Studies on Metal Carbonate Equilibria 26. The Hydrogen Carbonate Complex of Manganese(II) in Acid Solutions and a 3 M (Na)ClO₄ Ionic Medium at 25°C. Determination of the Solubility Product of MnCO₃(s)

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Complex formation in the system Mn(II)–H₂O–CO₂(g) has been studied in a 3 M ClO₄⁻ medium at 25°C using an EMF method. The equilibrium concentration of the H⁺ ions, $[H^+] \equiv h$, was measured using a glass electrode.
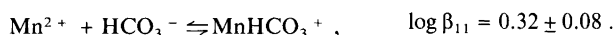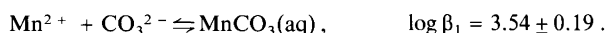
The data could be explained by the chemical model given below.

$$Mn^{2+} + H_2O + CO_2(g) \rightleftharpoons MnHCO_3^+ + H^+, \qquad \log \beta_{111} = -7.56 \pm 0.08.$$
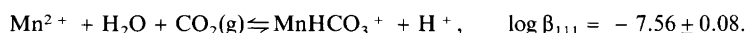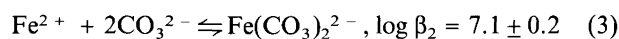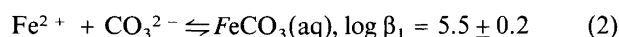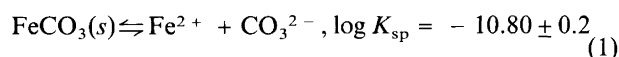
The equilibrium constant β_{pqr} refers to 3 M NaClO₄ as solvent. The error quoted is a maximum deviation evaluated graphically.

The Mn(II) system was studied in the range $3.0 < -\log h < 6.1$. The total concentration of the Mn^{2+} ions, B_T, was kept constant during the titrations at 0.1, 0.2 and 0.3 M, respectively. The partial pressure of CO₂(g), a, was kept constant and had the following values: 0.3 and 0.5 atm, respectively, at each B_T-level.
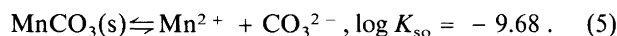
The solubility studies in 3 M (Na)ClO₄ resulted in the following results:

$$MnCO_3(s) \rightleftharpoons Mn^{2+} + CO_3^{2-}, \qquad \log K_{so} = -9.78 \pm 0.04.$$

$$Mn^{2+} + CO_3^{2-} \rightleftharpoons MnCO_3(aq), \qquad \log \beta_1 = 3.54 \pm 0.19.$$

$$Mn^{2+} + HCO_3^- \rightleftharpoons MnHCO_3^+, \qquad \log \beta_{11} = 0.32 \pm 0.08.$$

This work is part of a series of investigations made in this laboratory in order to study the formation of metal carbonate complexes. The results obtained have been used in the study of speciation and migration of several metal ions present in ground and surface water systems. For example, the following metal carbonate complexes were studied: La(III) carbonates,[1] Hg(I) and Hg(II) carbonates,[2] Zn(II) carbonates,[3,4] Pb(II) carbonates in the acid[5] and alkaline[6] range, Be(II) carbonates[7] and U(VI) and Th(IV) carbonates.[8] Moreover, the solubility product of FeCO₃(s)[9] was studied in 1 M (Na)ClO₄ ionic medium, and the following results were obtained by extrapolation to the infinite dilution standard state:

$$FeCO_3(s) \rightleftharpoons Fe^{2+} + CO_3^{2-}, \log K_{sp} = -10.80 \pm 0.2 \tag{1}$$

$$Fe^{2+} + CO_3^{2-} \rightleftharpoons FeCO_3(aq), \log \beta_1 = 5.5 \pm 0.2 \tag{2}$$

$$Fe^{2+} + 2CO_3^{2-} \rightleftharpoons Fe(CO_3)_2^{2-}, \log \beta_2 = 7.1 \pm 0.2 \tag{3}$$

For the Mn^{2+}–H₂O–CO₂(g) system, the following results, valid in 3 M NaClO₄, have been published in the literature:[10a,b,c]

$$Mn^{2+} + HCO_3^- \rightleftharpoons MnHCO_3^+, \log \beta_{BHL} = 0.45. \tag{4}$$

$$MnCO_3(s) \rightleftharpoons Mn^{2+} + CO_3^{2-}, \log K_{so} = -9.68. \tag{5}$$

