[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, WAYNE UNIVERSITY]

The Hydrolysis of Ferrous Chloride at 25°[1]

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The purpose of this work was to obtain data on the magnitude of the hydrolysis reaction of iron(II) chloride. These data serve to evaluate the character of the ions in dilute solution, the free energy of the reactions involved and the basicity of the metal hydroxide. Methods for the preparation of pure water, exhibiting a neutral *p*H, and iron(II) chloride dihydrate, free of ferric ion or adsorbed free acid, were developed. The data indicate that the hydrolysis of ferrous chloride in the range of 0.02 to 0.08 molal is represented by the reaction: $Fe^{++} + H_2O \leftrightarrows FeOH^+ + H^+$. The equilibrium constant, K_1, for this reaction is equal to 1.20×10^{-8} and the corresponding standard free energy change, $\Delta F°$, is 11000 cal. per mole. The secondary basic dissociation constant, K_{b2}, of ferrous hydroxide determined by calculation is 8.3×10^{-7} and the free energy change for the dissociation process is 8300 cal. per mole. From the magnitude of the hydrolysis and the dissociation constants determined in this research, it can be concluded that ferrous hydroxide, with respect to its secondary dissociation, is a relatively weak base being about 100-fold weaker than ammonium hydroxide, NH_4OH ($K_b = 1.8 \times 10^{-5}$), and about 10-fold stronger than hydroxylamine, NH_2OH ($K_b = 1.7 \times 10^{-8}$).

The purpose of this investigation was to calculate the hydrolysis constant of ferrous chloride from measurements of the *p*H as a function of salt concentration. No reliable data on the hydrolysis of ferrous chloride in aqueous solutions are given in the literature, for two reasons. In the first place, the preparation of the pure salt uncontaminated by ferric ion or free acid presents certain technical problems. Secondly, the accurate measurement of the hydrogen ion activity in ferrous chloride solutions is relatively difficult since the solutions have an extremely small buffer capacity and are readily subject to oxidation. For this reason the water and aqueous solutions must be protected from atmospheric contamination of acidic or basic nature; in particular the exclusion of CO_2 and NH_3 is essential. In addition it is necessary, in the case of easily oxidizable substances such as ferrous chloride, to ensure the absence of molecularly dissolved oxygen.

Experimental

Purification of Water.—For the purpose of this investigation, conductivity water prepared by distillation from alkaline permanganate solution in the Barnstead conductivity still was transferred together with three to five drops of H_2SO_4 to a 3-liter all-Pyrex glass still and redistilled under a CO_2-free atmosphere. After repeated flushings with purified hydrogen, the water was transferred directly into the hydrolysis cell which had previously been purged of atmospheric gases. Such treatment yielded water consistently giving a *p*H of 6.9 to 7.2 at 25° and was always used within one week of preparation.

Preparation of $FeCl_2$.—The salt used in this investigation was prepared by recrystallization of Merck reagent grade ferrous chloride in the presence of hydrochloric acid and electrolytic iron under an atmosphere of purified nitrogen. All the necessary operations of reduction, filtration, recrystallization and drying were performed in a single gas-tight apparatus. This apparatus consists of two 550-ml. round bottom Pyrex flasks each provided with a stopcock and ground glass joint necks. A glass tube fitted at each end with a ground joint and having a sintered glass filtering disk (medium porosity) sealed into its center, serves to connect the two flasks.

A typical preparation of ferrous chloride was carried out as follows: 240 g. of Merck reagent $FeCl_2 \cdot 4H_2O$ was added to one of the flasks together with 200 ml. of conductivity water, 10 ml. of 38% hydrochloric acid and 8 to 10 g. of pure electrolytic iron. The apparatus was then assembled (long axis vertical) and a current of purified nitrogen passed through the assembly, escaping through a mercury trap. The salt was brought into solution by heating and the heating was continued until complete reduction had been assured. The apparatus was then inverted and the solution freed of unreacted iron by nitrogen pressure filtration through the sintered glass disk. After cooling and subsequent recrystallization of ferrous chloride, the unit was again inverted and the crystals pumped free of the mother liquor, the filtrate being forced out of the apparatus by the applied nitrogen pressure. The crystallized salt was partially dried by evacuating the apparatus overnight at room temperature. The procedure thus far yields a mixed hydrate which, though relatively stable when dry, suffers the disadvantage of not being of uniform composition. However, when evacuation is continued over a water-bath maintained at 80°, the salt looses water of hydration and absorbed HCl, the dehydration being accompanied by a vigorous effervescence of the solid material. The final product is a white powder with a very pale green tint and its analysis shows it to be the dihydrate, $FeCl_2 \cdot H_2O$ (*Anal.* Calcd. Fe, 34.30; Cl, 42.6. Found: Fe, 34.34; Cl, 43.5).

