

[CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND THE CHEMISTRY DEPARTMENT OF IOWA STATE COLLEGE]

**The Solubility, Activity Coefficients and Solubility Product of Manganese(II) Iodate<sup>1a</sup>**BY ANSON MACK HAYES<sup>1b</sup> AND DON S. MARTIN, JR.

The solubilities of manganese(II) iodate in water at temperatures from 3–90°, in aqueous solutions of sodium chloride at 3° and 25°, and in aqueous solutions of potassium iodate and manganese(II) perchlorate at 25° were determined. Mean ionic activity coefficients have been calculated from the solubilities. The solubility product at 25° was  $4.79 \times 10^{-7}$  and the standard heat of solution was 2280 calories/mole.

**Introduction**

Very little information is available about the solubility of manganese(II) iodate in water. Early workers indicated that it is quite insoluble and one value of 0.5 g./100 g. H<sub>2</sub>O is given for room temperature.<sup>2a,b</sup> The variation of solubility with temperature, the activity coefficients, and the activity product have not been previously described.

This investigation was initiated to supply information for kinetic studies in this Laboratory involving the oxidation of manganese(II) in solutions containing iodate. The solubility of manganese(II) iodate in water at various temperatures and in aqueous solutions of potassium iodate, manganese(II) perchlorate and sodium chloride were determined. The results have been used to compute the activity coefficients, the solubility product and the heat of solution of manganese(II) iodate.

**Experimental**

**Materials.**—Manganese(II) iodate was prepared by precipitation from aqueous solutions of reagent grades iodic acid and manganese(II) chloride. The precipitate was filtered on a glass sinter and washed several times. However, the extent of the washing was limited somewhat by the finite solubility of the salt. The vacuum-dried salt was analyzed for manganese and iodate. Results of these analyses indicated 13.5% manganese and 0.0296 equivalent/gram. Theoretical values for Mn(IO<sub>3</sub>)<sub>2</sub> are 13.57% manganese and 0.02965 equivalent/gram. Therefore, the anhydrous salt was formed. Freshly prepared samples were used for this work; upon long standing, decomposition was evidenced by the faint odor of iodine. Such decomposition was believed to be not sufficient to influence these results significantly.

Water redistilled from alkaline permanganate was used throughout; its conductivity was found to be about  $10^{-8}$  ohms<sup>-1</sup> cm.<sup>-1</sup>.

Reagent grade sodium chloride and potassium iodate were employed for the preparation of the solutions. Manganese perchlorate solutions were prepared by dissolving very pure manganese metal in perchloric acid. These solutions contained a small excess of perchloric acid which could be determined from the pH measurements.

**Analyses.**—The manganese determinations were made by oxidation to permanganate with periodic acid according to the procedure of Willard and Greathouse.<sup>3</sup> Manganese(II) iodate was also ignited to Mn<sub>2</sub>O<sub>4</sub>, and weighed. The iodate determinations were made iodometrically in acid solution. The sodium thiosulfate used to titrate the liberated iodine was standardized against potassium iodate prepared by the J. T. Baker Chemical Company by the procedure described by Willard and Furman.<sup>4</sup>

**Preparation of Solutions.**—All solutions were prepared by weighing dried salts and adding a measured volume of water to these salts in a glass-stoppered flask. Chloride and iodate concentrations of the original solutions were verified by standard titration procedures.

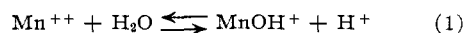
**Apparatus.**—A water thermostat with a temperature control of  $\pm 0.02^\circ$  was used for temperatures below 45°. Effective stirring and agitation were provided by means of a Burrel shaker. The point at 90° was obtained by a manually controlled water-bath.

