

Articles

Thermochemistry of Framework and Layer Manganese Dioxide Related Phases

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The energetics of a set of natural and synthetic manganese dioxides having a framework or a layer structure were determined by high-temperature solution calorimetry using sodium molybdate as a solvent. Enthalpies of formation of the metastable manganese dioxides were calculated from the measured values of the enthalpies of drop solution. The stability of the open structure depends mostly on the nature of and the amount of the tunnel (or interlayer) cation and on the degree of hydration. It depends less strongly on the topology of the structure itself and on the average oxidation state of manganese. The synthesis of these metastable microporous materials is not limited by the energetics of the structure.

Introduction

Manganese dioxide minerals are encountered on the Earth's surface as coatings and in massive deposits. They are also important deep-sea minerals. Several complex manganese oxides have been synthesized^{1–3} and some have potential applications as octahedral molecular sieve (OMS) materials.^{1,2} They also exhibit cation-exchange properties^{1,2} and some are microporous such as zeolites. Their large surface areas (up to 250 m²/g) give them possibilities for catalytic applications^{1,2} and they are also encountered in fuel cell and battery applications.⁴

Manganese dioxides, MnO₂, exhibit great structural complexity^{4,5}. Two main types of structures have been identified: three-dimensional (3D) octahedral framework and layer structures.

The framework phases consist of single or multiple chains of edge-sharing MnO₆ octahedra that share corners with other chains to produce a structure with

tunnels that are parallel to the chains. In some of the structures the tunnels are large enough to accommodate cations such as Ba²⁺, K⁺, and Pb²⁺. When extraframework cations are present, some of the Mn⁴⁺ is replaced by Mn³⁺ (or other lower valence cations, such as Fe³⁺) to maintain electroneutrality. The minerals hollandite,^{6–8} cryptomelane,⁹ and coronadite¹⁰ form an isostructural series with the general formula A_xB₈O₁₆, where A represents large cations (Ba²⁺, K⁺, Pb²⁺) and B represents Mn or other octahedral cations. The structure is built of double chains of MnO₆ octahedra that combine to form square cross-sections tunnels that are two octahedra on a side (2 × 2). For these open structures, the large cations in the tunnels are necessary to prevent collapse of the framework. Other manganese oxides with different tunnel sizes are romanechite¹¹ (2 × 3) and todorokite^{12,13} (3 × 3). The degree of hydration of these phases is also variable. Manganese oxides that have a layer structures include birnessite,¹⁴ chalcophanite,¹⁵ and lithiophorite.¹⁶ The layers of manganese octahedra are held together by O–H–O bonds, and OH is an integral part of the structure.

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Table 1. Structure and Composition of Studied Samples

phase	structure	composition	reference and origin
hollandite	octahedral framework 2 × 2 tunnel	K _{0.12} Mn _{1.00} O ₂ ·1.55H ₂ O	OMS-2 (synthetic)
		K _{0.30} Mn _{1.00} O ₂ ·1.55H ₂ O	OMS-2* (synthetic)
		K _{0.30} Mn _{1.00} O ₂ ·1.55H ₂ O	OMS-2** (synthetic)
		hollandite (natural Ba)	127118 (Stuor Njuoskes, Sweden)
		Na _{0.0125} Al _{0.029} Si _{0.01} K _{0.005} Mn _{0.82} Fe _{0.165} Ba _{0.09} - Pb _{0.02} O ₂ ·0.099H ₂ O	89104 (Chindwara, India)
		cryptomelane (natural K)	10217 (Broken Hill, Australia)
romanechite	octahedral framework 2 × 3 tunnel	Na _{0.03} Al _{0.02} K _{0.12} Mn _{0.94} Fe _{0.0375} Sr _{0.016} Ba _{0.012} - O ₂ ·0.0375H ₂ O	
		coronadite (natural Pb)	
todorokite	octahedral framework 3 × 3 tunnel	Pb _{0.175} Mn _{0.99} Al _{0.006} Zn _{0.006} O ₂ ·0.19H ₂ O	C1818 (Schneeberg, Saxony, Germany)
		Ba _{0.132} Ca _{0.006} Na _{0.002} Mn _{1.00} O ₂ ·0.26H ₂ O	OMS-1 [†] (synthetic)
birnessite	layer structure	Mg _{0.19} Mn _{1.00} O ₂ ·0.75H ₂ O	OMS-1 [‡]
		Mg _{0.19} Mn _{1.00} O ₂ ·0.75H ₂ O	OL-1 (synthetic)
		K _{0.12} Mn _{1.00} O ₂ ·0.19H ₂ O	OL-1 (synthetic)
		K _{0.29} Mn _{1.00} O ₂ ·0.19H ₂ O	OL-1 (synthetic)

^a Samples of same composition, but different preparation methods are denoted with * and **, and † and ‡.