Purification of Gases.—The nitrogen and hydrogen gases used in this work were obtained from commercial cylinders and carefully purified by passing through a series of gas washing bottles containing aqueous solution of mercuric chloride, chromous sulfate and sodium hydroxide. Saturated aqueous mercuric chloride is used to remove sulfur containing compounds present in the commercial product. Aqueous chromous sulfate serves to remove possible traces of oxygen. This reagent has been found to be about fifty times more effective for this purpose than the commonly used alkaline pyrogallol.[2] The washing with dilute sodium hydroxide removes traces of CO_2 and acid vapors carried over by the gas stream. When used in conjunction with the hydrogen electrode, the gas (hydrogen) was finally passed through redistilled conductivity water maintained at 25°.

The Hydrolysis Cell.—The hydrolysis cell consisted of a 250-ml. Pyrex electrolytic beaker provided with a rubber stopper containing seven holes. Lead-ins provided for the glass, saturated calomel, and hydrogen electrodes, a thermometer, gas inlet and outlet tubes, and provision for adding water to the cell. The cell was partially immersed in a water reservoir maintained at 25 ± 0.10° and the solutions were agitated by a Pyrex encased iron bar rotated by a magnetic stirrer.

Measurement of *p*H.—The *p*H of the solutions was obtained by Beckman external general purpose glass and saturated calomel electrodes in conjunction with the Beckman Model G *p*H meter. The meter was calibrated at 25° with Beckman buffer solution at *p*H 7.00 ± 0.02 and with saturated potassium hydrogen tartrate[3] at *p*H 3.56 ± 0.02. Simultaneous *p*H determinations were made with a dual hydrogen electrode prepared according to Michaelis,[4] and its e.m.f. was observed by means of a Leeds and Northrup Model No. 7651 student potentiometer. *p*H values were obtained from the potential, *E*, of the hydrogen electrode by comparison of the measured potential of the salt solution with

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[1] From a dissertation submitted by Mr. Leo Wootner in partial fulfillment of the requirements for the Master's degree at Wayne University.

[2] H. W. Stone, THIS JOURNAL, **58**, 2591 (1936).

[3] R. G. Bates, G. D. Pinching and E. R. Smith, *J. Research Natl. Bur. Standards*, **45**, 418 (1950).

[4] L. Michaelis, "Potentiometry," Chapter XXVII, "Physical Methods of Organic Chemistry," Vol. I, Part II (A. Weissburger, ed.) Interscience Publ., Inc., New York, N. Y., 1949, p. 1722.

the potential in a buffer solution of known *p*H according to the relation

$$\Delta pH = \frac{\Delta E}{0.0591} \text{ at } 25°$$

This relation is valid for a series of measurements in which the potential of the reference electrode and the barometric pressure are constant at 25°. The agreement between the *p*H values obtained with the hydrogen and glass electrodes was excellent, being better than 0.02 *p*H unit which value represents the rated to accuracy of the Beckman *p*H meter. The glass electrode, however, was found to be more stable and reached equilibrium in pure water and in very dilute solutions much more rapidly than the hydrogen electrode.

Analysis of Iron.—The salt concentration of the hydrolysis solutions was determined by the weight of $FeCl_2 \cdot 2H_2O$ dissolved in a known weight of water. These weight concentrations were checked volumetrically by titration with potassium dichromate using diphenylamine sulfonate as internal indicator following the method of analysis given in Willard and Furman.[5] Samples which had a concentration of less than 0.01 molar were also checked by colorimetric determination carried out with the Beckman Model B spectrophotometer using *o*-phenanthroline to produce the colored complex. The procedure is described by Sandell.[6]

Analysis of Chlorine.—Chloride ion was determined volumetrically by the method of Volhard.[7]

Procedure.—The experimental procedure employed in obtaining the data was as follows. Atmospheric gases were displaced from the hydrolysis cell by passing a current of purified hydrogen through the cell. A measured quantity of redistilled conductivity water (oxygen free) was added to the cell which was suspended in a water-bath reservoir at 25° and the initial *p*H and/or potential of the pure water noted by means of glass and hydrogen electrodes, respectively. A weighed quantity of $FeCl_2 \cdot 2H_2O$ was then added to the cell and brought into solution by agitation with a magnetic stirrer after which the *p*H (potential) at 25° was again noted. In order to test for the presence of ferric ion formed by oxidation either before or during the measurements, a sample was withdrawn after the determination and added to a solution of potassium thiocyanate. No trace of the characteristic red color of ferric thiocyanate could be observed in this manner. In order to obtain reproducible *p*H values, it was found necessary to clean the electrodes carefully after each determination. This was accomplished by rinsing in hydrochloric acid and repeated washings with air-free redistilled conductivity water. Observations of the *p*H of the solutions were made until successive readings over a five-minute period showed no change, indicating the attainment of equilibrium. After determination of the equilibrium *p*H, aliquot samples were removed and analyzed volumetrically and/or colorimetrically by the methods previously noted.