Complex formation in the Mn(II)–H₂O–CO₂(g) system

In the system studied, the reacting species Mn^{2+}, H₂O and CO₂(g) can form a series of (pqr) complexes with the general composition $B_p(OH)_q(CO_2)_r^{2p-q}$ according to the formation reaction (6)

$$pB^{2+} + qH_2O + rCO_2(g) \rightleftharpoons B_p(OH)_q(CO_2)_r^{2p-q} + qH^+ \tag{6}$$
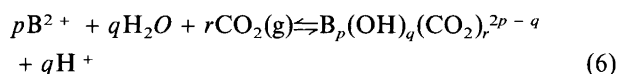
where $OHCO_2^- \equiv HCO_3^-$ and $(OH)_2CO_2^{2-} \equiv CO_3^{2-}$.

B^{2+} denotes the central metal ion. In the following, the ionic charges in subscripts will be omitted for clarity.

During this study the following were determined: the conditional (so-called concentration) constant, β^B_{pqr}, valid at constant level of B(II) and at the ionic strength $I = 3$ M; the equilibrium constant β_{pqr}, valid at trace levels of the species $i(c_i)$ in 3 M $NaClO_4$ as reference state; and β^0_{pqr}, the equilibrium constant in pure water as standard state. The definitions and notation are presented in Ref. 5.

The method of investigation used is similar to that described in Part 3[11] of this series, and is presented in Ref. 5. For the determination of the formation constants in the $Mn(II)-H_2O-CO_2(g)$ system, the self-medium method was used.[11,12] This means that high and constant concentrations were used for the total, analytical concentration of the central metal ion: $[Mn(II)] \equiv B_T$, such as 0.1, 0.2 and 0.3 M. The EMF measurements were carried out, for each B_T level, at two different partial pressure of $CO_2(g)$: 0.3 and 0.5 atm. The partial pressure of $CO_2(g)$, a, was calculated as follows:

$$a = (P - 0.0276) \times {}^o_o\, CO_2/100 \tag{7}$$

Here P is the atmospheric pressure in atm, and the value 0.0276 atm is the vapor pressure of water over 3 M $NaClO_4$. All measurements were made at $25.00 \pm 0.02 °C$ by using the equipment described earlier.[13]

Calculations and results. The calculation method was similar to that described in Refs. 5 and 11. Plots of $(h - H_T)/a$ vs. log h, shown in Fig. 1, turn out to be independent of a at a given value of B_T. Hence, for the predominant species $r = 1$.

Considering $[B^{2+}] \simeq B_T$, we have eqn. (8):

$(h - H_T)/a$

$$= \sum_p \sum_q q\beta_{pq1}B^p_T h^{-q} f(pq1)^{-1} f(Mn)^p f(H)^{-q} a^q_{H_2O} \tag{8}$$

At constant B_T, the composition of the test solutions is essentially constant. Hence, all activity factors are very near constant and we can use, first, the so-called conditional constants β^B_{pq1}. The value of function F, given by eqn. (9), turns out to be independent of h, indicating the formation of complexes with $q = 1$.

$$F \equiv (h - H_T)h/a$$

$$= \sum_p \sum_q q\beta^B_{pq1}B^p_T h^{-q+1} = \sum_q qK_q h^{-q+1} \tag{9}$$

The formal equilibrium constants K_1 and K_2 are defined as follows:

$$K_1 = \beta_{011} + \beta^B_{111}B_T + \beta^B_{211}B^2_T + \cdots \tag{10}$$

$$K_2 = \beta^B_{121}B_T + \beta^B_{221}B^2_T + \cdots \tag{11}$$

The intercept of the plot of F vs. h^{-1} is K_1, and $K_2 = 0$ in the present case.