**Procedure.**—Aqueous solutions in contact with solid manganese(II) iodate were shaken for 24 hours at 25° and 45° in glass-stoppered flasks. The volume of these solutions was approximately 200 ml. After withdrawing and analyzing 25-ml. aliquots from these samples, the flasks were placed in the other temperature bath and shaken for six hours. Aliquots were again withdrawn and analyses performed. Solubilities of the order of  $5 \times 10^{-3} m$  obtained at each temperature checked to within  $\pm 0.2\%$ . This was taken to indicate that reversible equilibrium had been attained at each temperature. Manganese(II) iodate was agitated at 3° and 25° with aqueous solutions of manganese(II) perchlorate and potassium iodate. The aliquots taken from these were accurately weighed so that an evaluation of the density could be made. Concentrations have been expressed in molalities (moles 1000 g. H<sub>2</sub>O) throughout.

The solutions containing manganese(II) perchlorate and sodium chloride were analyzed by adding hydrochloric acid and potassium iodide and titrating the liberated iodine with sodium thiosulfate. Aliquots from the solutions containing potassium iodate were oxidized to permanganate with periodic acid in the presence of sulfuric acid and compared colorimetrically in a Beckman model DU spectrophotometer at a wave length of 5260 Å. with a standard prepared by identical treatment from a standard solution of manganese(II) perchlorate. The solubilities of the pure salt at high temperatures were determined in an exactly similar fashion. The solid manganese(II) iodate was always present in considerable excess. The pH of each aliquot was taken with a Beckman model G pH meter to determine the hydrogen ion activity.

**Discussion and Results**

The observed solubilities of manganese(II) iodate in water and in aqueous solutions of sodium chloride, potassium iodate and manganese(II) perchlorate are presented in Table I. It is to be noted that about a pH 4 existed in most of the equilibrium solutions. It was estimated from the data of Fox, Swinehart and Garrett<sup>5</sup> in their determination of the solubility product of Mn(OH)<sub>2</sub> that the equilibrium constant must be less than  $10^{-10}$  for hydrolysis according to the reaction



Therefore, the hydrogen ion in the solutions was presumed to be due to the presence of hydrochloric acid which was not completely removed despite the several washings. This hydrochloric acid concentration, calculated from the pH by means of consistent activity coefficients, was included in the ionic strength given in Table I.

(5) R. K. Fox, D. F. Swinehart and A. B. Garrett, *THIS JOURNAL*, **63**, 1779 (1941).

(1) (a) Contribution No. 152 from the Institute for Atomic Research and the Chemistry Department of Iowa State College, Ames, Iowa. Work performed in the Ames Laboratory of the Atomic Energy Commission. (b) Present address: Research Department of the E. I. du Pont Co., Waynesboro, Va.

(2) (a) C. F. Rammelsberg, *Pogg. Ann.*, **55**, 66 (1842); (b) A. Ditte, *Ann. chim. phys.*, [6] **21**, 157 (1890).

(3) H. H. Willard and L. H. Greathouse *THIS JOURNAL*, **39**, 2366 (1917).

(4) H. H. Willard and N. H. Furman, "Elementary Quantitative Analysis," D. Van Nostrand Co., Inc., New York, N. Y., 1940, p. 269.

TABLE I  
SOLUBILITY DATA FOR MANGANESE(II) IODATE

Temp., °C.	mNaCl	mKIO <sub>3</sub>	mMn(ClO <sub>4</sub> ) <sub>2</sub>	mMn(IO <sub>3</sub> ) <sub>2</sub> × 10 <sup>3</sup>	pH	√μ <sub>±</sub>	γ <sub>±</sub>
3				5.68	4.03	0.131	0.783
3	0.01007			6.21	3.83	.170	.716
3	.02462			6.65	3.95	.211	.669
3	.0554			7.51	3.80	.280	.593
3	.1108			7.86	3.88	.367	.565
3	.407			9.02	3.91	.659	.493
25				6.58	4.03	.141	.749
25	.01007			6.94	3.84	.176	.710
25	.02462			7.61	3.94	.218	.647
25	.0554			8.36	3.80	.284	.589
25	.1108			8.96	3.86	.371	.550
25	.407			10.41	3.90	.662	.473
25		0.00688		4.74	4.13	.146	.722
25		.02213		2.11	4.28	.169	.689
25		.0622		0.685	4.10	.254	.557
25		.1091		0.301	4.43	.332	.509
25			0.01030	5.31	3.00	.219	.647
25			.00743	5.60	2.63	.204	.663
45				7.13	..	.146	..
90				8.54	..	.160	..