Data and Calculated Results

Since solutions of ferrous chloride are only moderately acidic, it can be assumed that the (hydrated) divalent iron ion accepts only one hydroxyl ion from the solvent, water, as represented by equation 1

$$Fe^{++} + H_2O \rightleftharpoons FeOH^{+} + H^{+} \qquad (1)$$

$$Fe^{++} + 2H_2O \rightleftharpoons Fe(OH)_2 + 2H^{+} \qquad (2)$$

ionic hydration and complex formation being neglected. The thermodynamic hydrolysis constants for the above equations are given by the relations

$$K_1 = \frac{a_{H^+}a_{FeOH^+}}{a_{Fe^{++}}}$$

and

$$K_2 = \frac{a_{H^{2+}}a_{Fe(OH)2}}{a_{Fe^{++}}}$$

In the calculation of the hydrolysis constant, it is assumed that the activity of the $FeOH^+$ ion is equal to the hydrogen ion activity in solutions of the same ionic strength, *i.e.*

$$a_{FeOH^+} = a_{H^+}$$

This will be approximately true in the dilute range of concentrations studied since the difference between the activity coefficients of the two species is probably negligibly small. In any case, we have no means of directly determining the activity of the $FeOH^+$ ion independently and this assumption must be made. The equilibrium expression may thus be evaluated by

$$K_1 = a^2_{H^+}/a_{Fe^{++}}$$

The activity of ferrous ion, Fe^{++}, has been calculated from the relation

$$a = m\gamma$$

where *m*, the molality, is obtained from the analytical data for the salt concentration, and γ is the mean activity coefficient of divalent iron. The activity coefficients are taken from the experimental determinations by Randall and Frandsen[8] on the assumption that the activities of the ferrous and chloride ions are equal at the same ionic strength.

The data together with the calculated constants are collected in Table I.

TABLE I

Moles $FeCl_2$/1000 g. H_2O	$a_{Fe^{++}}$	*p*H	$a_{H^+} \times 10^5$	$K_1 \times 10^8$
0.00089	0.0008	5.69	0.204	0.525
.0028	.0023	5.45	.355	.537
.0074	.0057	5.21	.617	.661
.0150	.0108	5.02	.955	.851
.0192	.0134	4.92	1.20	1.07
.0236	.0161	4.86	1.38	1.18
.0345	.0231	4.78	1.66	1.20
.0455	.0287	4.73	1.86	1.20
.0565	.0347	4.70	2.00	1.15
.0696	.0417	4.65	2.24	1.20
.0772	.0459	4.63	2.34	1.20

The data indicate that, at least in the concentration range of from 0.02 to 0.08 molal, the hydrolysis of ferrous chloride is accurately represented by equation 1 with a hydrolysis constant equal to 1.20×10^{-8}. In view of the very modest release of H^+ ion (*p*H 4.63) even at concentration of 0.0772 *m* iron(II) chloride, we can conclude that reaction (2) does not contribute significant amounts of H^+ ion. At any rate there is no way that the two contributions can be determined separately.

Since the thermodynamic treatment is most rigorous in extremely dilute solutions, it might appear anomalous that *K* does not exhibit a constant value for concentrations below 0.02 molal. Possibly the relatively high *p*H at these concentrations may lead to the separation of basic salts or hydroxides in the form of colloidal dispersions with the result that no definite reaction equilibrium could be expected.

As a check on the representative reactions of iron(II) hydrolysis, the *p*H of a series of solutions

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(5) H. H. Willard and N. H. Furman, "Elementary Quantitative Analysis," D. Van Nostrand Company, Inc., New York, N. Y., 1940, p. 246.

(6) E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, Inc., New York, N. Y., 1944, p. 271.

(7) E. H. Swift, "Introductory Quantitative Analysis," Prentice-Hall, Inc., New York, N. Y., 1950, p. 94.

(8) M. Randall and M. Frandsen, THIS JOURNAL, 54, 47 (1932).

was measured at constant ionic strength. Since the activity coefficient of an ion in dilute solution is a function of the total ionic strength of the solution, the activity coefficients of the ionic species, at constant ionic strength, will not vary with changes in the actual concentration of the species. An "equilibrium constant" can then be determined on the basis of concentration rather than activities of the ions involved in the reaction. This constant, however, is not of thermodynamic significance but serves only to characterize the reaction taking place. For these measurements, a weighed amount of $FeCl_2 \cdot 2H_2O$ was added to the cell together with sufficient recrystallized KCl to bring the total ionic strength to a value of 0.50. The data and results, tabulated in Table II, substantiate the conclusions arrived at by the "activity" method.