Estimation of $\beta_{111}(M\ atm^{-1})$. The equilibrium constant β_{111}, for the formation reaction

$$Mn^{2+} + H_2O + CO_2(g) \rightleftharpoons MnHCO_3^+ + H^+ \tag{12}$$

can be obtained from the B_T dependence of K_1. A plot of K_1 vs. B_T is given in Fig. 2, and is a straight line. This shows that the activity factors involved are quite constant. Moreover, the intercept of this plot is identical with β_{011} determined in 3 M $NaClO_4$. This fact indicates that the activity factors are not far from unity. According to Fig. 2, the species HCO_3^- and $Mn(OH)CO_2^+ \equiv MnHCO_3^+$ exist over the whole B_T range studied, and the slope yields the constant
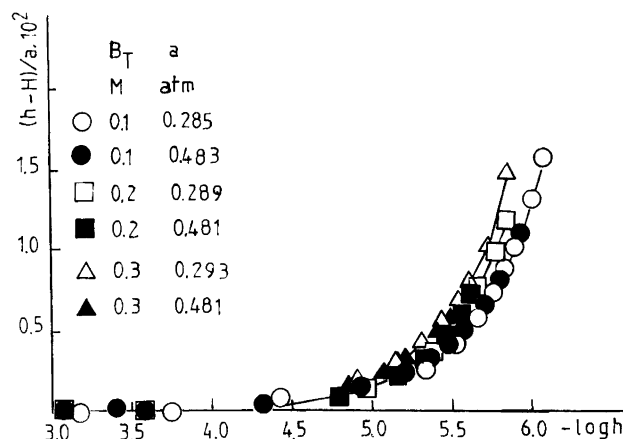
$$\log \beta^B_{111} = -7.57 \pm 0.08 \tag{13}$$

Fig. 1. The function $(h-H_T)/a$ plotted against log h. Symbols are experimental points. The full drawn curves represent the theoretical functions calculated with the following formation constants: $\beta^B_{111} = 2.691 \times 10^{-8}$ and $\beta_{011} = 1.031 \times 10^{-8}$ (cf. Ref. 11).
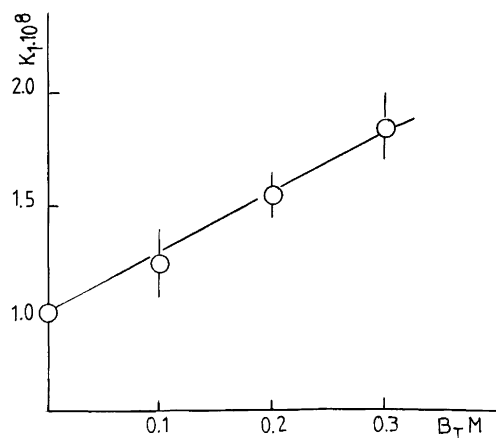

Fig. 2. Graphical determination of β^B_{111}. The formal equilibrium constant K_1, defined by eqn. (10), is plotted as a function of B_T. The vertical bars represent the experimental uncertainties.

For the ratio of the activity factors involved in eqn. (4) of Ref. 5 we can calculate

$$\log \beta_{pq1} = \log \beta_{pq1}^B - p \log f(B) + \log f(pq1) + q \log f(H) \tag{14}$$

$$1.0285 < \frac{f(111) f(H)}{f(B)} < 1.0101 \tag{15}$$

for the range $0.1 < B_T < 0.3$ M.

These ratios are quite constant. Hence, we can consider the average value 1.0193, which results in, for the equilibrium constant in a 3 M NaClO$_4$ reference state, the value

$$\log \beta_{111} = -7.56 \pm 0.08 \tag{16}$$

on the basis of eqn. (14).

The constant β_{111} can be recalculated into the more convenient form β_{11} according to the equation given below, valid for 3 M NaClO$_4$.

$$Mn^{2+} + HCO_3^- \rightleftharpoons MnHCO_3^+,$$
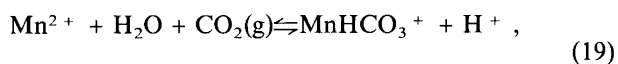with $\log \beta_{11} = 0.32 \pm 0.08$ \tag{17}
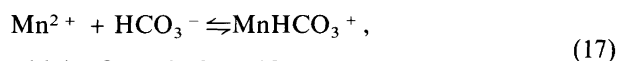
This value agrees well with $\log \beta_{11} = 0.45$ published in the literature.[10a]

