nickel(II) and zirconyl chlorides whose compositions lie within the ranges studied have been demonstrated as intermediates in the dehydration reactions. New hydrates have been found whose previous lack of identification may be traced to either (1) properties similar to those of known hydrates or (2) absence of thermodynamic data on the composition range wherein they exist. The results are summarized in Table I.

When hydration conditions for zirconyl chloride were adjusted so as to minimize uncertainties caused by hydrolysis, the results were analogous to those obtained by dehydration.

Acknowledgment.—To the Abbott Fund of Northwestern University and the Veterans Administration, the authors gratefully express their thanks for financial aid which helped to make this research possible.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Properties of Hydrates. II. Olation during Heterogeneous Dehydrations; Structural Formulas for Some Metal Dichloride Hydrates[1]

BY WILLIAM S. CASTOR, JR.,[2] AND FRED BASOLO

RECEIVED MAY 23, 1953

Compounds in each of the solid systems $MnCl_2 \cdot xH_2O$, $NiCl_2 \cdot xH_2O$ and $ZrOCl_2 \cdot xH_2O$ are characterized by the presence of coördinated hydroxyl groups and water molecules. As a consequence of the structural features deduced here, each of these systems reveals a peculiar dehydration behavior which can be interpreted as a series of olations. The number and kind of these condensations are determined by the number of hydroxyl groups and the geometry of the coördination. Each monomer first yields a diol dimer. The nickel and zirconyl complexes condense again, and the latter does so a third time, before olation is complete. Further dehydration then causes a decrease in coördination number from the symmetrical configuration first obtaining to the more usual symmetrical arrangement for each metal ion. The nickel and manganese salts remain chloro complexes, but the zirconyl salt probably does not. A structure suggested for the latter can account for its hydrolysis to 8-coördinated zirconia upon thermal decomposition. The stronger metal–chlorine bonds of the other complexes favor decomposition to anhydrous chlorides.

In the first paper of this series[3] it was shown that the hydrates of manganese(II) chloride are related by the reactions

$$
\begin{aligned}
MnCl_2 \cdot 4H_2O &= MnCl_2 \cdot 3^1/_2H_2O + {}^1/_2H_2O \\
MnCl_2 \cdot 3^1/_2H_2O &= MnCl_2 \cdot 3H_2O + {}^1/_2H_2O \\
MnCl_2 \cdot 3H_2O &= MnCl_2 \cdot 2H_2O + H_2O \\
MnCl_2 \cdot 2H_2O &= MnCl_2 \cdot H_2O + H_2O
\end{aligned}
$$

Similarly, the dehydration of $NiCl_2 \cdot 6H_2O$ proceeds first by a double loss of ${}^1/_2H_2O$; and dehydration of $ZrOCl_2 \cdot 9H_2O$ gives first a twofold loss of ${}^1/_2H_2O$, then a fourfold loss of ${}^1/_4H_2O$, and then again a double loss of ${}^1/_2H_2O$. This repeated occurrence of fractional hydrates is unusual, but perhaps only because other salts have not yet been scrutinized so closely. There is a certain regularity in the water losses, and it is the purpose of this paper to present an explanation of the phenomena involved.

Evidence for Coördination of Hydroxyl Groups.—The nature of the metal–oxygen bonds in hydrates has been the subject of numerous investigations,[4–13] and many conflicting hypotheses have been advanced. Although there is room for argument about details, the various data all seem consistent with the view that the linkages are generally ionic with some "covalent character."[14] Since manganese(II), nickel(II) and zirconium(IV) exhibit marked coördination tendencies, they might therefore be expected to show evidence for such "semi-covalent" bonding in their hydrates. Certain observations have, in fact, revealed the existence of coördinated hydroxyl groups in the systems of interest.

Despite repeated references[15,16] to the zirconyl ion as $Zr{=}O^{++}$, its existence as an oxy monomer is extremely doubtful. Schmid[17] suggested pyro-linkages as an improvement, and these are known to be possible.[18] Since a reasonable coördination for the zirconium ion must also be maintained, it can be concluded that the zirconyl ion is either an aquo-hydroxy monomer or some form of polymer. If

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[1] Based primarily upon a part of the thesis submitted by William S. Castor, Jr., to the Graduate School of Northwestern University in September, 1950, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] American Cyanamid Company, Calco Chemical Division, Piney River, Va.