Previous thermodynamic studies¹⁷ made on pure metastable manganese oxides and oxyhydroxides have shown that the enthalpy difference between 1 × 1 and 1 × 2 tunnel structures is very small, less than 6 kJ/mol. These results have suggested that the framework stability is not governed by the openness of the structure. The aim of this work is to measure the energetics of a series of metastable manganese dioxides (natural and synthetic) and to separate the effects of polymorphism, of extraframework cation content, and of hydration. The new information about structural stability will elucidate the question of the rich structural diversity of these compounds and perhaps direct the synthesis of new materials.

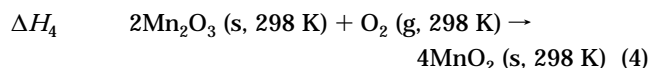
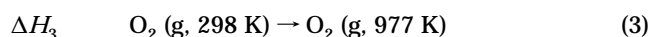
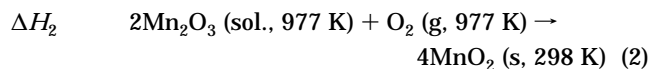
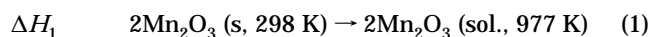
Experimental Methods

Sample Preparation and Characterization. The structure type and composition of the studied samples are summarized in Table 1. The hollandite, cryptomelane, coronadite, and romanechite mineral specimens are from the Smithsonian Institution collections. Chemical formulas were obtained by electron-microprobe analyses. Except for the coronadite, an atomic-absorption method was also used and the amount of water was determined with a DuPont moisture evolution analyzer.^{6,10} X-ray data already have been discussed elsewhere.^{7,10,11} Thermal behavior studies have shown that the most significant consequences of heating is the reduction of Mn⁴⁺, loss of water, and transformation into Mn₂O₃ or Mn₃O₄, admixed with other complex oxides in some cases.⁶

The synthetic samples (OMS-1, OMS-2, and OL-1) were made at the University of Connecticut. The 3 × 3 octahedral molecular sieve corresponding to natural todorokite (OMS-1) has been synthesized by autoclaving layer-structure manganese oxides¹ that are prepared by reactions of MnO₄⁻ and Mn²⁺. The synthetic cryptomelane (OMS-2) samples have been prepared using different methods, by refluxing or autoclaving an acidic solution of KMnO₄ and Mn²⁺ or by oxidation of Mn²⁺ under basic conditions.¹⁸ The layer structure birnessite (OL-1) was obtained by sol-gel synthesis from KMnO₄ and simple sugars.¹⁹ All the synthetic octahedral molecular sieves have been characterized by X-ray diffraction, thermogravimetric, SEM/EDX, and ICP analysis. The characterization details are given elsewhere.^{1,18,19}

Calorimetric Experiments. High-temperature calorimetric experiments were performed using a Tian Calvet twin

type calorimeter described in detail by Navrotsky.^{20–23} Drop solution calorimetry was used to determine the heat of solution of the manganese oxides. Samples were dropped from room temperature into a molten oxide solvent in the calorimeter at 977 K. Under an oxidizing atmosphere (a low rate of oxygen of 1.3 cm³/s through the calorimeter), all the Mn cations converted into the 3+ valence state in the melt. The heat effect measured both the enthalpy of reduction and the enthalpy of solution of the oxides. The calibration factor of the calorimeter was obtained by dropping α-Al₂O₃ (Aldrich, 99.99%) pellets of known mass and heat content into a calorimetric crucible with no solvent present. We choose sodium molybdate (3Na₂O·4MoO₃) as a solvent, because it dissolves Mn-based oxides easily.²⁴ The exact composition 3Na₂O·4MoO₃ was obtained by mixing Na₂MoO₄·2H₂O (Alpha Aesar, 99.5%) and MoO₃ (Alpha Aesar, 99.95%) and heating the mixed powder at 977 K. By simulation of the calorimetric experiment in a furnace, we checked that the samples totally dissolved in the solvent. We had some previous knowledge about the final oxidation state of manganese (3+) in lead borate,²⁵ but we had to make sure that it was the same in sodium molybdate. Pellets of MnO₂ and Mn₂O₃ phases were dropped in 3Na₂O·4MoO₃ in order to calculate the enthalpy of oxidation of Mn³⁺ to Mn⁴⁺, according to the following cycle:



