421. *The Hydrolysis of Manganese*(II) *Ion.*

By D. D. PERRIN.

The hydrolysis of manganese(II) ion has been studied potentiometrically over the range 15—42° at various ionic strengths (adjusted by addition of potassium nitrate). Results are interpreted quantitatively by assuming that the complex ion, $MnOH^+$, is formed. Values of the corresponding acid dissociation constant, $^*K_1$, have been obtained as a function of temperature and of ionic strength.

THERE is little reliable quantitative information about the hydrolytic equilibria of the bivalent metal ions from manganese to zinc. Nor, although polynuclear complex formation is of major importance in the hydrolysis of copper(II) ion,[1] is there much known concerning the significance of such equilibria in the hydrolysis of the other cations in this series. A detailed study on the hydrolysis of copper(II) was recently reported,[1] and the hydrolysis of manganese(II) ion has now been studied over a range of concentration, ionic strength, pH, and temperature. Studies of the other cations are in progress.

On the assumption that the principal reaction was $Mn_{aq}^{++} \rightleftharpoons MnOH^+ + H^+$, Chabarek, Courtney, and Martell[2] calculated, from the alkali titration curve of a solution about 0·01M in manganese(II) ion and 0·1M in potassium chloride, that $-\log {}^*K_1$ was 10·6 at 30°. The same assumption is implicit in the estimates, from distribution experiments,[3,4] of $\log K_1 = 4{\cdot}52$ at 20° and, from kinetic studies,[5] of $-\log {}^*K_1 = 9{\cdot}54$ at 100°. The present work validates this assumption and indicates that, up to the onset of precipitation, $MnOH^+$ is the major hydrolysed species for concentrations of manganese(II) ion ranging from 0·0005M to 0·1M.

---

[1] Perrin, *J.*, 1960, 3189.

[2] Chabarek, Courtney, and Martell, *J. Amer. Chem. Soc.*, 1952, **74**, 5057.

[3] Löfman, *Z. anorg. Chem.*, 1919, **107**, 241.

[4] Jellinek, " Lehrbuch der physikalischen Chemie," 2nd edn., Enke, Stuttgart, 1933, Vol. IV, p. 62.

[5] Kullgren, *Z. phys. Chem.*, 1913, **85**, 466.

EXPERIMENTAL

The potentiometric method, the recording pH meter, and the ancillary apparatus used in the present work have been described previously,[1] except that the Perspex stopper of the reaction vessel was replaced by a tightly fitting soft-rubber bung.

The procedure was as follows: a manganese chloride solution (100 ml.) of known concentration, ranging from 0·0005M to 0·1M and containing known (low) concentrations of hydrochloric acid and various amounts of potassium nitrate to alter the ionic strength, was titrated against 0·100M-potassium hydroxide (carbonate-free) solution, adequate time being allowed after each addition to ensure that equilibrium was attained. Hydrolysis constants were calculated from the initial concentration of manganese ion, the concentration of potassium hydroxide added, and the hydrogen-ion activity as measured by the glass electrode. Similar experiments, without manganese, were done in all cases to determine the concentration of free hydroxyl ion corresponding to the observed pH values: this was necessary because of the poor poise of the system over the pH range studied, which led to a sensitivity to adventitious traces of buffering species such as carbonate or silicate. To ensure that, initially, hydrolysis of manganese was negligible, all solutions were made 0·00025M in hydrochloric acid. During titrations, especially over the pH range 6—8·5, attainment of pH constancy (here defined as a drift of less than 0·002 pH unit in 5 min.) was slow, and an average titration at 20° took about 4 hr. Instrumental stability was good, but, especially at the higher temperatures, the electrodes cooled slightly during transfers between solutions and they had to be left for up to 0·5 hr. to attain an initial equilibrium. However, in all cases, when the electrode system was returned to buffer solution for checking at the end of the titration no final drift greater than 0·01 pH unit was observed.

Only low values of Z (the average number of hydroxyl ions bound per manganese atom) could be obtained before the onset of precipitation, as shown by a rapid downward drift of pH readings and the subsequent appearance of opalescence. Results up to this point could be interpreted quantitatively on the assumption that hydrolysis proceeded through the formation only of the mononuclear manganese–hydroxyl complex ion, $MnOH^+$, so that $^*K_1$ was given by

$$^*K_1 = \frac{[MnOH^+](a_{H^+})}{[Mn^{++}]} = \frac{([KOH^+] - [HCl] - [OH^-])(a_{H^+})}{([Mn^{++}]_T + [HCl] + [OH^-] - [KOH])}. \qquad (1)$$

Data from a typical experiment are presented in Table 1.

