Studies on Aqueous Soluble Carbonato Complexes of Mn^{II}, Mn^{III} and Mn^{IV}: Oxidation–Reduction Relationships

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Aqueous carbonato complexes of Mn^{II}, Mn^{III} and Mn^{IV} were prepared and investigated by UV–visible spectrophotometry and electrochemical techniques. Mn^{II} forms soluble anionic carbonato complexes in concentrated carbonate solutions. A complex with two CO_3^{2-} has been found in 1 M K_2CO_3 solutions. The value of its conditional formation constant is in the range $10^{5.7 \pm 0.3}$. The soluble Mn^{II} carbonato complexes are readily oxidized by air to Mn^{III} species. Mn^{IV} complexes were obtained by reduction of MnO_4^- ions or by oxidation of Mn^{II} in concentrated carbonate solutions. Insoluble solids, probably oxides, were often produced during the studied oxidation–reduction reactions.

The carbonato complexes of Mn and also of Tc and Re, all elements belonging to the Group VIIB, have not been thoroughly investigated, except for the almost insoluble MnCO$_3$, rhodochrosite,[1] one of the natural minerals of Mn. An acidic species of Mn^{II} with the formula MnHCO$_3^+$ has been found.[2] Its formation constant is rather small ($\log \beta = 1.275$ at 25 °C)[3] and by taking into account the presence of such species one introduces only small changes in the solubility product value of MnCO$_3$. A more complete knowledge of the equilibria involving Group VIIB ions in carbonate solutions is crucial to understanding many natural phenomena involving Mn^{II,III,IV} ions.

In connection with nuclear waste storage safety, it is necessary to investigate the stability of soluble carbonato species of Tc^{V,IV,III,II} which could participate in the transport of radioactive ^{99}Tc from storage sites to the biosphere.

The competition between OH$^-$, O^{2-} and CO_3^{2-} for the coordination sites of ions from Group VIIB is a key parameter for the stability of carbonato complexes at a given pH. Investigations of Mn complexes might be a useful first approach for the study of the Tc complexes, except for the higher stability of the Tc ions in oxidation states greater than II. In this paper we report the first results dealing with soluble manganese(II, III, IV) carbonato complexes.

Experimental

Products. MnO$_2$ was provided by the Institut des Matériaux de Nantes. Its crystallinity was poor, as shown by its X-ray powder diffraction diagram. Only broad lines of the Akthenskite MnO$_2$ structure (JC-PDS 30-820) were observed. MnCO$_3$ was an Aldrich product, 37744-9, 99.9% pure. All other chemicals were Prolabo products of analytical grade and were used without further purification.

Apparatus.

Electrochemistry. A Radiometer Analytical SA set was used. This comprised (1) A Trace Lab 150, which included a polarograph MDE 150 and a solid rotating electrode EDI 101 T. Trace lab 150 permits one to use most electroanalytical methods. It is computer-driven by a program under Windows 3.1 provided by Radiometer. (2) A Volta Lab 32, which includes a galvano potentiostatic unit DEA 332 with a programmable interface IMT 101. A Volta Master 2 program, also provided by the manufacturer, was used to drive this unit.

Spectrophotometry. A double-beam UV–visible spectrophotometer 21016C from Shimadzu, operating between 190 and 900 nm, was used for the spectroscopic investigations.

Solid structural investigations. Some of the solids obtained in this work were analyzed by X-ray powder diffraction techniques, using a Phillips PW 1710 diffractometer. Energy-dispersive X-ray analyses were performed using an EDX microprobe (Oxford

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Instruments) coupled with a Leica Stereoscan 440 scanning electron microscope.

Procedures.

Dissolution of MnCO₃ into K₂CO₃ solutions. The solubility of $MnCO_3$ in carbonate solutions under oxidic and anoxidic conditions was investigated. The concentration of Mn was determined by γ-counting of $MnCl_2$ labelled by ^{54}Mn. ^{54}Mn disintegrates by electron capture with a 312-day half-life. Counting its 834.84 keV γ-rays served to monitor the Mn concentrations. For these experiments constant ionic strength was calculated by applying the equation

$$I = \frac{1}{2} \sum \gamma_i c_i$$

and was maintained at $I = 4.4$ by addition of KCl. The chloride complexes of Mn^{II} are very weak, $\beta_{11} = 1(5)$ and play a minor role in the reactions investigated here. At room temperature equilibria were obtained after 100 h. To avoid oxidation of Mn^{II}, small amounts of hydrazine 10^{-2} M were daily added to the solutions. The oxidation of the Mn^{II} carbonato complexes by O_2, MnO_4^-, was carried out and followed by voltammetry at a rotating platinum electrode. The solids obtained during this study were analyzed by X-ray diffraction and electron microscopy.