where s means solid; sol., solution; and g, gas; $\Delta H_4 = \Delta H_1 + \Delta H_2 + \Delta H_3$, with ΔH_1 and ΔH_2 being the measured enthalpies and $\Delta H_1 = 2(168.2 \pm 2.6)$ kJ/mol and $\Delta H_2 = -4(126.3 \pm 1.2)$ kJ/mol (see Table 4). ΔH_3 is the heat content of oxygen, $\Delta H_3 = 22.02$ kJ/mol,²⁵ and $\Delta H_4 = -146.8 \pm 7.1$ kJ/mol.

The enthalpy of oxidation, -146.8 ± 7.1 kJ/mol, calculated from the measured values when the experiments were done

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Table 2. Enthalpy of Drop Solutions of Manganese Dioxides in 3Na₂O·4MoO₃, at 977 K

composition ^a	FW (g/mol O ₂)	ΔH drop sol. (kJ/mol) in 3Na ₂ O·4MoO ₃ at 977 K
OMS-2 (synthetic) (K _{0.12})	119.55	167.5 ± 2.5(10)
OMS-2* (synthetic) (K _{0.3})	128.56	187.3 ± 3.4(7)
OMS-2** (synthetic) (K _{0.3})	128.56	186.6 ± 2.0(6)
hollandite (natural Ba)	104.96	110.3 ± 1.7(4)
cryptomelane (natural K)	94.85	121.1 ± 1.2(6)
coronadite (natural Pb)	126.58	123.8 ± 1.5(6)
romanechite (natural)	109.89	134.5 ± 0.6(5)
OMS-1 [†] (synthetic) (Mg _{0.19})	108.51	185.9 ± 3.8(4)
OMS-1 [‡] (synthetic) (Mg _{0.19})	108.51	183.6 ± 2.2(9)
OL-1 (synthetic) (K _{0.125})	95.20	152.1 ± 1.8(8)
OL-1 (synthetic) (K _{0.29})	103.04	152.4 ± 5.2(6)

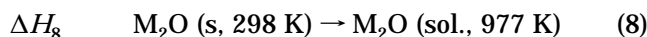
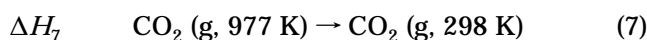
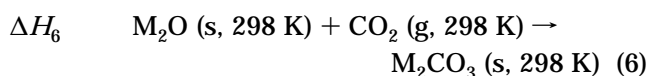
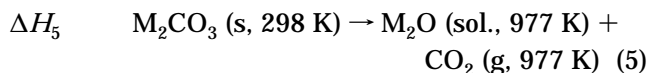
^a See footnote a of Table 1.

in sodium molybdate, is close to the value obtained for the lead borate solvent, -148.5 ± 28.2 kJ/mol,²⁵ and confirms that Mn cations dissolve in the 3+ valence state in 3Na₂O·4MoO₃. Furthermore, the enthalpy determined by calorimetry is in excellent agreement with the only experimental enthalpy value of Otto²⁶ (-162.2 kJ/mol), obtained by oxygen pressure measurements.

Results and Discussion

The measured enthalpies by drop solution methods in 3Na₂O·4MoO₃, at 977 K of framework and layer manganese dioxides are summarized in Table 2. The similar values obtained for a set of two samples of identical composition (but different preparation methods), 187.3 ± 3.4 and 186.6 ± 2.0 kJ/mol for synthetic OMS-2 and 185.9 ± 3.8 and 183.6 ± 2.2 kJ/mol for OMS-1, show the reproducibility of the method. The average value is 187.0 ± 2.0 kJ/mol for OMS-2 and 184.3 ± 2.0 kJ/mol for OMS-1. The determination of the enthalpy of formation (from the oxides) of the cation-doped manganese dioxides requires the values of the enthalpy of a drop solution of the simple oxides which enter the composition of the complex oxides.