Activity coefficients of the manganese(II) iodate in the aqueous solutions of sodium chloride were evaluated at 3° and 25° from the changes of solubility with ionic strength.

The solubility at zero ionic strength was obtained by extrapolation to zero ionic strength of the convenient, simple expression from the interionic attraction theory for a 2-1 electrolyte given below.

$$\log \gamma_{\pm} = \frac{-S\mu_m^{1/2}}{1 + A\mu_m^{1/2}} \quad (2)$$

where

$\gamma_{\pm}$  is the mean ionic activity coefficient

$\mu_m$  is the ionic strength

$S$  is the limiting slope (1.017 at 25° and 0.981 at 3° from tables in Harned and Owen<sup>6</sup>)

$A$  is a constant

In place of  $\gamma_{\pm}$  was substituted  $m_0/m$  where  $m$  is the molality of a saturated solution and  $m_0$  the corresponding value extrapolated to zero ionic strength. Thus when  $\log m$  was expressed as a function of  $\sqrt{\mu}$ , the constants  $m_0$  and  $A$  were deter-

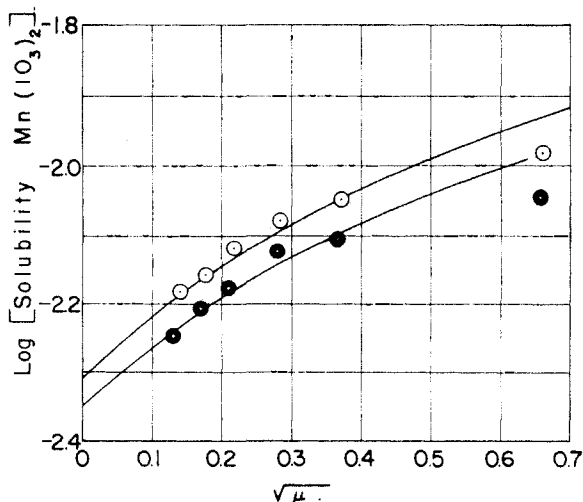


Fig. 1.—Solubility of  $Mn(IO_3)_2$  in aqueous NaCl solutions: ●, 3°; ○, 25°.

(6) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1950, p. 587.

mined from the smoothed function in the region of low ionic strengths. The values of these constants were: at 3°,  $m_0 = 4.45 \times 10^{-3}$ ,  $A = 1.11$ ; at 25°,  $m_0 = 4.93 \times 10^{-3}$ ,  $A = 1.18$ . The values for  $A$  correspond to  $\delta$  values of 3.4 and 3.6 Å., respectively.<sup>6</sup> The fit of the calculated solubilities is illustrated in Fig. 1 in which the curves represent the functions defined by expression 2.

Since the solubility product for a 2-1 electrolyte is given by

$$K_{sp} = 4 m_0^3 \quad (3)$$

the values  $3.52 \times 10^{-7}$  for 3° and  $4.79 \times 10^{-7}$  for 25° were indicated.

Mean ionic activity coefficients were computed from the relation

$$K_{sp} = \gamma_{\pm}^3 m^2 (IO_3^-) m_{Mn^{++}} \quad (4)$$

Values of  $\gamma_{\pm}$  for the experimental solutions have been included in Table I and these values for 25° have been plotted as a function of ionic strength in Fig. 2 which also includes a  $\gamma_{\pm}$  for  $MnCl_2$  as reported by Robinson and Stokes.<sup>7</sup> The magnitude of the activity coefficients indicates that manganese(II) iodate may be considered a highly dissociated electrolyte. However, the somewhat lower values in iodate solutions may be due to the formation of complexes to some extent.