[3] W. S. Castor, Jr., and F. Basolo, THIS JOURNAL, **75**, 4804 (1953).

[4–13] The references are intended to be illustrative, not complete.

[4] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1950, p. 114.

[5] J. P. Hunt and H. Taube, *J. Chem. Phys.*, **18**, 757 (1950).

[6] H. L. Friedman, H. Taube and J. P. Hunt, *ibid.*, **18**, 759 (1950).

[7] J. P. Hunt, A. C. Rutenberg and H. Taube, THIS JOURNAL, **74**, 268 (1952).

[8] H. J. Emeléus and J. S. Anderson, "Modern Aspects of Inorganic Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1947, pp. 154ff.

[9] C. A. Beevers and C. M. Schwartz, *Z. Krist.*, **91**, 168 (1935).

[10] L. Hackspill and A. P. Kieffer, *Ann. chim.*, [10], **14**, 227 (1930).

[11] A. W. Thomas, "Colloid Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1934, pp. 141ff.

[12] J. Louisfert, *J. phys. radium*, **8**, 45 (1947).

[13] M. Prasad, S. S. Dharmatti, C. R. Kanckar and N. S. Biradar, *J. Chem. Phys.*, **17**, 813 (1949).

[14] O. K. Rice, "Electronic Structure and Chemical Binding," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 421–426.

[15] F. P. Venable, "Zirconium and Its Compounds," American Chemical Society Monograph Series, New York, N. Y., 1921, p. 32.

[16] W. B. Blumenthal, *J. Chem. Education*, **26**, 472 (1949).

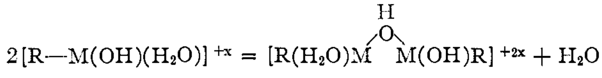
[17] P. Schmid, *Z. anorg. allgem. Chem.*, **167**, 369 (1927).

[18] Consider, for example, the structures of the dioxides [R. W. G. Wyckoff, "Crystal Structures," Interscience Publishers, Inc., New York, N. Y., 1948, Sec. I, Chap. IV, text pp. 3–4] and of the oxysulfide [J. D. McCullough, L. Brewer and L. A. Bromley, *Acta Cryst.*, **1**, 287 (1948)].

monomeric forms exist, they should show one or more reactions characteristic of coördinated hydroxyl groups. One such reaction, a polymerization, has been observed in chloride[19] and perchlorate[20] solutions and carefully studied in the case of the perchlorate.[21] Although the condensation has not yet been completely characterized, it has previously been related to coördinated hydroxyl groups in the zirconium species.[22]

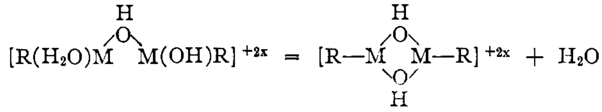
The observations and arguments of Meerwein[23] provide evidence for coördinated hydroxyl groups in the hydrates of nickel(II) and manganese(II) chlorides. Concentrated solutions of these salts exhibit acidic hydrogens which cannot be attributed to hydrolysis, but can be understood in terms of H[M(OH) . . .] groupings. The effect disappears rapidly upon dilution. In each case the remainder of the coördination sphere of the cation must be satisfied by anions and/or undissociated water molecules. Since coördinated ligands present in concentrated solutions are probably also in evidence in the crowded environment of the highest solid hydrates, the literature cited indicates that these compounds are aquohydroxy complexes.

