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The Equilibria of Manganese Hydroxide, $Mn(OH)_2$, in Solutions of Hydrochloric Acid and Sodium Hydroxide

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The purpose of this paper is to present data on the solubility of manganese hydroxide in solutions of sodium hydroxide and of dilute hydrochloric acid. These data make possible the evaluation of the equilibria constants for the reaction of manganese hydroxide with hydrogen ions and with hydroxyl ions, the equilibria constants for the basic dissociation, the acidic dissociation, the solubility product constant and the corresponding free energy values. In addition to this they give several necessary values which are to be used later in the determination of the Mn/Mn^{++} couple.

Early work is at variance with respect to the value of the solubility product and the water solubility of manganese hydroxide. Sackur and Fritzmann² and Britton³ report 4×10^{-14} at 18° and 1.3×10^{-18} , respectively, for the solubility product of manganese hydroxide. Investigators reporting values of the water solubility (g. mole/liter) are:

Sackur and Fritzmann ² (at 18°)	2.15×10^{-5}
Bodländer ⁴	2.5×10^{-4}
Herz ⁵	6×10^{-8}
Tamm ⁶ (at 18°)	2×10^{-4}

No work is reported which can be used to show the complete record of the behavior of manganese

hydroxide in acid and in basic solutions; data for that record are presented in this paper.

Procedure

The general procedure is similar to that in previous papers.^{7,8}

All work was carried out in an atmosphere of nitrogen, purified by a purification train as described by Garrett and Heiks.³

Conductivity water (2×10^{-6} mho) was used for the preparation of all solutions. This water was boiled free of oxygen and stored under nitrogen.

Hydrochloric Acid Solutions.—Grasselli c. p. hydrochloric acid was used; standard solutions (oxygen free) were prepared by dilution of a sample which had been standardized with standard alkali using phenolphthalein as an indicator.

Sodium hydroxide solutions were prepared by dissolving Baker and Adamson reagent sodium hydroxide pellets in conductivity water which had previously been boiled free of carbon dioxide and oxygen; saturated barium hydroxide solution was added in slight excess to precipitate all the carbonate. The alkali was standardized with potassium acid phthalate using phenolphthalein as an indicator.

Manganese hydroxide was prepared from reagent quality manganese chloride (Baker and Adamson) by the method described by Johnston, Cuta and Garrett⁹ for the preparation of silver oxide. A slight excess of sodium hydroxide was maintained throughout this preparation in order to eliminate the formation of a basic salt. This method of preparation gave a product ($Mn(OH)_2$) of very slight color and with no indication of oxidation. This product was then washed twelve times with conductivity water by centrifugation. After the eighth washing no evidence of

(1) Present address: Colton Laboratory, Hiram College, Hiram, Ohio.

(2) Sackur and Fritzmann, *Z. Elektrochem.*, **15**, 845 (1909).

(3) Britton, *J. Chem. Soc.*, **127**, 2118 (1925).

(4) Bodländer, *Z. physik. Chem.*, **27**, 55 (1898).

(5) Herz, *Z. anorg. Chem.*, **22**, 279 (1900).

(6) Tamm, *Z. physik. Chem.*, **74**, 496 (1910).

(7) Garrett, Vellenga and Fontana, *THIS JOURNAL*, **61**, 367 (1939).

(8) Garrett and Heiks, *ibid.*, **63**, 562 (1941).

(9) Johnston, Cuta and Garrett, *ibid.*, **55**, 2311 (1933).

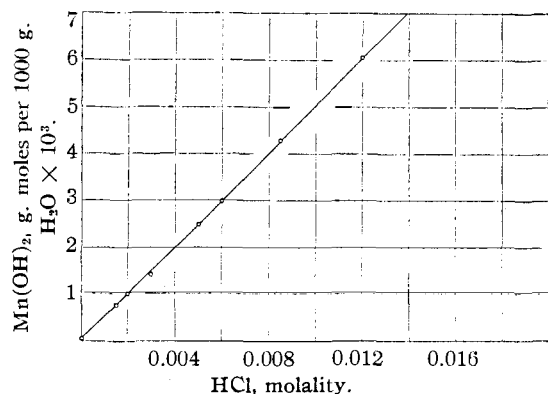


Fig. 1.

chloride ions could be obtained by addition of silver nitrate. By necessity this was taken as an indication of removal of excess hydroxyl ion. The four additional washings were used to ensure complete removal of extraneous ions. From this product a pair of samples was prepared for each desired concentration of acid or alkali. Equilibrium was approached from supersaturation (S) and from undersaturation (U); an equilibrium period of approximately eight days at $25 \pm 0.02^\circ$ was used.