Here we used the value[10a] of $\log \beta_{011} = 7.88$, which was obtained by combining the proper equilibrium constants for the equilibria of carbonic acid.
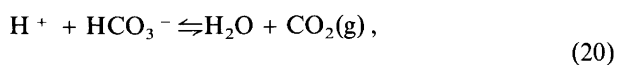
However, from the point of view of speciation of ions in surface and ground water systems, the formation constant β_{111}°, valid in the pure water standard state, is important. This recalculation can be done through eqn. (28) in Ref. 5. Hence, we have

$$\log \beta_{111}^\circ = \log \beta_{111} + 2D(3) + [\bar{\epsilon}(MnHCO_3, ClO_4)$$

$$+ \bar{\epsilon}(H, ClO_4) - \bar{\epsilon}(Mn, ClO_4)][ClO_4] \tag{18}$$
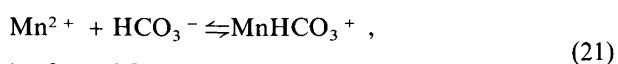
Here, the interaction coefficient $\bar{\epsilon}(MnHCO_3, ClO_4)$ is not known. Therefore, the term which includes this interaction coefficient was taken from the Zn–H$_2$O–CO$_2$(g) system,[3] as an approximation. Hence, we used the following interaction coefficients: $\bar{\epsilon}(H, ClO_4) = 0.18$,[14] $\bar{\epsilon}(MnHCO_3, ClO_4) \simeq \epsilon(ZnHCO_3, ClO_4) = 0.20$[3] and $\bar{\epsilon}(Mn, ClO_4) \simeq \epsilon(Mn, ClO_4) = 0.38$, which was calculated from the activity coefficient of manganese perchlorate solutions.[15] Hence, we obtain $\log \beta_{111}^\circ = -7.07 \pm 0.08$. This equilibrium constant can be recalculated into the more convenient form β_{11}°:

$$Mn^{2+} + H_2O + CO_2(g) \rightleftharpoons MnHCO_3^+ + H^+,$$
$$\log \beta_{111}^\circ = -7.07 \pm 0.08 \tag{19}$$

$$H^+ + HCO_3^- \rightleftharpoons H_2O + CO_2(g),$$
$$\log \beta_{011}^\circ = 7.83^1 \tag{20}$$

$$Mn^{2+} + HCO_3^- \rightleftharpoons MnHCO_3^+,$$
$$\log \beta_{11}^\circ = 0.76 \pm 0.08 \tag{21}$$

Determination of the solubility product of MnCO$_3$(s)

Method of investigation. Crystalline MnCO$_3$(s) was equilibrated with two groups of solutions. The composition of the solutions in group 1 and 2 is presented in Tables 1 and 2.

Through the solutions of group 1, 100% CO$_2$(g) was bubbled, through group 2 N$_2$(g) or Ar(g). For group 1 samples were taken every third day, for group 2 every fifth day, until EMF values were obtained stable within 1–2 mV. The pH of the investigated solutions were measured with a Metrohm combined glass electrode. The E_0-value of the combined electrode was measured before and after the sample was taken, determined in a 10 mM HClO$_4$ + 3 M NaClO$_4$ solution. The average value of E_0 was used in the calculation of the pH of the investigated solutions. The samples were filtrated using a Millipore filter (Minisart, pore size 0.45 μm). 5.00 ml of the filtrated solution were diluted to 50.0 ml, and the total Mn(II) content of the obtained solutions was measured using inductively coupled plasma (ICP) atomic emission spectroscopy. The solubility product was determined at 25.0 ± 0.3 °C.

Interpretation of the solubility measurements. The measured $Mn(II)_T$ values were interpreted by assuming the presence of the species Mn^{2+}, $MnHCO_3^+$, $MnCO_3$(aq) and $Mn(CO_3^{2-})_2^{2-}$. Hence, the total concentration of Mn(II) can be written as follows:

$$Mn(II)_T = [Mn^{2+}] + [MnHCO_3^+] + [MnCO_3(aq)]$$

$$+ [Mn(CO_3^{2-})_2^{2-}] \tag{22}$$

Considering the equilibrium constants, we can write

$$Mn(II)_T = [Mn^{2+}][1 + \beta_{11}[HCO_3^-] + \beta_1[CO_3^{2-}]$$

$$+ \beta_2[CO_3^{2-}]^2] \tag{23}$$

From the definition of the solubility product we have

$$[Mn^{2+}] = K_{so}/[CO_3^{2-}] \tag{24}$$

Table 1. Composition of the test solutions used in the solubility studies of MnCO$_3$(s), in the measurements of group 1.