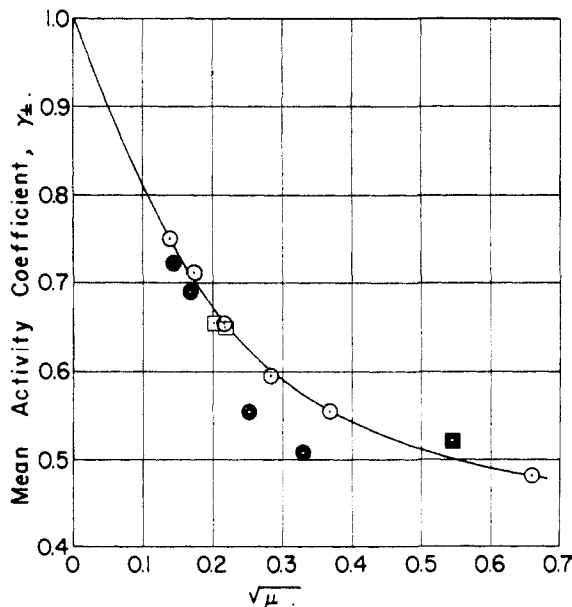
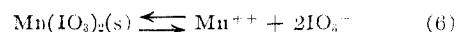


Fig. 2.—Mean ionic activity coefficient ( $\gamma_{\pm}$ ) for  $Mn(IO_3)_2$  in various solutions at 25°: ○, NaCl; ●,  $KIO_3$ ; □,  $Mn(ClO_4)_2$ ; ■, activity coefficient for manganese chloride reported by Robinson and Stokes.

The heat of solution of manganese(II) iodate was calculated from the dependence of the solubility product upon temperature by the well-known thermodynamic relation

$$\Delta H^{\circ} = -2.303R \Delta(\log K_{sp}) / \Delta(1/T) \quad (5)$$

The value obtained was 2,280 calories/mole from the variation in the temperature interval 3-25° for the reaction



(7) R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **36**, 1137 (1940).

Assuming that  $\Delta H^0$  is independent of temperature over this range and from the  $\Delta F^0$  of 8,610 cal. given by the solubility product at 25°, the  $\Delta S^0$  for reaction 6 is -21.2 e.u. Using -19.1 e.u. as the standard entropy<sup>8</sup> of  $Mn^{++}$  and +28.0 e.u. for  $IO_3^-$ ,<sup>9</sup> the

(8) A. F. Kapustinskii, *J. Phys. Chem. (U. S. S. R.)*, **15**, 220 (1941).

(9) W. M. Latimer, K. S. Pitzer and W. V. Smith, *THIS JOURNAL*, **60**, 1829 (1938).

standard entropy of solid manganese(II) iodate was calculated to be 58.1 e.u. This value may be compared with 54 e.u. which would be obtained by the use of the tables given by Latimer<sup>10</sup> for the entropies of ions in solids.

(10) W. M. Latimer, *ibid.*, **73**, 1480 (1951).

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## The Persulfate-Iron(II) Initiator System for Free Radical Polymerizations<sup>1</sup>

BY J. W. L. FORDHAM AND H. LEVERNE WILLIAMS

In dilute aqueous solutions of acrylonitrile and under a nitrogen atmosphere the oxidation of iron(II) by persulfate is a second order reaction, probably the bimolecular reaction:  $Fe^{++} + S_2O_8^{--} \rightarrow Fe^{+++} + SO_4^{\cdot-} + SO_4^{\cdot-}$ . The rate constant of the second order reaction at weak ionic strengths of the solution is expressed by the Brønsted-Debye-Hückel equation for a reaction between two oppositely charged divalent ions. The calculated product of the ionic charges of the reactants has a value of -4.15 at 0° and -3.80 at 10°. In the temperature range from 0 to 10° the rate constant at infinite dilution is given by  $k_0 = 1.0 \times 10^{11} e^{-12,100/RT}$  l. mole<sup>-1</sup> sec.<sup>-1</sup>.

In the presence of 2,2'-bipyridine the addition of the first two molecules of complexing agent to the ferrous ion does not destroy the reactivity of the complex with persulfate. However, with the formation of the tribipyridine complex its reactivity is destroyed. The rate constant of the second order reaction is unchanged in the presence of the emulsifiers Agent 140 BK and Daxad 11 but is increased in the presence of Nacconol NRSF.