Reduction of the MnO₄⁻ ions by the solvent. The standard potentials of the couples MnO_4^-/MnO_4^{2-} (0.54 V vs. SHE); and MnO_4^-/Mn^{IV} (0.64 V vs. SHE) at a pH around 12 are higher than the potential of the O_2/H_2O couple (0.51 V vs. SHE). This means that Mn^{VII} (MnO_4^-) and Mn^{VI} (MnO_4^{2-}) ions are thermodynamically unstable in carbonate solutions at a pH in the range from 11 to 12. This instability is increased if carbonate complexes of Mn^{IV} are more stable than the oxide MnO_2. MnO_4^- ions were reduced by water when heating their carbonate solutions at temperatures close to 100 °C. For MnO_4^- solutions in 5 M K_2CO_3, 0.5 M $KHCO_3$ 2 h of heating were necessary to observe the complete disappearance of Mn^{VII}. UV–visible spectrophotometry was used to follow this reduction. As some solids were formed during the reduction the spectra were recorded after careful filtration of the solutions through 0.25 or 0.45 μm millipore filters. Extended reaction times were necessary to achieve reduction of MnO_4^-, contained in less concentrated carbonate solutions, especially at lower pH.

Dissolution of MnO₂ into a melted eutectic of K₂CO₃ and Na₂CO₃. 0.1 g MnO_2 was carefully mixed and ground with 50 g of a K_2CO_3/Na_2CO_3, 0.5 mol fraction. This powder was heated to 800 °C, at which point the melted carbonates rapidly dissolved the MnO_2 to give a red solution. The surface of the melt in contact with air changed color from red to green, indicating the partial oxidation of MnO_2 to MnO_4^{2-} ions. After being cooled the solidified salts were dissolved in a 1 M $KHCO_3$ solution, then the green color disappeared rapidly due

to Mn^{VI} disproportionation. Finally a red solution was obtained. The UV–visible spectrum showed that it was the same Mn species as obtained by reduction of MnO_4^- ions by H_2O.

Leaching of MnO₂ by aqueous carbonate solutions. The solutions and the solids obtained by leaching MnO_2 by various carbonate solutions were investigated. The influence of pH, carbonate concentrations, temperature of leaching and agitation was studied.

Chemical analysis. The oxidation state of Mn in the solids and the solutions was determined by spectrophotometric analysis of formed Fe^{III} by the oxidation of a deoxygenated solution of $FeSO_4$ in sulfuric acid mixed with the sample. This procedure is based on the fact that all ions of Mn in higher oxidation states than II are reduced by Fe^{II} into Mn^{II} in an acidic solution of sulfate. The Mn content in the samples was analysed by spectrophotometry after oxidation of all Mn^{II} ions into MnO_4^- by sodium persulfate in the presence of catalytic amounts of Ag^+ ions. This standard procedure is described in Ref. 4.

