[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Properties of Hydrates. I. Kinetic Identification of Compounds Formed between Salts and Water[1,2]

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Hydrate compositions can be determined kinetically if the rate of reaction is observed at sufficiently frequent intervals. Either dehydration or hydration procedures can be used, since the method is based primarily upon the heterogeneous character of the reactions. All hydrates known from equilibrium investigations in the regions studied kinetically were found for the greater portion of the systems $CaCl_2$–H_2O, $MnCl_2$–H_2O, $NiCl_2$–H_2O and $ZrOCl_2$–H_2O. In all but the first case new hydrates were discovered, and reasons for their previous lack of identification are suggested. The method is especially valuable for distinguishing hydrates with similar decomposition pressures and shows promise for those which tend to decompose by some side reaction such as hydrolysis.

Thermodynamic methods are customarily employed for the identification of definite compounds in salt–water systems. However, this approach possesses practical disadvantages for hydrates with similar decomposition pressures or those which tend to decompose by side reactions. Consequently, a kinetic procedure has been developed for determining which compositions represent chemical individuals.

Although other forms of this method have had limited use,[4–7] the kinetic approach has not yet achieved general recognition or acceptance. This may be attributed to the fact that the theoretical aspects have not been clearly understood, a situation which has caused doubtful conclusions to be drawn from inadequate measurements of hydration and dehydration rates.[8] However, when correctly applied, the kinetic procedure for hydrate identification is simpler and more sensitive than the usual equilibrium methods.

Theoretical

Numerous workers have found that at constant temperature heterogeneous reactions of the type $solid_1 = solid_2 + gas$ proceed autocatalytically.[9] Thus, the rate *vs.* composition curve for a single such reaction often starts at a low value and increases before it falls toward zero. If two of these reactions occur consecutively, in the region of composition corresponding to the intermediate compound both are slow. A minimum therefore occurs in the gross rate of reaction at or near the composition of the intermediate, making its identity apparent.

This rate minimum will be detectable as long as overlap of the bounding decomposition curves does not become too large from simultaneous occurrence of the two reactions. Too infrequent observation of the rate can cause apparent overlap because the experimental data yield a difference curve which approaches the true rate curve only as the composition increment approaches an infinitesimal. Consequently, observations must be made frequently, and time lapses must be smaller for faster reactions. Increments on the composition axis small enough to identify compounds with great differences in composition and reaction rate may be much too large to distinguish substances which differ only slightly in one or both of these respects.

Experimental Method

Salt hydrates were allowed to gain or lose water at 25 ± 0.1° in hygrostats. Four systems—$CaCl_2 \cdot xH_2O$, $MnCl_2 \cdot xH_2O$, $NiCl_2 \cdot xH_2O$ and $ZrOCl_2 \cdot xH_2O$—were investigated. The dehydration of calcium chloride was followed by periodic chloride analysis of a large sample in a desiccator containing concentrated sulfuric acid. The reactions were sufficiently slow and the sample large enough that perturbation of the system by sampling was slight.

Dehydration of $MnCl_2 \cdot 4H_2O$ and $NiCl_2 \cdot 6H_2O$ was considerably more rapid than that of $CaCl_2 \cdot 6H_2O$. Therefore, these studies were made by following the loss in weight of fixed samples dried in desiccators containing magnesium perchlorate. The samples were analyzed for chloride before and after dehydration. This technique is decidedly more sensitive and convenient than the first.

The rates of decomposition of the higher hydrates of zirconyl chloride over magnesium perchlorate or sodium hydroxide were much too rapid to be measured satisfactorily by either of the above techniques. These reactions were finally studied by following the loss in weight of a sample placed upon the pan of a thermostated, desiccated analytical balance.[10] This technique offers the added important advantage that hydrolysis over an inert desiccant is suppressed because liberated hydrogen chloride remains in the vicinity of the sample.

Results

Limitations of space do not permit tabulation of the observations and the rates calculated therefrom.[11] However, for the present purpose it is sufficient to note that the individual decomposition curves exhibit the qualitative shape to be anticipated from the theoretical considerations and that in the cases of otherwise known intermediates the kinetic studies reveal hydrates of correct composition. These facts are best illustrated by the graphs given. It should be observed that the individual decomposition curves are not merely inverted parabolas, but they all have the same quali-

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[1] Presented before the Division of Physical and Inorganic Chemistry, 118th Meeting of the American Chemical Society, Chicago, Ill., September 3–8, 1950.

[2] Based 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.