Identification of the Olation Reaction.—A common property of aquohydroxy complexes is their ability to undergo the olation reaction[11,24]



$$2[\mathrm{R{-}M(OH)(H_2O)}]^{+x} = [\mathrm{R(H_2O)M}\overset{\mathrm{H}}{\diagup\mathrm{O}\diagdown}\mathrm{M(OH)R}]^{+2x} + \mathrm{H_2O}$$

If the condensing species are identical, a second olation leads to the formation of a *cis*-diol bridge



$$[\mathrm{R(H_2O)M}\overset{\mathrm{H}}{\diagup\mathrm{O}\diagdown}\mathrm{M(OH)R}]^{+2x} = [\mathrm{R{-}M}\underset{\mathrm{H}}{\overset{\mathrm{H}}{\overset{\diagup\mathrm{O}\diagdown}{\diagdown\mathrm{O}\diagup}}}\mathrm{M{-}R}]^{+2x} + \mathrm{H_2O}$$

A single hydroxyl group in the monomer results in the elimination of one H_2O/M in two steps of $^1/_2H_2O$ each. If the R groups in the above formulations were such that each metal atom in the diol dimer still retained one coördinated, unshared hydroxyl group and at least one coördinated water molecule, olation could proceed. However, since the condensing species would then be dimers, four consecutive losses of $^1/_4H_2O$ per metal atom would occur. Additional hydroxyl groups would permit still further condensation.

Heretofore, the olation reaction has been studied chiefly in solution,[24] but the concept has been extended to the hydrous oxides by Thomas, Graham and others.[11,25,26] The water losses described are those found in the dehydration of $MnCl_2 \cdot 4H_2O$, $NiCl_2 \cdot 6H_2O$ and $ZrOCl_2 \cdot 9H_2O$.[3] Since other evidence also points to formulation of these compounds as aquohydroxy complexes, it seems necessary to conclude that the repeated occurrences of fractional hydrates result from olation condensations.

Fixing the Initial Coördination Numbers.—To ascertain the coördination number of the metal atom in an aquohydroxy complex, we must rely upon an assumption which has been invoked frequently in the past.[10] It may be stated as follows: simple hydrate water will be lost more readily than the constitutional water of the aquohydroxy complex. The statement is not axiomatic, for it implies a thermodynamic criterion and kinetic considerations are neglected. However, upon the basis of this reasonable assumption, it may be concluded that the olating species contain no uncoördinated water.

The half-hydrates characteristic of a primary olation occur directly upon dehydration of either $MnCl_2 \cdot 4H_2O$ or $NiCl_2 \cdot 6H_2O$. In the case of zirconyl chloride, half-hydrates occur at two places in the dehydration—during decomposition of $ZrOCl_2 \cdot 9H_2O$ and of $ZrOCl_2 \cdot 7H_2O$. However, the 8-hydrate decomposes to lose $^1/_4H_2O$ four times, the behavior expected for olation condensation of a diol dimer, so the first olation begins with the decomposition of the 9-hydrate. It appears, therefore, that $MnCl_2 \cdot 4H_2O$, $NiCl_2 \cdot 6H_2O$ and $ZrOCl_2 \cdot 9H_2O$ are aquohydroxy monomers in which all the water is coördinated.

Since both the manganese and nickel salts have been shown to contain acidic hydrogens,[23] the chloride ions must be included in the coördination sphere with the water. Because the monomers are stable in equilibrium with an aqueous solution, the alternative treatment would be equivalent to writing a non-existent hydrolysis. Noting that the dehydration behavior of zirconyl chloride reveals olations characteristic of three hydroxyl groups, it appears that $ZrOCl_2 \cdot 9H_2O$ also contains a Meerwein-type acidic hydrogen. Hence, the same argument about chloride coördination should apply.

Upon the basis of the foregoing discussion, it is possible to write preliminary structural formulas for the three monomers and examine the coördination numbers of the metal ions[27]

$$\begin{aligned}
\mathrm{MnCl_2 \cdot 4H_2O} &= \mathrm{H[Mn(H_2O)_3(OH)Cl_2]}\\
\mathrm{NiCl_2 \cdot 6H_2O} &= \mathrm{H[Ni(H_2O)_5(OH)Cl_2]}\\
\mathrm{ZrOCl_2 \cdot 9H_2O} &= \mathrm{H[Zr(H_2O)_7(OH)_3Cl_2]}
\end{aligned}$$

These notations are tentative because the argument has not yet been carried far enough to completely fix the number of acidic hydrogens. However, the one shown in each case above is the minimum, and additional acidity could not influence the determination of the coördination number.