Sedimentation, Filtration and Analysis.—The samples were allowed to sediment for a period of about seven days and were filtered through a Jena glass filter. They were then oxidized to permanganate with potassium periodate in presence of phosphoric acid and analyzed spectrophotometrically by the procedure described by Mehlig¹⁰ and by Willard and Greathouse.¹¹

The pH Values.—These measurements were made with a glass electrode calibrated to pH 10 by means of standard buffers.¹²

The Data

The data are collected in Tables I, II and III and shown graphically in Figs. 1 and 2. Figure 2 shows the complete record of manganese hydroxide in dilute acid and in sodium hydroxide solution. By necessity one must extrapolate the curve from water solubility to approximately 1 molar sodium hydroxide due to the fact that the solubility through this range is so slight that no method is available for analysis. However, on the basis of the nature of the rest of the solubility

(10) Mehlig, *Ind. Eng. Chem., Anal. Ed.*, **11**, 274 (1939).

(11) Willard and Greathouse, *THIS JOURNAL*, **39**, 2366 (1917).

(12) The instruments were calibrated at pH 4 with potassium acid phthalate-NaOH buffer (*cf.* Clark and Lubs buffer mixture) and with citric acid-sodium acid phosphate (*cf.* MacIlvaine, *J. Biol. Chem.*, **49**, 183 (1921)). The latter buffer system was used to calibrate the instrument to pH 8. At pH 8 the citric acid-sodium acid phosphate buffer calibration was checked with the boric acid-sodium hydroxide buffer (*cf.* Clark and Lubs buffer mixtures) which was then used to obtain the calibration to pH 10. Special care was observed in securing a glass electrode that would come to equilibrium quickly in this pH range. This was necessary since the pH of the unbuffered manganese hydroxide solutions might be expected to change very rapidly due to absorption of carbon dioxide. Several electrodes were investigated and two different ones were used to obtain the pH values in this range in which it is notoriously difficult to work.

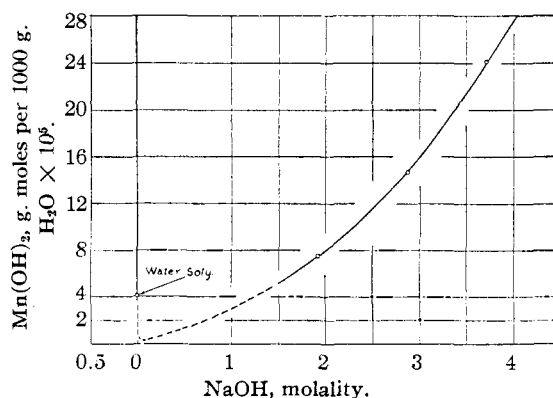


Fig. 2.

curve in acid and in alkali, it seems very probable that this represents the solubility curve through that region.

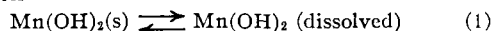
TABLE I

THE SOLUBILITY OF MANGANESE HYDROXIDE IN WATER	
Prepn.	Moles Mn(OH) ₂ for 1000 g. H ₂ O
1	4.04×10^{-5}
1	3.91×10^{-5}
1	4.14×10^{-5}
2	3.73×10^{-5}
2	4.10×10^{-5}
2	4.56×10^{-5}
Average 4.1×10^{-5}	

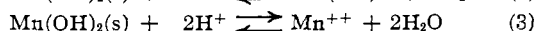
The high solubility of manganese hydroxide in acid solution and its low solubility in alkali solutions give a qualitative indication of the fact that manganese hydroxide is a strong base. This seems to be further verified by the observation that manganese salts do not hydrolyze appreciably. The complete verification of this prediction is given in the subsequent calculation of the acidic and basic constants of manganese hydroxide.

The following equations probably indicate the reaction that manganese hydroxide undergoes in water, in acid, and in alkali.