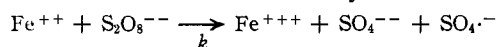
### Introduction

The persulfate-iron(II) reaction has not yet been studied extensively as a source of free radicals although this system will initiate acrylonitrile polymerization.<sup>2</sup> However it has been postulated that the reaction produces sulfate radical ions which are able to initiate the oxidation chain for alcohols.<sup>3</sup> Saal<sup>4</sup> studied the rate of the reaction in the presence of different concentrations of the electrolytes potassium chloride, magnesium chloride and magnesium sulfate but he neglected the bimolecular terminating step between the iron(II) and the sulfate radical ions and "his method of expressing concentrations is obscure and apparently burdened with typographical errors".<sup>5</sup>

In view of the lack of reliable data on the rate constant of the oxidation of iron(II) by persulfate this study was undertaken. Determinations of the rate constant at various ionic strengths of the solution were made in order to determine the rate constant at infinite dilution. The effect of adding the iron(II) complexing agent 2,2'-bipyridine and various emulsifiers was investigated.<sup>5a</sup>

### Theoretical

If the  $SO_4^{\cdot-}$  radical ion formed by the reaction



reacts solely with a monomer molecule to initiate polymerization, then in the absence of interfering

(1) Presented before the Division of Inorganic and Physical Chemistry, American Chemical Society, Cleveland, Ohio, April, 1951.

(2) R. G. R. Bacon, *Trans. Faraday Soc.*, **42**, 140 (1946).

(3) J. H. Merz and W. A. Waters, *Faraday Soc. Discussions*, **2**, 179 (1947).

(4) R. N. J. Saal, *Rec. trav. chim.*, **47**, 385 (1928).

(5) C. V. King and O. F. Steinbach, *THIS JOURNAL*, **52**, 4779 (1930).

(5a) Subsequent to the preparation of this paper the work by Kolthoff, Medalia and Raaen has been published (*ibid.*, **73**, 1733 (1951)) extending considerably the knowledge of the persulfate-iron(II) reaction under various conditions. Their data do not alter any of the considerations in this paper.

side reactions the iron(II) should disappear by a second order reaction and eq. 1 should be valid.

$$\ln(1 - (b - a)/[Fe^{++}]) = -(b - a)kt + \ln a/b \quad (1)$$

where  $a = [S_2O_8^{--}]_0$  and  $b = [Fe^{++}]_0$ .

Preliminary experimental data indicated that the initial reaction involving traces of atmospheric oxygen, very difficult to remove experimentally, results in an increase in the initial rate of iron(II) disappearance and a decrease in the value of  $(b - a)$  for the subsequent oxygen-free reaction. Consequently the difference between the initial concentrations of iron(II) and persulfate cannot be used to determine the value of  $(b - a)$  for the oxygen-free reaction. But when  $a < b$  and  $t \rightarrow \infty$

$$b - a = [Fe^{++}]_{\infty} \quad (2)$$

Hence under these conditions eq. 1 becomes

$$\ln(1 - [Fe^{++}]_{\infty}/[Fe^{++}]) = [Fe^{++}]_{\infty}kt + C \quad (3)$$

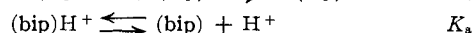
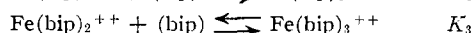
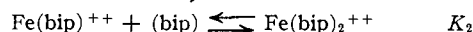
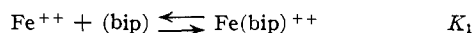
where  $C = a$  constant.

Since the reaction is ionic, the observed rate constant will be dependent on the activity coefficients of the reactants and the activated complex. In dilute solutions the equation of the observed rate constant should be given by

$$\log k = \log k_0 - 4 \frac{A\mu^{1/2}}{(DT)^{3/2}} \quad (4)$$

where  $k_0 =$  rate constant at infinite dilution;  $A =$  a constant;  $D =$  dielectric constant of the medium;  $T =$  temperature; and  $\mu =$  ionic strength of the solution.

When 2,2'-bipyridine (bip) is added to the system the following equilibria are assumed to be valid.



When the total bipyridine concentration and the pH of the solution are adjusted so that practically