Results and discussion

Manganese(II). The solubility of $MnCO_3$ at room temperature in potassium carbonate at a constant pH of 11.6 and an ionic strength of 4.4 as a function of carbonate concentration is plotted in Fig. 1 on a bilogarithmic scale. The slope of the straight line is close to 1. That means that one CO_3^{2-} ion is added to the insoluble $MnCO_3$ to form a soluble dicarbonato species. The formation constant of this species, $\beta_{12} = Mn(CO_3^{2-})_2^{2-}/(Mn^{2+})(CO_3^{2-})^2$, can be evaluated in the presence of solid $MnCO_3$ by taking into account the value of $MnCO_3$ solubility product, $K_{S0} = 10^{-9.68}$, at an ionic strength of 3, allowing the concentration of Mn^{2+} to be calculated,[5] with the result $\beta_{12} = 10^{5.7}$. As was observed, the value of the experimental solubility product values are sensitive to the degree of the insoluble solid crystallinity: an error of ± 0.3 log units in β_{12} could be easily made using this solubility method. The UV–visible spectrum of the colorless solution obtained by dissolving $MnCO_3$ in deaerated aqueous 4 M in K_2CO_3 and 1 M in $KHCO_3$ is shown in Fig. 2a. This spectrum has been
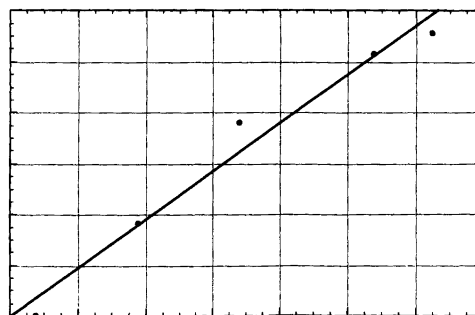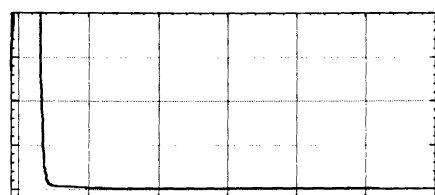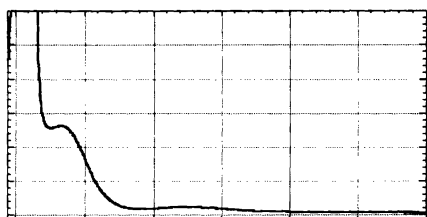

Fig. 1. Solubility of Mn^{II} in potassium carbonate solutions as a function of CO_3^{2-} ion concentrations. Ionic strength, $I = 4.4$.

2a

2b

Fig. 2. UV–visible absorption spectrum of a 10^{-3} M MnCO$_3$ solution in 4 M K$_2$CO$_3$ and 1 M KHCO$_3$: (a) anoxidic conditions or in the presence of hydrazine; (b) solution in contact with air during 3 days.
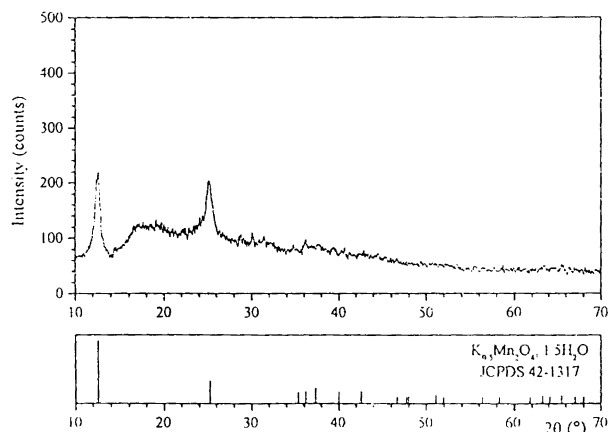

Fig. 3. X-Ray diffusion pattern of the solid precipitated from 0.001 M MnCO$_3$ in 4 M K$_2$CO$_3$ and 1 M KHCO$_3$ after 8 days of contact with air, compared with the JCPDS42-1317 reference file of K$_{0.5}$Mn$_2$O$_4 \cdot$ 1.5H$_2$O.

attributed to Mn^{II}, after checking the oxidation state of manganese by the spectrophotometric titration of Fe^{III}, following the procedure described in the Experimental section. The addition of small quantities of hydrazine (NH$_2$NH$_2$) maintained manganese in the divalent state, even in the presence of air. The species of manganese(II) observed in these conditions are probably anionic carbonato species with formula Mn(CO$_3$)$_2$(OH)$_y^{(4+y-2)-}$. The number of OH$^-$ ions will be considered later after the investigation of the pH influence upon the Mn^{II} solubility.