The initial coördination numbers deduced above for the Mn(II), Ni(II) and Zr(IV) ions are 6, 8 and 12, respectively. All are compatible with the expectation of symmetrical configurations in predominantly ionic complexes, but the smaller symmetrical arrangements with coördination numbers 4, 6 and 8 might have been anticipated. The enhancement is very probably related to one previously observed. Pauling[28] lists several cations whose co-

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(19) M. Adolf and W. Pauli, *Kolloid-Z.*, **29**, 173 (1921).

(20) G. Jander and K. F. Jahr, *Kolloid-Beihefte*, **43**, 295 (1935).

(21) R. E. Connick and W. H. Reas, THIS JOURNAL, **73**, 1171 (1951).

(22) R. E. Connick and W. H. McVey, *ibid.*, **71**, 3182 (1949).

(23) H. Meerwein, *Sitzber. Ges. Beforder. ges. Naturw. Marburg*, **64**, 119 (1930); *Chem. Zentr.*, **101**, **II**, 1962 (1930).

(24) H. J. Emeléus and J. S. Anderson, ref. 8, pp. 128–131.

(25) R. P. Graham and A. W. Thomas, THIS JOURNAL, **69**, 816 (1947).

(26) R. P. Graham and A. E. Horning, *ibid.*, **69**, 1214 (1947).

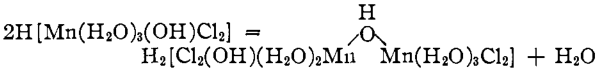
(27) The system of notation used throughout this paper necessarily emphasizes the covalent properties of essentially ionic bonds. Attention is directed primarily to the coördination of the metal ions, but the oxygen ions are allowed their usual coördination numbers.

(28) L. Pauling, ref. 4, p. 381.

ordination to oxygen in essentially ionic solids is enlarged by the effect of covalent groupings in the lattice, and it has long been known that the water molecules in hydrates exert a pronounced influence upon the crystal structure.[29]

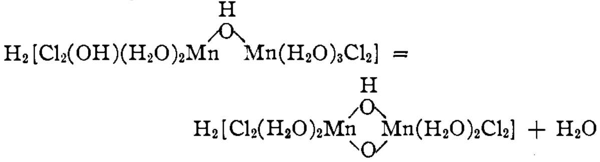
This explanation of the large initial coördination numbers suggests that a decrease in coördination may occur during dehydration. Visual evidence for such a change exists in the $MnCl_2 \cdot xH_2O$ and $NiCl_2 \cdot xH_2O$ systems. The colored cations in these salts have unpaired electrons,[30] so the number of semi-covalent metal–oxygen bonds can influence the color. A change from pale pink to deep pink occurs during dehydration of $MnCl_2 \cdot 3H_2O$, and one from green to yellow accompanies dehydration of $NiCl_2 \cdot 4H_2O$.[3]

$MnCl_2 \cdot xH_2O$.—As a consequence of previous arguments, $MnCl_2 \cdot 4H_2O$ may be formulated as $H[Mn(H_2O)_3(OH)Cl_2]$ or $H_2[Mn(H_2O)_2(OH)_2Cl_2]$. The latter notation applies if the second ionization is sufficiently large to provide evidence for two hydroxyl groups yet too small to be detected by Meerwein's techniques.[23] The dehydration behavior indicates one diolation. For the monobasic configuration, this would be



$$2H[Mn(H_2O)_3(OH)Cl_2] = H_2[Cl_2(OH)(H_2O)_2Mn \overset{\overset{H}{}}{\diagup O \diagdown} Mn(H_2O)_3Cl_2] + H_2O$$

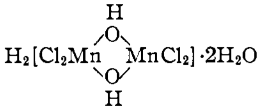
followed by



$$H_2[Cl_2(OH)(H_2O)_2Mn \overset{\overset{H}{}}{\diagup O \diagdown} Mn(H_2O)_3Cl_2] = H_2[Cl_2(H_2O)_2Mn \overset{\overset{H}{}}{\diagup O \diagdown}\!\!\!\underset{\underset{H}{}}{\diagdown O \diagup} Mn(H_2O)_2Cl_2] + H_2O$$

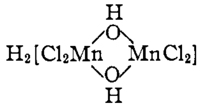
If the monomer were dibasic, the diol dimer could condense again; but for the monobasic alternative illustrated above, further dehydration is likely only if the complex changes to one with smaller coördination number. $MnCl_2 \cdot 3H_2O$ decomposes directly to $MnCl_2 \cdot 2H_2O$ with a color change from very pale pink to deep pink, so the condensations are correct as written.