TABLE 1.

Evaluation of $^*K_1$ from potentiometric titration.

$[MnCl_2]$ = 0·00500M. [HCl] = 0·000255M. Temp. 25°.
Titrated with 0·100M-KOH. $[MnOH^+]$ assumed = [KOH] − [HCl] − $[OH^-]$.

[KOH] (μM)	pH	[KOH] − [HCl] − $[OH^-]$ (μM)	$[Mn^{++}]$ (μM)	Z	−log $^*K_1$
0	3·640	—	—	—	—
100	3·859	—	—	—	—
200	4·340	—	—	—	—
250	5·705	—	—	—	—
255	6·844	—	—	—	—
260	7·410	4·4	4996	0·0009	(10·47)
270	8·011	12·7	4987	0·0025	(10·61)
280	8·314	20·8	4979	0·0042	10·69
290	8·498	28·9	4971	0·0058	10·73
300	8·619	37·2	4963	0·0074	10·74
320	8·766	54·6	4945	0·0109	10·72
340	8·886	71·7	4928	0·0143	10·72
360	8·977	89	4911	0·0178	10·72
400	9·084	125	4875	0·0250	10·68
				Average	10·71

Effect of Ionic Strength and Temperature on $^*K_1$.—The values of −log $^*K_1$ listed in Table 2 were calculated by using equation (1). They indicate that −log $^*K_1$ is relatively insensitive to ionic strength, changing by less than 0·4 logarithm unit as I varies from 0·015 to 1·51. [A similar insensitivity is shown by log $^*\beta_{22}$ for copper(II) ion.[1]] The estimates of −log $^*K_1$ at I = 1·5, obtained from results for $[Mn^{++}]_T$ = 0·0050M and 0·100M, agree within experimental error, and results at I = 0·00176 for $[Mn^{++}]_T$ = 0·00050M and at I = 0·0153 for $[Mn^{++}]_T$ = 0·0050M differ only by an amount close to that predicted from the limiting Debye–Hückel equation. This constancy of −log $^*K_1$ over a 200-fold variation in concentration of manganese(II) ion strongly supports the conclusion that no significant amounts of polynuclear complexes are formed under these conditions.

TABLE 2.

Effect of ionic strength on log $^*K_1$ at 20°.

$MnCl_2$ solutions, containing low concentrations of HCl and varied concentrations of KNO_3, titrated with 0·100M-KOH. Values of $-\log {}^*K_1{}^\circ$ calculated from $-\log {}^*K_1$ by using eqn. (2) with $\alpha = 1$ and $\beta = 0{\cdot}40$.

pH range	$[Mn^{++}]_T$ (M)	I	Z	$-\log {}^*K_1 \pm$ range (no. of obs.)	$-\log {}^*K_1{}^\circ$
9·012—9·833	0·00050	0·00176	0·016 —0·092	10·81 ± 0·03 (7)	10·75
8·535—9·375	0·0050	0·0153	0·0048—0·0326	10·88 ± 0·04 (7)	10·72
8·254—9·238	0·0050	0·0403	0·0021—0·0182	10·96 ± 0·05 (6)	10·73
8·525—9·301	0·0050	0·0653	0·0026—0·0181	11·08 ± 0·05 (6)	10·80
8·460—9·354	0·0050	0·115	0·0025—0·0170	11·12 ± 0·06 (6)	10·78
8·322—9·398	0·0050	0·215	0·0016—0·0166	11·17 ± 0·04 (7)	10·78
8·670—9·454	0·0050	0·315	0·0035—0·0206	11·17 ± 0·05 (7)	10·76
8·588—9·392	0·0050	0·615	0·0024—0·0144	11·25 ± 0·03 (6)	10·84
8·648—9·310	0·0050	1·015	0·0046—0·0196	11·04 ± 0·06 (6)	10·68
7·916—8·528	0·100	1·500	0·0009—0·0037	10·99 ± 0·03 (12)	10·76
8·893—9·413	0·0500	1·515	0·0072—0·0248	11·05 ± 0·04 (6)	10·82