Manganese(III). In contact with air, the colorless solutions of Mn^{II} darkened and their UV–visible spectrum changed as shown in Fig 2b. Two new bands, with maximum absorption at 274 and 450 nm, appeared. After several hours a black solid precipitated. Its X-ray powder diagram, reproduced in Fig. 3, accords with the JCPDS 42-1317 reference file diagram, corresponding to K$_{0.5}$Mn$_2$O$_4 \cdot$ 1.5H$_2$O. The small crystallite size, 10–13 nm, calculated by applying the Scherrer formula,[6] showed that the sample was poorly crystallized. A Mn : K ratio close to 4 was determined by an energy-dispersive X-ray analysis, statistically performed on the grains of the sample using an EDX microprobe Oxford instrument coupled with a Leica Stereoscan 440 scanning electron microscope. Apparently, at a pH around 10.8, the final state of the Mn^{II} carbonato complexes in the presence of oxygen is a Mn^{IV}/Mn^{III}/K mixed oxide. The soluble Mn^{III} carbonato complexes are metastable species which can

be observed for several days. At a pH close to 11, however, O^{2-} ions seem to be able to replace the carbonate ligand in the first coordination sphere of Mn^{III}. The formation of the K$_{0.5}$Mn$_2$O$_4 \cdot$ 1.5H$_2$O is probably due to the occurence of a thermodynamic sink which favors the partial oxidation of Mn^{III} into Mn^{IV} by oxygen. As potassium ions are contained in the solid and participate to the structure stability, it is premature to conclude that this behavior is general, because a change in the potassium concentration or its replacement by another cation may change the reaction path and the nature of the final products.

The voltammogram at the rotating platinum electrode, of a potassium carbonate solution, 5×10^{-4} M in Mn^{II}, in contact with air for two days, is shown in Fig. 4. It can be seen that the Mn^{II}–Mn^{II+x} couple in the carbonate medium looks reversible at the platinum electrode. Its formal potential in 5 M K$_2$CO$_3$ and 0.5 M KHCO$_3$ is $+0.07$ V vs. the Ag/AgCl electrode, which yields $+0.29$ V vs. the normal hydrogen electrode. A slope analysis of the voltamperometric curve, by plotting log $I/I_d - I$ as a function of the potential, yields 0.065 V. This indicates that one has to deal with an one electron quasi-reversible reaction. One may therefore conclude
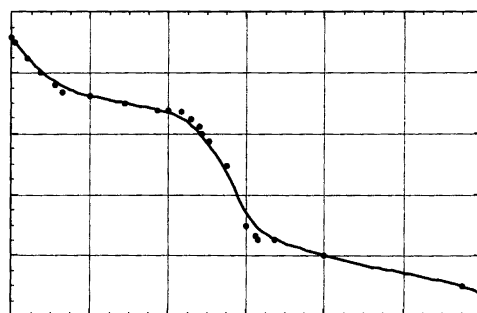

Fig. 4. Voltammogram of a 5×10^{-4} M MnCO$_3$ in 4 M K$_2$CO$_3$ and 1 M KHCO$_3$ after 2 days of contact with air (rotating platinum electrode 1000 r.p.m.).

that the Mn^{II}/Mn^{III} couple is close to reversible at the platinum electrode in carbonate–bicarbonate solutions around a pH of 11.2. The strong shift of the Mn^{III}/Mn^{II} formal potential to lower values when replacing an acidic medium $[E'_0(Mn^{III} - Mn^{II}) = 1.51$ V vs. NHE] by a carbonate medium shows clearly that the carbonate complexes of Mn^{III} are more stable than the corresponding Mn^{II} complexes. However, because of the O^{2-}, OH^-/CO_3^{2-} competition for the Mn^{III} coordination sites being apparently favorable to the oxides ions, the Mn^{II} carbonato complexes are more easily observed at high pH. The electrochemical evidence for the oxidation of Mn^{II} carbonato complexes into soluble Mn^{III} carbonato complexes shown in Fig. 4 was corroborated by UV-visible spectrophotometry. The absorption bands of aged solutions of Mn^{II} carbonato species in contact with air, shown in Fig. 2b, can be attributed to Mn^{III} because further oxidation of Mn with MnO_4^- gave rise to a new spectrum, attributed to manganese(IV) or a species of Mn^V other than MnO_4^{3-}, which possesses a completely different UV–visible spectrum.[7] The highly intense bands appearing in the spectra of the Mn ions at higher oxidation state than II ($\varepsilon_M = 10^4$) are probably due to charge transfer rather than d–d transitions. The spectrum of Mn^{III} changes with the pH of the solution, even for small changes in the carbonate concentration, indicating that mixed hydroxo–carbonato complexes are formed. The relative intensity of the absorption bands at 450–274 nm (Table 1), decreases with pH, showing that the 450 nm band is probably due to the presence of hydroxo groups in the first coordination sphere of manganese(III). The UV band at 274 nm is probably due to CO_3^{2-}–Mn^{III} charge-transfer transitions, and the band at 450 nm could be attributed to some Mn^{III}–Mn^{III} electron transfer, the two metal ions being present in a polymeric species in which the metal ions are linked by OH bridges. The red shift for the electron transfer bands when some CO_3^{2-} ions are replaced by OH^- has already been observed in U^{VI} hydroxocarbonato complexes.[8]