| [(Na)clO$_4$]/M	[NaHCO3]/M	CO$_2$(g)(%)
3.000		100
3.000	0.005	100
3.000	0.007	100
3.000	0.010	100
3.000	0.020	100
3.000	0.030	100
3.000	0.040	100
3.000	0.060	100
3.000	0.080	100
3.000	0.100	100

Table 2. Composition of the test solutions used in the solubility studies of $MnCO_3(s)$, in the measurements of group 2.

[(Na)ClO$_4$]/M	[NaHCO$_3$]/M	[Na$_2$CO$_3$]/M
3.000	0.050	0.005
3.000	0.100	0.010
3.000	0.150	0.020
3.000	0.025	0.0025
3.000	0.075	0.0075
3.000	0.125	0.0125
3.000	0.005	0.005
3.000	0.010	0.010
3.000	0.015	0.015
3.000	0.020	0.020
3.000	0.030	0.030
3.000	0.040	0.040

Hence, we can write

$$Mn(II)_T[CO_3^{2-}] = K_{so} + K_{so}\beta_{11}[HCO_3^-]$$

$$+ K_{so}\beta_1[CO_3^{2-}] + K_{so}\beta_2[CO_3^{2-}]^2 \qquad (25)$$

Results for group 1. The concentration of the CO_3^{2-} ions was calculated from eqn. (26).

$$CO_2(g) + H_2O \rightleftharpoons 2H^+ + CO_3^{2-} ,$$

with $\log K_{Po} = -17.44$ $\qquad (26)$
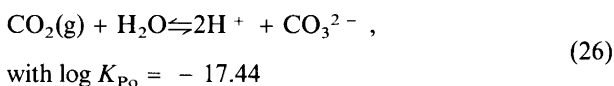
This equation was obtained by combining the proper equilibrium constants for the carbonic acid equilibria, given in Ref. 16.

The evaluation of K_{so} was made in two steps. First the presence of $MnHCO_3^-$ was neglected and K_{so1} was determined as the intercept obtained by plotting $Mn(II)_T[CO_3^{2-}]$ vs. $[CO_3^{2-}]$. This plot resulted in $K_{so1} = 1.76 \times 10^{-10}$. Then the value of the term $K_{so1}\beta_{11}[HCO_3^-]$ was calculated using the preliminary value of K_{so1} and the known value of β_{11}. A new plot of $F_1 \equiv Mn(II)_T[CO_3^{2-}] - K_{so1}\beta_{11}[HCO_3^-]$ vs. $[CO_3^{2-}]$ gave a better value of K_{so2}. Hence, we have eqn. (27).

$$F_1 \equiv Mn(II)_T[CO_3^{2-}] - K_{so1}\beta_{11}[HCO_3^-]$$

$$= K_{so2} + K_{so2}\beta_1[CO_3^{2-}] + K_{so2}\beta_2[CO_3^{2-}]^2 \qquad (27)$$

The intercept of the plot F_1 vs. $[CO_3^{2-}]$ results in

$$\log K_{so2} = -9.78 \pm 0.04 . \qquad (28)$$

This value agrees well with that presented in the literature:[10a,c] $\log K_{so} = -9.68$. The plot in question results in a straight line and is presented in Fig. 3. This means that the species $Mn(CO_3^{2-})_2^{2-}$ is not present. From the slope $(= K_{so2}\beta_1)$ we can calculate

$$\log \beta_1 = 3.72 \pm 0.03 \qquad (29)$$

for the equilibrium

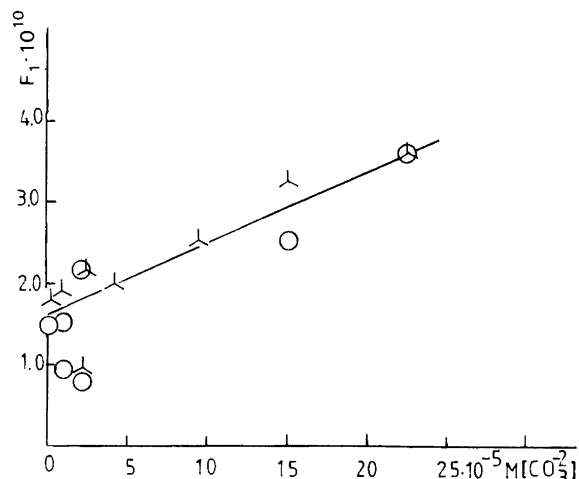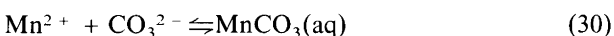$$Mn^{2+} + CO_3^{2-} \rightleftharpoons MnCO_3(aq) \qquad (30)$$