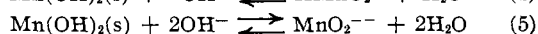
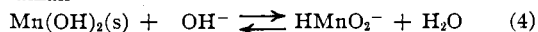
In water



In acid



In alkali



The Equilibria in Acid Solutions.—An inspection of the data in Table II indicates that in all cases the manganese hydroxide must have dissolved as the result of reaction with two hydrogen

TABLE II
THE SOLUBILITY OF MANGANOUS HYDROXIDE IN DILUTE HYDROCHLORIC ACID

Moles of HCl per 1000 g. H ₂ O	Approach to equilibrium	Moles of Mn(OH) ₂ per 1000 g. H ₂ O × 10 ³	m _{H⁺} from glass electrode data taken from smoothed curve	$K_3 = \frac{m_{Mn^{++}} + \gamma_{Mn^{++}}}{m_{H^+}^2 \gamma_{H^+}^2} a_{H_2O}^2$
0.000		4.1		
.00150	S	73.8	6.3×10^{-10}	1.7×10^{15}
.00150	U	75.2		
.00200	S	101	8.0×10^{-10}	1.4×10^{15}
.00200	U	103		
.00300	S	139	8.0×10^{-10}	2.1×10^{15}
.00300	U	143		
.00500	S	250	1.0×10^{-9}	2.2×10^{15}
.00500	U	247		
.00600	S	292	1.2×10^{-9}	1.8×10^{15}
.00600	U	304		
.00850	S	438	1.6×10^{-9}	1.4×10^{15}
.00850	U	422		
.0120	S	600	2.0×10^{-9}	1.2×10^{15}
.0120	U	610		
.0160	S	800	2.0×10^{-9}	1.6×10^{15}
.0160	U	810		
.0200	S	990	2.0×10^{-9}	1.2×10^{15}
.0200	U	980		

Av. value $K_3 = 1.6 \times 10^{15}$
 $\Delta F_{298}^0 = -20,800$ cal.

TABLE III
THE SOLUBILITY OF MANGANOUS HYDROXIDE IN SODIUM HYDROXIDE

Moles of NaOH per 1000 g. H ₂ O	Approach to equilibrium	Moles of Mn(OH) ₂ per 1000 g. H ₂ O, × 10 ³	$K_4 = \frac{m_{HMnO_2} - \gamma_{HMnO_2}}{m_{OH^-} \gamma_{OH^-} a_{H_2O}}$
1.924	U	7.53	3.8×10^{-6}
2.880	S	15.0	4.8×10^{-6}
2.880	U	14.4	
3.72	S	23.3	6.1×10^{-6}
3.72	U	25.0	
4.14	S	28.6	6.6×10^{-6}
4.14	U	29.8	

ions (see Equation 3 above) in order that the hydrogen ion concentration be reduced to the very low values indicated by the pH values. Hence, if any of the Mn(OH)⁺ ions are present they must be so in very small amounts. This suggests that Equation 3 accounts, in the main, for the increased solubility in acid solutions; further support of this conclusion will be obtained in the discussion of the solubility product values obtained.

Hence from Equation (3)

$$Mn(OH)_2(s) + 2H^+ = Mn^{++} + 2H_2O$$

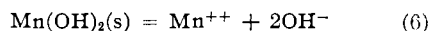
$$K_3 = \frac{m_{Mn^{++}} + \gamma_{Mn^{++}} a_{H_2O}^2}{m_{H^+}^2 \gamma_{H^+}^2}$$

or by the simplification suggested in previous cases⁸

$$K_3 = \frac{m_{Mn^{++}} + \gamma_{Mn^{++}}^2 a_{H_2O}^2}{m_{H^+}^2}$$

The values of $m_{Mn^{++}}$ and m_{H^+} are taken from Table II; the values of γ_{HCl} are given by Harned and Ehlers¹³ and the values of a_{H_2O} are calculated from Raoult's law. From these data $K_3 = 1.6 \times 10^{15}$ (variation 1.2×10^{15} to 2.2×10^{15} over the concentration range $m_{HCl} = 0.0015$ to 0.02). The corresponding $\Delta F_{298}^0 = -20,800$ cal.

The Solubility Product Constant, K_6 .—From the value of K_3 the solubility product constant, K_6 , may be calculated with the aid of the ion product, K_w , of water for the equation



$$K_6 = \frac{K_3 K_w^2}{a_{H_2O}^2} = m_{Mn^{++}} \gamma_{Mn^{++}} m_{OH^-}^2 \gamma_{OH^-}^2$$

$$K_6 = 1.6 \times 10^{-13}$$

and the corresponding $\Delta F_{298}^0 = 17,400$ cal.

This value may be compared with the similar value calculated from the water solubility data on the assumption of complete dissociation; hence

$$K_6 = 4a_{Mn^{++}}^3 = 2.8 \times 10^{-13}$$

$$\Delta F_{298}^0 = 17,150$$
 cal.