TABLE II

Moles $FeCl_2$/1000 g. H_2O	pH	$K_1 \times 10^8$
0.022	4.41	6.9
.036	4.30	6.7
.045	4.26	6.8
.050	4.23	6.9
.071	4.16	6.8

The second basic dissociation constant, K_{b2}, of ferrous hydroxide for the reaction

$$FeOH^+ \leftrightarrows Fe^{++} + OH^-$$

can be calculated from the hydrolysis constant and the ion product of water

$$K_{b2} = \frac{a_{Fe^{++}} a_{OH^-}}{a_{FeOH^+}} = \frac{K_w}{K_1}$$

$$K_{b2} = \frac{1 \times 10^{-14}}{1.12 \times 0^{-8}} = 8.3 \times 10^{-7}$$

The standard free energy of the reaction governed by the thermodynamic constant may be calculated from the expression

$$\Delta F^\circ = -RT \ln K$$

This gives, for the free energy of the hydrolysis of ferrous chloride

$$\Delta F^\circ = 11000 \text{ cal./mole}$$

and, for the free energy of the secondary dissociation of ferrous hydroxide

$$\Delta F^\circ = 8300 \text{ cal./mole}$$

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[CONTRIBUTION FROM WESTINGHOUSE RESEARCH LABORATORIES]

The Viscosities of Aqueous Solutions Containing Metal Chelates Derived from Ethylenediaminetetraacetate[1]

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The viscosities of dilute aqueous solutions containing divalent metal chelates of ethylenediaminetetraacetate have been determined. For comparison the viscosities of solutions containing the simple dihydrogen-, monohydrogen- and ethylenediaminetetraacetate anions also have been studied. The viscosities of all such solutions can be related to concentration by the equation of Jones and Dole. The Jones–Dole viscosity B-coefficients characteristic of the simple anions increase in the order dihydrogen-, monohydrogen-, ethylenediaminetetraacetate. B-coefficients characteristic of the metal chelates were found to be related to quantities involving metal ion electronegativity (or second ionization potential of the metal), and reciprocal metal cation radius. The results obtained suggest that all the chelates studied, with the exception of the lead chelate, have similar structures in solution, involving the same number of ligand groups donated by the ethylenediaminetetraacetate ion to the metal cation.

Ethylenediaminetetraacetic acid has received considerable attention in recent years due to the ability of the ethylenediaminetetraacetate (EDTA) ion to react with a large number of different metal ions in solution to form water soluble metal chelates.[2] Despite the great amount of work done on such reactions, there is comparatively little information available concerning the structures of such complexes in solution, particularly in regard to the number of reactive groups of the EDTA ion actually bonded to the metal atom. It was felt that a study of some of the fundamental physical properties of aqueous solutions containing such chelates might prove profitable in this respect. A study has accordingly been made of the viscosities of dilute solutions containing the chelates resulting from the reaction of EDTA with a number of different divalent metal cations. For comparison, viscosities were also determined for solutions containing the EDTA ion itself and two other anions derived from ethylenediaminetetraacetic acid (H_4 EDTA), through the stepwise loss of protons: dihydrogen ethylenediaminetetraacetate (H_2 EDTA), and monohydrogen ethylenediaminetetraacetate (HEDTA).

Experimental

Reagents.—Bersworth reagent grade disodium dihydrogen ethylenediaminetetraacetate (Na_2H_2EDTA) dihydrate was further purified by the method of Blaedel and Knight.[3] Ethylenediaminetetraacetic acid was prepared by acidifying a solution of the disodium salt, filtering and washing the precipitate, and drying the precipitate at 110°.[4] Approximately one molar metal nitrate solutions were prepared and standardized as described previously.[4] The standard sodium and potassium hydroxide solutions employed were carbonate free. Disodium calcium ethylenediaminetetraacetate ($Na_2CaEDTA$) and the corresponding Mg compound ($Na_2MgEDTA$) were kindly donated by the Alrose Chemical Company. They were purified by dissolving in a small

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(1) Presented, in part, at the Cincinnati Meeting of the American Chemical Society, April, 1955.

(2) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hill, Inc., New York, N. Y., 1952.

(3) W. J. Blaedel and H. J. Knight, *Anal. Chem.*, **26**, 741 (1954).

(4) R. G. Charles, THIS JOURNAL, **76**, 5854 (1954).