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

[4] G. F. Smith, O. W. Rees and V. R. Hardy, THIS JOURNAL, **54**, 3513 (1932).

[5] R. Membrauer, *Z. physik. Chem.*, **A172**, 64 (1935).

[6] C. Lieber, *ibid.*, **A182**, 153 (1938).

[7] A. S. Mikulinskii and E. N. Podtymchenko, *J. Phys. Chem. (U.S.S.R.)*, **8**, 600 (1936).

[8] B. N. Ghosh, *J. Indian Chem. Soc.*, **18**, 472 (1941).

[9] A recent example which also affords an excellent entrance to the literature can be found in the work of L. L. Bircumshaw and J. Edwards, *J. Chem. Soc.*, 1800 (1950).

[10] W. S. Castor, Jr., and F. Basolo, *J. Chem. Education*, **28**, 380 (1951).

[11] A complete tabular presentation of the results can be found in the thesis identified in note 2.

tative shape. The rate depressions approximately midway between the hydrate-minima in the figures are a general characteristic of the hydrate decomposition curves. It has been suggested that similar depressions in the rates of other single heterogeneous reactions are of kinetic origin.[12,13] They should not be taken to indicate additional intermediates.

Dehydration of Difficultly Hydrolyzable Chlorides.—Figure 1 shows the dehydration of wet calcium chloride obtained by recrystallizing the C.P. 6-hydrate from cold water. The existence of previously known[14] 6-, 4- and 2-hydrates is revealed in the expected manner.

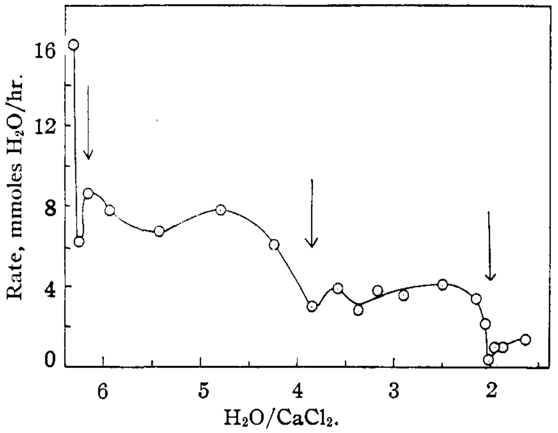

Fig. 1.—Dehydration of calcium chloride: Arrows indicate 6-, 4- and 2-hydrates.

The dehydration of C.P. $MnCl_2·4H_2O$ shown in Fig. 2 similarly reveals the existence of compounds containing 4, 3.5, 3, 2 and 1 molecules of water.

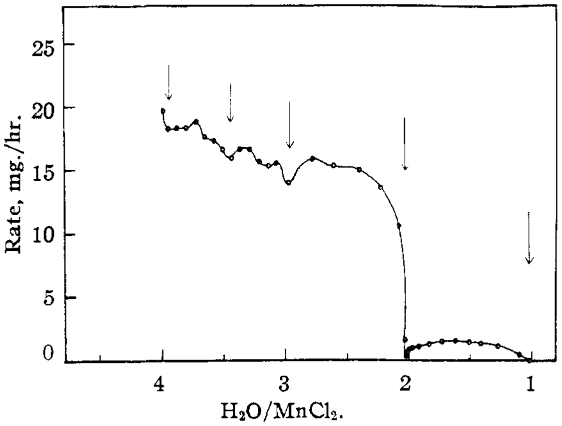

Fig. 2.—Dehydration of manganese(II) chloride: Arrows indicate 4-, 3.5-, 3-, 2- and 1-hydrates.

Although thermodynamic measurements have revealed the more distinctive 4-, 2- and 1-hydrates,[15] the 3.5- and 3-hydrates have not been previously described. This is probably because of their marked resemblance to $MnCl_2·4H_2O$, for all three of these compounds exhibit the same pale pink color and similar average rates of dehydration. The latter similarity indicates that very little difference exists in the equilibrium vapor pressures at 25°. The more distinctive 1- and 2-hydrates differ considerably in their ease of dehydration, not only between themselves but also from the three higher hydrates. Both are deep pink.