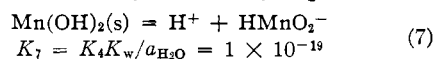
The agreement is excellent. The assumption of complete dissociation is a very probable one in such dilute solutions (10^{-5} molal) and in the case of a compound which gives every appearance of being a strong base. The values are probably reliable to the extreme of the variation between

(13) Harned and Ehlers, THIS JOURNAL, 55, 2179 (1933).

them and probably represent the best values so far obtained. It is improbable that the value for the water solubility should be less than that obtained in this research. The water had a conductivity of 2×10^{-6} mhos and a pH of approximately 6.8. It was boiled to remove oxygen and carbon dioxide and stored under nitrogen. The chance for the presence of extraneous hydrogen ions in the samples was reduced to a minimum. On the other hand, the chance for the presence of hydroxyl ions was probably greater for the samples of manganese hydroxide were precipitated in alkaline solutions and washed with conductivity water. Of necessity the absence of chloride ions was used as an indirect test for the removal of the last traces of hydroxyl ions. A small amount of extraneous hydroxyl ions would, by common ion effect, greatly reduce the solubility of manganese hydroxide (see Fig. 2). The value of the water solubility obtained in this research seems to us to be the most probable one, not only due to the care observed in the preparation of the samples, but also to the fact that the water solubility values obtained from different preparations of manganese hydroxide are in good agreement (see Table I).

The Equilibrium in Alkaline Solutions.—If manganese hydroxide is a strong base then we may expect its hydrogen ion dissociation to be very slight, particularly the second dissociation. Unfortunately, the solubility is so slight in the range where it is possible to calculate these acid dissociation values that no data were obtained. However, the constant for Equation 4 has been

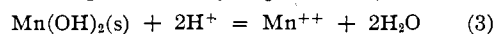
evaluated through the range $m_{\text{NaOH}} = 1.0$ to 4.0 (see Table III). The variation in the value of K_4 through this range is from 3.8×10^{-5} to 6.6×10^{-5} . Using the value of $K_4 = 1 \times 10^{-5}$ as the most probable value (obtained by extrapolation of a plot of K_4 vs. m_{NaOH} to $m_{\text{NaOH}} = 0$) gives the value of $\Delta F_{298}^0 = 7000$ cal. This makes possible the evaluation of the acid dissociation constant, K_7 , for the reaction represented by Equation 7



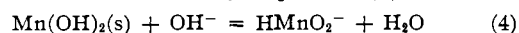
Acknowledgment.—We wish to thank Professors W. Brode and W. MacNevin for aid in the analyses of these solutions.

Summary

The solubility of manganese hydroxide has been determined in water, in dilute hydrochloric acid and in sodium hydroxide at $25 \pm 0.02^\circ$. The data indicate that manganese hydroxide is a strong base. The main reaction taking place in acid solution is represented by Equation (3)



and in basic solution by Equation (4)



The value of the solubility product calculated from Equation (3) is 1.6×10^{-13} ; the value obtained from the water solubility data is 2.8×10^{-13} . The value of K_4 is 1×10^{-5} which gives the value for the ion product of the acidic dissociation, $\text{Mn(OH)}_2 = \text{H}^+ + \text{HMnO}_2^-$, of 1×10^{-19} .

COLUMBUS, OHIO

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, TENNESSEE VALLEY AUTHORITY]

Phosphorus-Halogen Compounds from Phosphorus Pentoxide and Halides. Properties of Phosphorus Trifluoride and Phosphorus Oxyfluoride*

BY GRADY TARBUTTON, E. P. EGAN, JR., AND S. G. FRARY

The reaction of non-volatile halides with phosphorus pentoxide has been mentioned in the literature, but the conditions of the experiments and the properties of the products formed have not been thoroughly investigated. Schultze¹ prepared phosphoryl trifluoride by the action of phosphorus pentoxide on a fluoride, and Thorpe and Hambly² obtained the same compound from

phosphorus pentoxide and cryolite. Lucas and Ewing,³ however, reported that phosphorus pentafluoride, not phosphoryl trifluoride, was obtained by heating a mixture of phosphorus pentoxide and calcium fluoride. Curtis, Copson and Abrams⁴ stated that the reaction between phosphorus pentoxide and sodium chloride yielded volatile phosphorus chlorides and that this type of reac-

* Original manuscript received April 22, 1940.

(1) H. Schultze, *J. prakt. Chem.*, (2) **21**, 443 (1880).

(2) T. E. Thorpe and J. F. Hambly, *J. Chem. Soc.*, **55**, 759 (1889).

(3) H. J. Lucas and F. J. Ewing, *THIS JOURNAL*, **49**, 1270 (1927).

(4) H. A. Curtis, R. L. Copson and A. J. Abrams, *Chem. and Met. Eng.*, **44**, No. 3, 140-142 (1937).