Manganese(IV). Soluble manganese(IV) carbonato complexes were obtained through three procedures: by boiling $KMnO_4$ in carbonate solutions, by oxidizing Mn^{II} by MnO_4^- ions or by dissolving MnO_2 into melted K_2CO_3–Na_2CO_3 eutectic at 800 °C and then dissolving

Table 1. Effect of pH on the optical density ratio (R) at 274–450 nm bands in the UV–visible spectra of various 10^{-3} M Mn^{III} carbonato complexes.

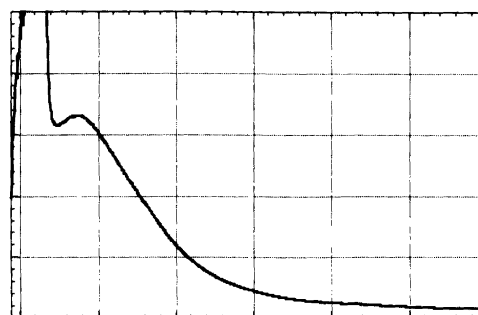| K_2CO_3 /mol l^{-1}	$KHCO_3$ /mol l^{-1}	pH	R
6	0	> 12.5	1.6
4.3	0.33	11.3	6.5
3.5	0.5	11	8.9
4	1.5	10.6	8.7
0.2	2	9.2	28

Fig. 5. UV–visible absorption spectrum of a 5×10^{-4} M $KMnO_4$ solution in 5 M K_2CO_3 and 0.5 M $KHCO_3$. Mn^{VII} was reduced by boiling for 2 h.

the cooled solidified melt into an aqueous solution of $HKCO_3$.

Reduction of $KMnO_4$ by H_2O. 5×10^{-4} to 2×10^{-3} M solutions of $KMnO_4$ into 5 M K_2CO_3–0.5 M $KHCO_3$ solutions were heated in a boiling water bath. After 2 h the rose color of permanganate vanished and was replaced by a brown to yellow color, the UV visible spectrum is shown in the Fig. 5. The oxidation state of manganese was determined using the procedure described in the Experimental section, and a value close to 4 was found. Solids are formed from the yellow–brown solutions during the reduction of MnO_4^- ions by the solvent. If boiling is pursued the color of the solution disappears and all the manganese is precipitated. Unfortunately, these solids were amorphous, and XRD was not useful for their identification. The voltammogram of a carbonate solution of Mn^{IV} is shown in Fig. 5. It can be seen that this curve corresponds to one or several irreversible electrochemical steps. Owing to this irreversibility, it was not possible to assign a number of electrons for this reduction, probably involving polymeric species. Oxidation of Mn^{III} in Mn^{IV} was not seen in the voltammogram of a Mn^{III}/Mn^{II} mixture, shown in Fig. 3. This indicates that the reversible formal oxidation potential of the Mn^{III}/Mn^{IV} couple is probably higher than the solvent oxidation potential. Unlike the Mn^{III} complex the UV–visible spectra of carbonate solutions of Mn^{IV} were not useful to distinguish the various species being present because only very broad bands were detected.