Since coördination number 5 is very uncommon,[31] the dihydrate should probably be formulated



$$H_2[Cl_2Mn \overset{\overset{H}{}}{\diagup O \diagdown}\!\!\!\underset{\underset{H}{}}{\diagdown O \diagup} MnCl_2] \cdot 2H_2O$$

with one molecule of simple hydrate water per metal atom. The 4-coördinated structure is supported by the fact that $MnCl_2 \cdot 2H_2O$ decomposes directly to $MnCl_2 \cdot H_2O$



$$H_2[Cl_2Mn \overset{\overset{H}{}}{\diagup O \diagdown}\!\!\!\underset{\underset{H}{}}{\diagdown O \diagup} MnCl_2]$$

As would be predicted from its structure, the monohydrate is exceptionally resistant to dehydration.[3]

$NiCl_2 \cdot xH_2O$.—Discussion already given limits the formulation of $NiCl_2 \cdot 6H_2O$ to either $H[Ni(H_2O)_5(OH)Cl_2]$ or $H_2[Ni(H_2O)_4(OH)_2Cl_2]$. Dehydration has shown $NiCl_2 \cdot 5.5H_2O$ and probably $NiCl_2 \cdot 5H_2O$,[3] so at least one diolation occurs. Intermediates were not detected in the further dehydration to $NiCl_2 \cdot 4H_2O$, but since the color change did not yet occur, a second diolation probably did. This choice of the dibasic alternative, $H_2[Ni(H_2O)_4(OH)_2Cl_2]$, for the monomer leads directly to the formulations

$$NiCl_2 \cdot 5H_2O = H_4[Cl_2(OH)(H_2O)_3Ni{-}(OH)_2{-}Ni(H_2O)_3(OH)Cl_2]$$

$$NiCl_2 \cdot 4H_2O = H_4[Cl_2(H_2O)_2Ni{-}(OH)_4{-}Ni(H_2O)_2Cl_2]$$

and these are seen to be consistent with the observed color change upon dehydration of the latter. The direct formation of $NiCl_2 \cdot 2H_2O$ then predicts

$$NiCl_2 \cdot 2H_2O = H_4[Cl_2Ni{-}(OH)_4{-}NiCl_2]$$

In agreement with this structure, $NiCl_2 \cdot 2H_2O$ is extremely resistant to dehydration. The indicated 6-coördination of Ni^{++} is that to be expected, and the greater acidity of the nickel hydrates is consistent with the usual order of stability of nickel(II) and manganese(II) complexes.[32]

For simplicity, the ol-linkages in the above formulations have been indicated by $[\ldots Ni{-}(OH)_n{-}Ni \ldots]$. Except in the case of a single diol bridge, the formal notation of multiple ol linkages in this manner is not meant to imply that all are formed between the same two metal atoms. A tetraol configuration is, in fact, sterically impossible for the octahedrally coördinated Ni^{++} of $NiCl_2 \cdot 2H_2O$. Consequently, it does not exist in the 8-coördinated $NiCl_2 \cdot 4H_2O$ either. A chain of diol linkages is considered more probable than a cyclic tetramer, but either is possible on the basis of data now available.[33]

$ZrOCl_2 \cdot xH_2O$.—Except for uncertainty about the number of acidic hydrogens, prior considerations fix the structure of $ZrOCl_2 \cdot 9H_2O$ as $H[Zr(H_2O)_7(OH)_3Cl_2]$. Two consecutive losses of $^1/_2H_2O/Zr$ produce a diol dimer, $ZrOCl_2 \cdot 8H_2O$, which is further characterized by four subsequent losses of $^1/_4H_2O/Zr$ to give $ZrOCl_2 \cdot 7H_2O$. A double loss of $^1/_2H_2O$ to $ZrOCl_2 \cdot 6H_2O$ then reveals olations with a third hydroxyl group on each zirconium atom.