The Debye–Hückel theory predicts that, at 20°, log $^*K_1$ should vary with ionic strength according to the equation:

$$-\log {}^*K_1{}^\circ = -\log {}^*K_1 - 1{\cdot}506 I^{\frac{1}{2}}/(1 + \alpha I^{\frac{1}{2}}) + \beta I, \qquad (2)$$

where $^*K_1{}^\circ$ is the thermodynamic acid dissociation constant and α and β are constants. If the arbitrary but reasonable values of $\alpha = 1$ (corresponding to an average distance of approach of 3 Å for the oppositely charged ions) and $\beta = 0{\cdot}40$ are assigned, the results in Table 2 lead, over the entire range of ionic strength studied (0·00176—1·515), to $-\log {}^*K_1{}^\circ = 10{\cdot}76 \pm 0{\cdot}08$. Theoretical uncertainties inherent in equation (2) and in the values of α and β become less important at lower ionic strengths, so that only results for $I \leqslant 0{\cdot}315$ have been included in obtaining the final value, at 20°, of $-\log {}^*K_1{}^\circ = 10{\cdot}76 \pm 0{\cdot}04$. By replacing the factor, 1·506 at 20°, with the corresponding theoretical values which range from 1·494 at 15° to 1·575 at 42°, equation (2) has also been used to afford $-\log {}^*K_1{}^\circ$ at other temperatures from the experimental results for $-\log {}^*K_1$ over the range, 15—42°. The values in Table 3 have been obtained by taking $\alpha = 1$ and $\beta = 0{\cdot}40$, as at 20°.

TABLE 3.

Thermodynamic acid dissociation constants of manganese(II) ion from 15° to 42°.

In all cases, $[MnCl_2]$ = 0·0005M for I = 0·00176, and 0·005M for I = 0·0153, 0·0403.

	$-\log {}^*K_1{}^\circ$					
I	15°	20°	25°	30°	36°	42°
0·00176	10·93	—	10·63	10·35	10·15	10·04
0·0153	10·96	—	10·55	10·41	10·24	10·14
0·0403	10·91	—	10·59	10·37	10·18	10·11
Av. (± range)	10·93 ±0·03	10·76 [a] ±0·04	10·59 ±0·04	10·38 ±0·03	10·19 ±0·05	10·10 ±0·06

[a] From Table 2.

DISCUSSION

Although the equation $-\log {}^*K_1{}^\circ = 3150/T$, where T is in °K, reproduces the values in Table 3 within 0·02 logarithm unit at all temperatures except 42° (difference 0·08), the experimental uncertainty is too great to permit calculation of the entropy change for the reaction, $Mn_{aq}{}^{++} \rightleftharpoons MnOH^+ + H^+$, by using the identities, $-\Delta G^\circ = \boldsymbol{R}T \ln {}^*K_1$; $d(-\Delta G^\circ)/dT = \Delta S^\circ$. Qualitatively, however, it can be concluded that the change in entropy must be small.

Because of its five 3*d*-electrons, Mn^{++} is spherically symmetrical and possesses the extra stability associated with ions containing five half-filled *d*-orbitals. The weak crystal-field strength of hydroxyl ion is insufficient to cause spin-pairing of the *d*-electrons in $MnOH^+$, so that there is no crystal-field stabilization. As an approximation, Mn^+ might therefore be expected to resemble the cations of Group 2A. Two quantitative comparisons can be made, based on suggested linear relations between $-\log {}^*K_1$ values and either z^2/r (where z is the cation valency and r is the cation crystallographic radius)[6] or ionization potentials.[7] From crystal radii[8] and $-\log {}^*K_1$ for Ca^{++} (12·70[9]) and Mg^{++} (11·42[10]), a value of $-\log {}^*K_1 = 12{\cdot}1$ at 25° is predicted for Mn^{++}, *i.e.*, 1·5 logarithm units less acid than found. Similarly, from the second ionization potentials of calcium, magnesium, and manganese (11·82, 14·96, 15·70 ev[11]) the estimate is $-\log {}^*K_1 = 11{\cdot}1$. Here also Mn^{++} is predicted to be a weaker acid than is experimentally observed. In both cases, because these relations are based on electrostatic considerations, the deviations probably indicate that covalent bond formation in $MnOH^+$ is also significant.

Department of Medical Chemistry, John Curtin School of Medical Research,
Institute of Advanced Studies, Australian National University,
Canberra, Australia.

[*Received, October* 19*th*, 1961.]

---

[6] Davies, *J.*, 1951, 1256.

[7] Irving and Williams, *J.*, 1953, 3192.

[8] Goldschmidt, *Skrifter Norske Videnskaps-Akad. Oslo*, 1926, **8**, 69; *Ber.*, 1927, **60**, 1263.

[9] Davies and Hoyle, *J.*, 1951, 233.

[10] Stock and Davies, *Trans. Faraday Soc.*, 1948, **44**, 856.

[11] Moore, "Atomic Energy Levels," Nat. Bur. Standards Circular 467, 1958, Vol. III.