The simple oxides that are very hygroscopic were dried before the calorimetric experiments (Table 3). The enthalpy of the drop solution of BaO, Na₂O, K₂O, and SrO (Table 4) was known for lead borate solvent,^{28,29} but we had to measure it in sodium molybdate. These values were determined from the measured drop solution enthalpy of the corresponding carbonates (Table 3), according to the following thermochemical cycle:²⁸⁻³⁰

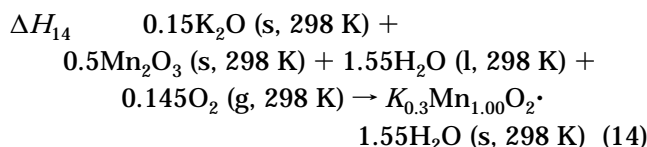
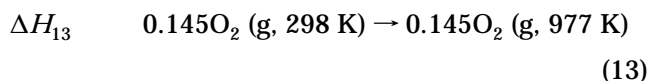
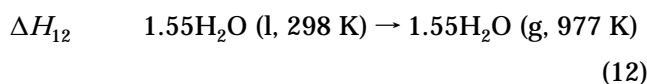
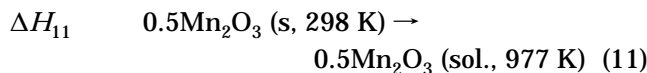
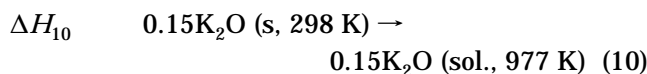
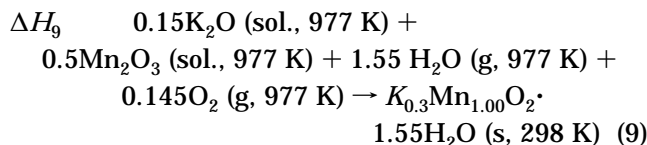


(for BaCO₃ and SrCO₃, replace M by N = M/2)

$\Delta H_8 = \Delta H_5 + \Delta H_6 + \Delta H_7$. ΔH_5 is the measured enthalpy. ΔH_6 is the enthalpy of formation of carbonates from the oxides at 298 K; see ref 31 for BaCO₃ and for SrCO₃ and ref 32, for Na₂CO₃ and for K₂CO₃. ΔH_7 is the heat content of CO₂.³²

Al₂O₃ and SiO₂ do not dissolve in sodium molybdate. We neglected the contribution of the enthalpy of dissolution of those oxides when we calculated the enthalpy of formation of natural hollandite, cryptomelane, and coronadite. However, this approximation should not affect the results significantly because of the minor content of SiO₂ and Al₂O₃.

The enthalpy of formation from the oxides, at 298 K, of the MnO₂-based phases has been calculated from the measured values of the enthalpies of the drop solution. An example of a thermodynamic cycle is shown here for synthetic OMS-2 ($K_{0.3}\text{Mn}_{1.00}\text{O}_2 \cdot 1.55\text{H}_2\text{O}$). In this case, the reaction is equilibrated by incorporation of gaseous oxygen.



where ΔH_9 , ΔH_{10} and ΔH_{11} are the measured enthalpies. ΔH_{12} and ΔH_{13} are the heat content of oxygen and water, respectively,³² and ΔH_{14} ($=\Delta H_9 + \Delta H_{10} + \Delta H_{11} + \Delta H_{12} + \Delta H_{13}$) is the enthalpy of formation of the oxides at 298 K of $K_{0.3}\text{Mn}_{1.00}\text{O}_2 \cdot 1.55\text{H}_2\text{O}$.

The enthalpies of formation from the oxides of the manganese dioxides are reported in Table 5 and in Figure 1. Note that we treat H₂O as simply another oxide component. Note further that, since Mn₂O₃ is the reference state for manganese, the extent of oxidation diminishes with increasing tunnel cation content.