Although the fact that the zirconium salts are colorless prevents visual detection of the expected change in coördination number, this change could be located from the number of Meerwein-type acidic hydrogens. One might expect $Zr(OH)_2(aq.)^{++}$ to be less acidic than $Mn(aq.)^{++}$, thereby limiting these hydrogens to one. Since experimental data on this point are not available, the formulation $H_2[(H_2O)_2Zr{-}(OH)_6{-}Zr(H_2O)_2]Cl_4$ deduced for $ZrOCl_2 \cdot 4H_2O$ on this basis must be considered tentative. Still, it is interesting to note that this structure is consistent with the hydrolysis behavior in dry air[3,17] and the 8-fold coördination to oxygen found in the three established structural

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[29] A. F. Wells, "Structural Inorganic Chemistry," The University Press, Oxford, 1945, pp. 362–381.

[30] L. Pauling, ref. 4, pp. 27–28.

[31] H. P. Klug, E. Kummer and L. Alexander, THIS JOURNAL, **70**, 3064 (1948).

[32] F. A. Snavely and W. C. Fernelius, *Science*, **117**, 15 (1953).

[33] G. Lundgren and L. G. Sillén [*Arkiv Kemi*, **1**, 277 (1949)] found the structure of $Th(OH)_2CrO_4 \cdot H_2O$ to be built up of infinite zigzag-formed chains of composition $[Th(OH)_2{}^{++}]_n$ like those favored here. Finite CrO_4 groups are between the chains, so that each Th atom is surrounded by 8 O atoms; and the additional water is contained in holes in the lattice.

modifications of zirconia.[18] The stronger metal–chlorine bonds deduced for the analogous nickel and manganese complexes favor decomposition to anhydrous chlorides as observed.[34]

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[34] F. Ephraim, "Inorganic Chemistry," P. C. L. Thorne and E. R. Roberts, Ed., Interscience Publishers, Inc., New York, N. Y., 1947, p. 269.

Acknowledgment.—To the Abbott Fund of Northwestern University and the Veterans Administration, the authors gratefully express their thanks for financial aid which helped to make this study possible.

EVANSTON, ILLINOIS

[CONTRIBUTION OF DEPARTMENT OF CHEMISTRY OF CLARK UNIVERSITY]

Thermodynamics of Metal Chelate Formation. I. The Third and Fourth Dissociation Constants of Ethylenediaminetetraacetic Acid

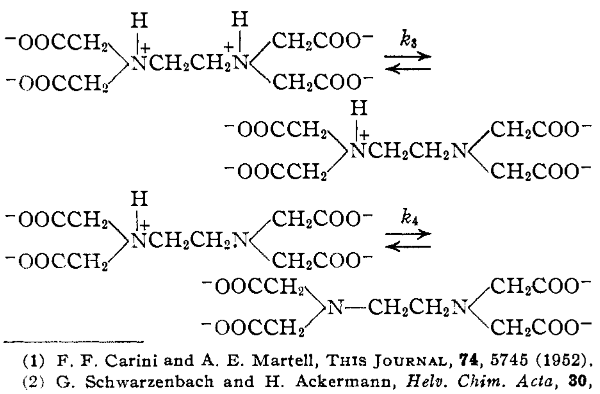
BY F. F. CARINI AND A. E. MARTELL

RECEIVED APRIL 27, 1953

The potentials of the hydrogen–silver–silver chloride cell have been measured in buffer solutions containing acid salts of ethylenediaminetetraacetic acid. The e.m.f. data obtained without liquid junction were extrapolated to infinite dilution with the aid of the Debye–Hückel limiting law, and the thermodynamic equilibrium constants associated with the dissociation of the third and fourth protons were determined. The standard free energy changes for these reactions at 0, 5, 10, 15, 20, 25 and 30° were calculated, and the corresponding values of $\Delta H°$ and $\Delta S°$ applying over this temperature range are reported.