Reduction of $KMnO_4$ by $MnCO_3$. By mixing gradually, at room temperature, a 10^{-3} M solution of $MnCO_3$ with a 10^{-3} M solution of $KMnO_4$ into 4.5 M K_2CO_3 plus 1.5 M $KHCO_3$, $KMnO_4$ is first reduced to a Mn^{III} carbonato species which has a UV–visible spectrum as shown in Fig. 2b. Further oxidation led to a solution of which the UV–visible spectrum is similar to the spectrum shown in Fig. 5. The voltammogram of this last solution is close to that of the Mn^{IV} solutions voltammograms represented Fig. 6. Thus it can be concluded that we dealt with the reactions
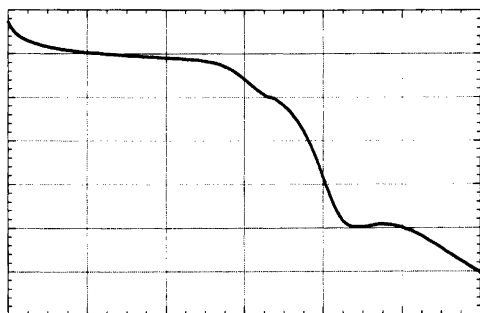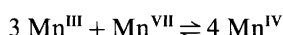
$$4\,Mn^{II} + Mn^{VII} \rightleftharpoons 5\,Mn^{VII}$$
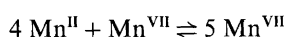
Fig. 6. Voltammogram of a 5×10^{-4} M reduced $KMnO_4$ solution in 5 M K_2CO_3 and 0.5 M $KHCO_3$ (rotating platinum electrode 1000 r.p.m.). Mn^{VII} was reduced by boiling for 2 h.

and

$$3\, Mn^{III} + Mn^{VII} \rightleftharpoons 4\, Mn^{IV}$$

Reaction of MnO_2 with aqueous carbonate solutions and the melted K_2CO_3–Na_2CO_3 eutectic. The reaction of MnO_2 with aqueous carbonate solutions at room temperature or at 100 °C led to very dilute Mn^{III} carbonato species of which the UV–visible spectrum is similar to the Mn^{III} spectrum obtained by the procedure described above. The X-ray diffraction of the amorphous solid from the reaction was not informative. However, as we started with a poorly crystallized sample of MnO_2, Akhtensite-JCPDS reference file30-820, the loss of crystallinity and the detection of small amounts of soluble Mn^{III} indicate a chemical reaction. The probable thermodynamic sink for Mn in potassium carbonate solution is the mixed oxide which is formed by partial reduction of MnO_2 by the solvent via the formation of soluble Mn^{III} carbonato complexes.

MnO_2 is dissolved rapidly into melted K_2CO_3–Na_2CO_3, 1/1 eutectic, at 800 °C. It gives a deep red melt. In the presence of air some color change from red to green is observed at the surface of the melt, which indicates partial conversion of the Mn^{IV} carbonato species into $Mn^{VI}O_4^{2-}$ ions. The solidified melt was dissolved into a $KHCO_3$ solution. The voltammogram and the UV–visible spectrum of the solution showed that Mn^{IV} carbonato was obtained. The concentration of Mn and its stability in solution was higher than for the Mn^{IV} solutions prepared by the other procedures. Increased stability with increased concentrations in manganese can be due to the presence of polymeric species, probably mixed hydroxocarbonate complexes, in which the metals are linked by hydroxo bridges. After several months a black solid could be isolated from the solution.

Conclusion

This study has shown that all ions of Mn, from II to IV, can form carbonato species soluble in aqueous solutions. In the high-pH range investigated here, species can lead to insoluble compounds, probably oxides. Only one has been identified as $K_{0.5}Mn_2O_4 \cdot 1.5H_2O$. It is the final

product of $Mn^{II}(CO_3)_2^{2-}$, oxidation by air, first into Mn^{III} soluble carbonato species, followed by a further oxidation to the identified insoluble product. Mn^{IV} gives mixed hydroxocarbonato species when in contact with concentrated carbonate solutions. When K^+ ions are present the precipitation of $K_{0.5}Mn_2O_4 \cdot 5H_2O$ is favored. The determination of the quantitative relationships between these species will be an important piece of work because of the numerous parameters which govern the competition between the ligands: OH^-, O^{2-}, CO_3^{2-} for bonding to the metal. Solubility products of simple oxides, hydroxides and insoluble carbonates must be known. Oxidation–reduction reactions in which the solvent and dissolved oxygen can play a role must be precise. The pH of the medium is obviously an important parameter, as it influences the values of all the other parameters. As mentioned in the Introduction, solid $Mn^{II}CO_3$, isomorphous with calcite, is the only known carbonate of Group VII B metallic ions. It dissolves into carbonate solutions to give one anionic carbonato or hydroxocarbonato species which posseses two CO_3^{2-} ions.