Fig. 3. Graphical determination of the solubility product K_{so} and the equilibrium constant β_1, the latter one for the formation of the species $MnCO_3(aq)$. The function F_1 is plotted vs. $[CO_3^{2-}]$. The measurements in group 1 are considered.

Results for group 2. Plotting F_2 vs. $[CO^{2-}_3]$ we have

$$F_2 \equiv Mn(II)_T[CO_3^{2-}] - K_{so2}\beta_{11}[HCO_3^-]$$

$$= K_{so2} + K_{so2}\beta_1[CO_3^{2-}] \qquad (31)$$

This plot is presented in Fig. 4. The intercept is equal to K_{so2}. From the slope we can calculate

$$\log \beta_1 = 3.54 \pm 0.19 \qquad (32)$$

This value agrees within the experimental uncertainty with that obtained for group 1. The formation of $Mn(CO_3^{2-})_2^{2-}$ could not be detected.

Recalculation of the solubility equilibria to the pure water standard state. Our equilibrium constants, K_{so2} and β_1, can be recalculated into the pure water standard state. For these values we have
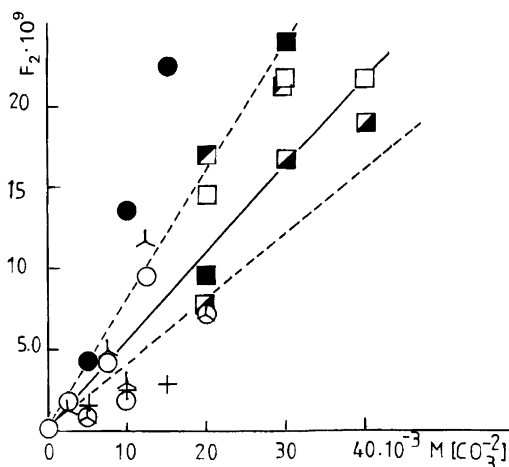
Fig. 4. Graphical determination of the solubility product K_{so2} and the formation constant β_1 for the measurements in group 2.

$$K^o_{so} = [Mn^{2+}][CO_3^{2-}]f(Mn)f(CO_3)$$

$$\equiv K_{so2}f(Mn)f(CO_3) \tag{33}$$

$$\beta^o_1 = [MnCO_3(aq)][Mn^{2+}]^{-1}[CO_3^{2-}]^{-1}f(CO_3)^{-1} \tag{34}$$

The activity factors involved can be calculated according to eqn. (7) in Ref. 5. We use the same value for ε(Mn, ClO$_4$) as before. The interactions between the Mn^{2+} and HCO$_3^-$, moreover, CO$_3^{2-}$ are neglected. Hence, we have

$$\log K^o_{so} = \log K_{so2} - 8D(3) + \varepsilon(Mn, ClO_4)[ClO_4]$$

$$+ \varepsilon(CO_3, Na)[Na^+] \tag{35}$$

$$\log K^o_{so} = -10.61 + \varepsilon(CO_3, Na)[Na^+] \tag{36}$$

$$\log \beta^o_1 = \log \beta_1 + 8D(3) - \varepsilon(Mn, ClO_4)[ClO_4]$$

$$- \varepsilon(CO_3, Na)[Na^+] \tag{37}$$

$$\log \beta^o_1 = 4.55 - \varepsilon(CO_3, Na)[Na^+] \tag{38}$$

Using the interaction coefficient ε(Na, CO$_3$) = − 0.05,[17] the following results can be calculated

$$\log K^o_{s0} = -10.76 \pm 0.04 \tag{39}$$

$$\log \beta^o_1 = 4.70 \pm 0.03 \tag{40}$$

Experimental

Chemicals. Solutions of NaClO$_4$, NaHCO$_3$, NaOH, AgClO$_4$ and HClO$_4$ were prepared from reagents of analytical grade. They were analysed as described earlier.[13]