In order to carry out a potentiometric study of the thermodynamics of reactions between metal ions and the ethylenediaminetetraacetate anion, it is first necessary to study the thermodynamic changes associated with the combination of the anion with hydrogen ions. Since it has been shown in a previous publication[1] that it is possible to calculate the stabilities of the alkaline earth chelates from potentiometric measurements involving only the third and fourth ionization constants of ethylenediaminetetraacetic acid, it was decided to first restrict our investigation to the determination of these thermodynamic equilibrium constants over a range of temperatures.

With the exception of the work mentioned above, no thermodynamic constants have been determined for this amino acid, and no studies have been made of the effect of temperature on the equilibria. Previous investigations by Schwarzenbach and Ackermann[2] and by Cabell[3] were carried out at 25° and in a neutral salt medium of 0.1 ionic strength. In addition to usefulness in the study of complexing of metal ions, the heats and entropies of ionization of ethylenediaminetetraacetic acid are interesting in view of the complex structure and high charge of the basic substances involved. The equilibria under investigation may be represented by



$$^{-}OOCCH_2(HN^{+})(CH_2)_2(N^{+}H)CH_2COO^{-} \ldots$$

The differences between the third and fourth dissociation constants are too large in view of present methods of predicting dissociation constants of organic substances. It was hoped that the thermodynamic changes involved would help to explain this discrepancy.

Experimental

The method employed for the determination of thermodynamic dissociation constants consisted of the extrapolation to zero ionic strength of the electromotive force of cells without liquid junction containing a buffer system consisting of appropriate ethylenediaminetetraacetate anions. The cells employed may be divided into two general classes

I. Pt–H_2, $K_2H_2V(m_1)$, $K_3HV(m_2)$, $KCl(m_3)$, AgCl–Ag
II. Pt–H_2, $K_3HV(m_1)$, $K_4V(m_2)$, $KCl(m_3)$, AgCl–Ag

where H_4V represents ethylenediaminetetraacetic acid.

Cell I, which contained the di- and tripotassium salts of ethylenediaminetetraacetic acid was used for the evaluation of k_3, and cell II, containing the tri- and tetrapotassium salts of ethylenediaminetetraacetic acid, was employed for the determination of k_4. The electromotive forces of these cells were measured from 0 to 30°. The values for 0° were evaluated by extrapolation of data taken at slightly higher temperatures.

Materials and Equipment.—The ethylenediaminetetraacetic acid was obtained through the courtesy of the Bersworth Chemical Company, Framingham, Massachusetts. It was further purified by two successive recrystallizations from water. The buffer solutions employed in cells of type I and II were made up by adding to the purified ethylenediaminetetraacetic acid the required amount of carbonate-free standard potassium hydroxide solution, prepared by the method of Schwarzenbach and Biedermann,[4] and standardized against potassium acid phthalate in the usual manner. The potassium chloride used was freed from bromide contamination by recrystallization from water and 95% ethanol as outlined by Pinching and Bates.[5]

The silver–silver chloride electrodes were prepared by the method of Shedlovsky and MacInnes,[6] and the platinum–hydrogen electrodes were made according to the directions outlined in Weissberger.[7] Tank hydrogen was first passed through a deoxo purifier, a presaturator, and then through

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[1] F. F. Carini and A. E. Martell, THIS JOURNAL, **74**, 5745 (1952).

[2] G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **30**, 1798 (1942).

[3] M. J. Cabell, A. E. R. E. Report C/R 813, Ministry of Supply, Harwell, Berks., England, 1951.

[4] G. Schwarzenbach and W. Biedermann, *Helv. Chim. Acta*, **31**, 331 (1948).

[5] G. Pinching and R. Bates, *J. Research Natl. Bur. Standards*, **37**, 311 (1946).

[6] T. Shedlovsky and D. A. MacInnes, THIS JOURNAL, **58**, 1970 (1936).

[7] A. Weissberger, "Physical Methods of Organic Chemistry," Second Edition, Vol. II, Interscience Publishers, Inc., New York, N. Y., 1949, p. 1722.