson, ibid. 7, 453 (1939).
[4] W. H. Zachariasen, J. Am. Chem. Soc. 62, 1011 (1940).
[5] P. Torkington, J. Chem. Phys. 17, 357 (1949).
[6] P. Torkington, J. Chem. Phys. 17, 1026 (1949).
* See footnote d of reference 6.