In Fig. 3 the dehydration behavior of C.P. $NiCl_2·6H_2O$ reveals the formation of 5.5-, 4- and 2-hydrates and suggests the existence of a 5-hydrate. The initial composition was a little too dry to allow kinetic detection of $NiCl_2·6H_2O$. Only $NiCl_2·2H_2O$ is yellow, the other compounds being green. As in the similar case of manganese (II) chloride, only the more distinctive 6-, 4- and 2-hydrates have been identified by conventional equilibrium methods.[16] Chloride determinations required in connection with the study of these three hydrate systems were made by titration with 0.1 *M* silver nitrate, using dichlorofluorescein as indicator.[17]

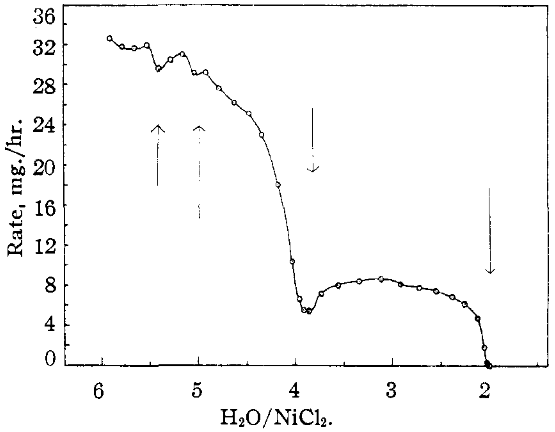

Fig. 3.—Dehydration of nickel(II) chloride: Solid arrows indicate 5.5-, 4- and 2-hydrates. Broken arrow indicates possible existence of 5-hydrate. The initial composition contained too little water to reveal the 6-hydrate.

Dehydration of Zirconyl Chloride.—Although the method of Young and Arch[18] was sometimes used, zirconyl chloride was usually prepared by evaporating to saturation on the steam-bath a solution prepared from 30 g. of $ZrCl_4$, 15 ml. of 36% hydrochloric acid and 200 ml. of water. After cooling, the product was collected upon a filter and could be freed of excess HCl by washing with acetone or drying over sodium hydroxide until odorless. In the latter case, the Cl/Zr ratio decreased rapidly to 2.00 and then slowly. Chloride analyses were made by titration in 0.13 *M* nitric acid with 0.1 *M* mercurous nitrate, using brom phenol blue as indicator.[19] Zirconium was determined as the dioxide either after ammonia precipitation of the hydrous oxide or by direct thermal decomposition of the chloride hydrates.

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[12] A. Sieverts and H. Theberath, *Z. physik. Chem.*, **100**, 463 (1922).

[13] J. Y. Macdonald, *J. Chem. Soc.*, 832, 839 (1936).

[14] B. Roozeboom, *Z. physik. Chem.*, **4**, 31 (1889).

[15] K. Sano, *J. Chem. Soc. Japan*, **59**, 846 (1938); **60**, 366 (1939).

[16] I. H. Derby and V. Yngve, THIS JOURNAL, **38**, 1439 (1916).

[17] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Company, New York, N. Y., 1943, p. 571.

[18] R. C. Young and A. Arch, "Inorganic Syntheses," Vol. II, W. C. Fernelius, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 121.

[19] I. M. Kolthoff and W. D. Larson, THIS JOURNAL, **56**, 1881 (1934).

The identity of the familiar 8-hydrate[20,21] was confirmed by the observation that drier compositions apparently stopped hydrating when the composition $ZrOCl_2 \cdot 8H_2O$ was reached over a saturated aqueous solution of ammonium chloride at 25°. Schmid's identifications of 6- and 4-hydrates[21] were confirmed by showing that the former is the equilibrium composition over saturated aqueous sodium hydroxide and the latter over magnesium perchlorate or concentrated sulfuric acid. The 4-hydrate could not be thermally dehydrated in air without extensive hydrolysis.

A typical dehydration of acetone-washed zirconyl chloride over magnesium perchlorate is shown in Fig. 4. Slight hydrolysis caused an apparent shift to high water contents because the compositions were calculated from the chloride analysis of the product neglecting hydrolysis. The resulting uncertainty is too small to hamper interpretation of the data. With support for $ZrOCl_2 \cdot 6^1/_2H_2O$ from other, shorter dehydrations, Fig. 4 reveals the existence of zirconyl chloride hydrates with 8, 7.75, 7.5, 7.25, 7, 6.5 and 6 moles of water.