Mn(ClO$_4$)$_2$ stock solution was made by dissolving MnCO$_3$·XH$_2$O in an excess of HClO$_4$, both Merck p.a. quality. As the MnCO$_3$·XH$_2$O was partly oxidized, it dissolved only partly. Therefore, 30% H$_2$O$_2$ p.a. was added to the mixture in question, until all MnCO$_3$(s) dissolved. The excess of H$_2$O$_2$ was decomposed by boiling. The Mn(II) content of the stock solution was determined gravimetrically as MnNH$_4$PO$_4$·H$_2$O.[18] The analyses agreed to within ± 0.1%. The hydrogen-ion concentration in the Mn(ClO$_4$)$_2$ stock solution was determined potentiometrically, as described in Ref. 13, with the help of Gran plot.[19]

Methods. The experimental details of the EMF measurements are described in Ref. 5. At the pH measurements of the solubility studies, the combined glass electrode resulted in creeping EMF values. These were measured as a function of time and extrapolated to the time when the combined electrode was put into the test solution.

MnCO$_3$(s) was precipitated from Mn(ClO$_4$)$_2$ solution by adding calculated amount of NaHCO$_3$ solution. Ar(g) was bubbled through the mixture for a few days in order

for recrystallisation of the precipitate to be achieved. Then the MnCO$_3$(s) precipitate was filtered by decantation and washed with distilled water until ClO$_4^-$ ions could not be detected by concentrated KCl solution. The precipitate was dried at 105°C. Its quality was checked by powder X-ray determination. We obtained the same results as those given for pure MnCO$_3$(s).

Discussion

From the magnitude of the equilibrium constants β$_{11}$ and β$_1$, for the formation of MnHCO$_3^+$ and MnCO$_3$(aq), it is obvious that the bonding of the HCO$_3^-$ ion is monodentate, and that of the CO$_3^{2-}$ ion is bidentate. For example, the equilibrium constant for the formation of manganese acetate (MnAc$^+$) at zero ionic strength is log β$^o_{11}$ = 1.30 ± 0.10. This value was calculated using literature values[10d] of log β$_{11}$, *I* and the specific ion interaction theory. In the present work we obtained log β$^o_{11}$ = 0.76 ± 0.08.

Experimental values of the equilibrium constants for other ligands with the possibility of bidentate coordination are given in Table 3. (These values have been recalculated to the pure water standard state.)

The equilibrium constants for the Mn(II) and Fe(II) carbonate complexes are approximately the same, but the Fe(II) complex is somewhat more stable, as expected from a ligand field contribution for Fe(II) [but not for Mn(II)].

Also the bidentate oxalate complexes have a magnitude comparable with that of the carbonate complexes. In this case the Mn(II) complex is somewhat weaker than the corresponding Fe(II) complex.

There was no experimental evidence for the formation of Mn(CO$_3^{2-}$)$_2^{2-}$ in the carbonate concentration range investigated. Such a complex was indicated in a previous study of the Fe(II)–carbonate system.[9] However, the experimental evidence for the formation of anionic complexes in the later study is rather weak, and it would be desirable to have additional experiments at higher carbonate concentrations.

Table 3. Comparison of the formation constant log β$_1$ for the reaction L^{2-}+M^{2+} ≡ ML(aq), where the ligand is a bidentate one and the metal ion is Mn^{2+} and Fe^{2+}. The temperature is 25°C.

Ligand: Metal ion	CO$_3^{2-}$ (carbonate)		(COO$^-$)$_2$ (oxalate)	
	I	log β$_1$	*I*	log β$_1$
Mn^{2+}	3.0	3.54±0.19[a]	0.1	3.2[c]
Mn^{2+}	0	4.70±0.19	0	4.04
Fe^{2+}	0	5.5±0.2[b]	1.0	3.05[c]
Fe^{2+}	−	−	0	4.36

[a]Present work. [b]Ref. 9. [c]Ref. 10d.

Finally, it should be mentioned that the calculated theoretical titration curves agree well with the experimental ones in Fig. 1.

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