Mn^{III}, like Fe^{III}, is not known to form stable carbonato species because of its high tendency to be hydrolysed. However, the carbonato complexes of Mn^{III} have been identified in this work, at least as intermediate species, during the oxidation of Mn^{II} carbonate complexes by oxygen. In nature some rare minerals contain carbonate and Mn^{III}, for example, desautelstite, $Mg_6Mn^{III}_2(OH)_{16}CO_3 \cdot 4H_2O$.[9]

Mn^{IV} is also found with carbonate ions in rare minerals like jouravskite, $Ca_3Mn^{IV}(OH)_6CO_3SO_4 \cdot 12H_2O$, but the structure of this natural Mn^{IV} compound has shown that the Mn^{IV} ions are surrounded by six OH^- ions.[10] In the present study it has been found that soluble Mn^{IV} carbonato species can be obtained in solution as the result of several reactions: reduction of MnO_4^- ions, oxidation of Mn^{II} ions and dissolution of MnO_2 in molten salts. Here again the stability of these carbonato species toward the oxo or hydroxo species in aqueous solutions has to be investigated more completely to tell if they are transient or thermodynamically stable species. The identification of all solids being in equilibria with the solutions has not been achieved completely because most of them were amorphous. The speciation of the soluble complexes is not complete. However, the occurence of several carbonated species has been established. One remaining task is that of investigating the carbonato complexes in a larger pH range. Most of the present work was carried out in the pH range 10–11.5, in which the concentrations of CO_3^{2-} ions are the highest and are favorable for the formation of carbonato species. However, a more complete investigation must be undertaken to determine precisely the existence of mixed OH^-/CO_3^{2-} ligand complexes. Our present understanding of the reactions taking place in potassium carbonate media, in the pH range from 10.5 to 11.5, in oxidic environments is shown schematically in Fig. 7. The mixed
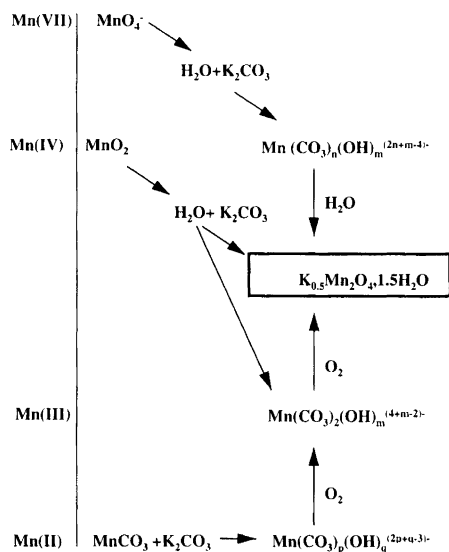
Mn(VII) | MnO$_4^-$

H$_2$O+K$_2$CO$_3$

Mn(IV) | MnO$_2$ Mn (CO$_3$)$_n$(OH)$_m^{(2n+m-4)-}$

H$_2$O+ K$_2$CO$_3$ H$_2$O

K$_{0.5}$Mn$_2$O$_4$,1.5H$_2$O

O$_2$

Mn(III)   Mn(CO$_3$)$_2$(OH)$_m^{(4+m-2)-}$

O$_2$

Mn(II) | MnCO$_3$ +K$_2$CO$_3$ $\longrightarrow$ Mn(CO$_3$)$_p$(OH)$_q^{(2p+q-3)-}$

Fig. 7. Main oxidation, reduction and complexation reactions proposed for Mn ions in contact with 5 M K$_2$CO$_3$ at pH 10.8.

Mn valence oxide III/IV ($K_{0.5}Mn_2O_4 \cdot 1.5H_2O$) presents a well in which all the species of all the oxidation states are transformed, after a more or less long period of time, by reduction with water or oxidation by oxygen.

Coming back to the purpose for which this investigation was undertaken, the transportation of Tc via soluble species obtained in the presence of carbonates, we must take into account the very low concentration range of the metal, where the solubility product of the solids might not be reached and where the occurrence of soluble species and sorption on the surfaces are the predominant features.

However, the present investigation is a strong incentive for the research of the soluble carbonates of Tc^{IV} in a large pH range. Their stability toward insoluble oxides or complexes with humic acid must be specified. Oxidation into very mobile TcO_4^- is also a key factor for the environmental behavior of Tc. For all these reactions kinetic factors will play a more important role than the for the equivalent Mn^{IV} reactions.

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