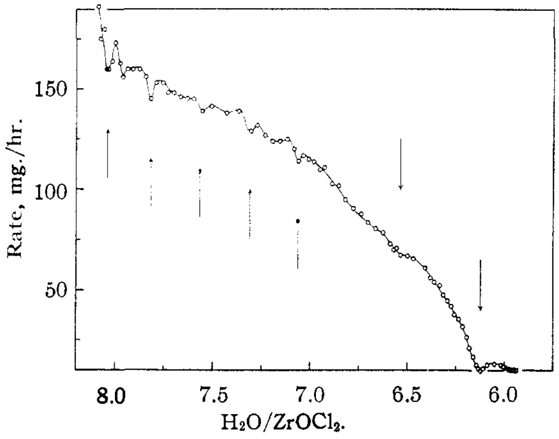

Fig. 4.—Dehydration of zirconyl chloride over magnesium perchlorate. Arrows indicate 8-, 7.75-, 7.5-, 7.25-, 7-, 6.5- and 6-hydrates. The sample was washed with acetone before dehydration.

Since preliminary X-ray diffraction measurements indicated that the moist crystals isolated from solution were not identical with $ZrOCl_2 \cdot 8H_2O$, kinetic evidence for higher hydrates was sought. The moist crystallization product was dehydrated over solid sodium hydroxide, the desiccant also serving to remove uncombined hydrogen chloride. Partial results of such a study are shown in Fig. 5. The higher hydrates found contain 8.5, 9, and probably 10 water molecules, but uncertainty as to the rate of loss of HCl leaves some doubt about the exact composition of the highest hydrate. No minima exist prior to those shown in Fig. 5, and continued dehydration gave first the 8-hydrate and then four consecutive losses of $^1/_4H_2O$ like those of Fig. 4. Other similar studies yielded comparable results, hydrolysis effects being most evident during the slower dehydrations over sodium hydroxide.

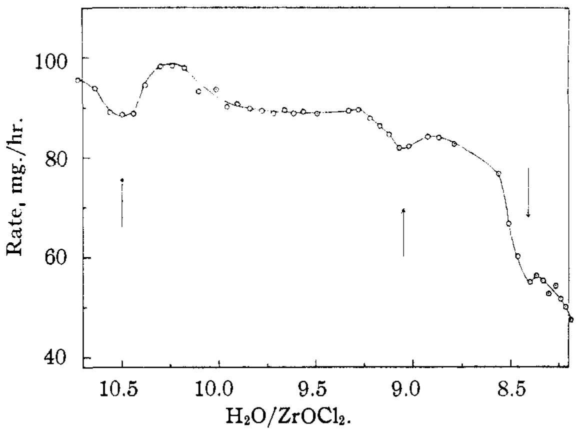

Fig. 5.—Dehydration of zirconyl chloride over sodium hydroxide: Arrow on left probably refers to a 10-hydrate; other arrows indicate 9- and 8.5-hydrates. Hydrogen chloride was lost simultaneously with the water.

Hydration.—Several attempts were made to investigate the hydration behavior of $ZrOCl_2 \cdot 4H_2O$. In the relatively moist atmospheres required, hydrolysis caused serious complications. Uncertainty as to the composition of the solid could be minimized by effecting rapid hydration, but faster rates were more difficult to measure accurately. There are, then, optimum conditions for the study of such reactions, but the hydration tendencies of the various compounds differ so widely that several sets of conditions are necessary. A humidity controlled by saturated aqueous ammonium chloride showed promise for the study of hydration rates between $ZrOCl_2 \cdot 7H_2O$ and $ZrOCl_2 \cdot 8H_2O$. The intermediate hydrates could be inferred from a comparison of two determinations. The 6-, 6.5- and 7-hydrates were easily detected during slower hydration over saturated aqueous cobalt(II) chloride, but hydrolysis severely complicated composition assignments at higher water contents.

Still other hydration conditions must be investigated before the hydrates found by dehydration can all be identified from the reverse reactions. However, where suitable conditions were found, hydration gave rate curves analogous to those obtained during dehydration. Although kinetic identification of hydrates may therefore be accomplished by changing the composition of a salt–water system in either direction, it seems far more practical to study easily hydrolyzable salts in the drier atmospheres possible during dehydration.

Conclusions

The validity of the kinetic method for hydrate identification seems well established. All previously known hydrates of calcium, manganese(II),

Table I

Hydrates Identified

$CaCl_2$	$MnCl_2$	$NiCl_2$	$ZrOCl_2$
6	4	5.5, (5)	(10)
4	3.5, 3	4	9
2	2	2	8.5, 8
	1		7.75, 7.5, 7.25, 7
			6.5, 6
			4

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(20) F. P. Venable, "Zirconium and Its Compounds," American Chemical Society Monograph Series, New York, N. Y., 1921, p. 67.

(21) P. Schmid, *Z. anorg. allgem. Chem.*, **167**, 369 (1927).

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.

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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]

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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.

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[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).

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[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).

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[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)].