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Table 3. Measured Enthalpies of Drop Solutions of Carbonates, in $3\text{Na}_2\text{O}\cdot 4\text{MoO}_3$, at 977 K

carbonate	origin and purity	heat treatment before experiment	FW (g/mol)	ΔH drop sol. (kJ/mol)
BaCO_3	Johnson Matthey, 99.99%	2 h, 500 °C	197.34	$123.9 \pm 1.0(5)^a$
Na_2CO_3	Aldrich, 99.995%	24 h, 100 °C	105.99	$150.6 \pm 1.4(8)$
K_2CO_3	Fisher, 99.9%	24 h, 100 °C	138.20	$129.1 \pm 2.7(8)$
SrCO_3	Johnson Matthey, 99.999%	2 h, 500 °C	103.62	$137.0 \pm 2.3(8)^a$

^a Values obtained from the work of McHale.²⁷

The structure, the cation content, the manganese oxidation state, and the degree of hydration vary in the different manganese dioxides. We have tried to separate the contribution of each of these parameters in order to point out the energetic trends.

Our previous studies showed that the enthalpy difference between several tunnel structures of pure MnO_2 or MnOOH composition is very small.¹⁷ Ramsdellite is higher in enthalpy than pyrolusite by only 5.4 ± 3.1 kJ/mol for the MnO_2 composition (Table 5). This small difference suggests that the framework stability is not strongly influenced by the openness of the structure. The present study is in agreement with this observation. We did not observe a direct correlation between the enthalpy of formation and the size of the tunnel (Figure 1). Analogous trends have been observed in silica zeolites. High-temperature solution calorimetry experiments have shown that the enthalpies of formation of a series of high silica zeolites are only 8–14 kJ/mol less exothermic than that of quartz, with only a weak dependence of enthalpy on density or cage size.³³

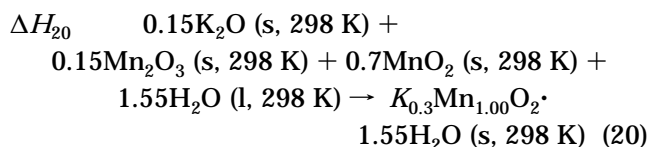
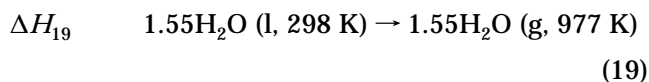
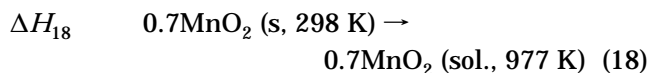
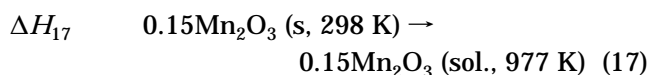
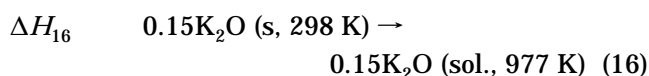
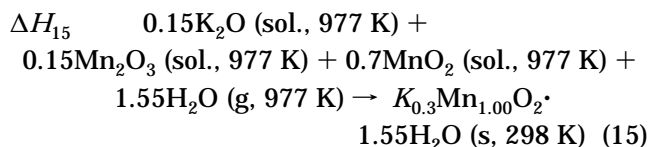
Rather, this work shows that the nature of the cations located inside the tunnel plays an important role in the energetics (see Figure 1). The enthalpy of formation becomes more negative with increasing cation content. Since the degree of oxidation diminishes with increasing cation content (no Mn^{3+} in MnO_2 but substantial Mn^{3+} in oxides with large concentration of extraframework cations) and the oxidation of $1/2\text{Mn}_2\text{O}_3$ to MnO_2 is exothermic (-36.7 kJ/mol of MnO_2 formed, see above), the observed trends suggest that the interaction of the alkali or alkaline earth cations with the framework is strongly exothermic and more than compensates for the effect of a lesser degree of oxidation.

For the same amount of cation, the incorporation of different types of cations has a strong effect on the enthalpy of formation of the framework manganese structure. For example, the trends in Figure 1 suggest that for a 2×2 tunnel, Ba has a greater stabilizing effect than K. The energetics are also somewhat different for different tunnel types (2×2 vs 2×3) and for the layer structure, with the same type of tunnel or interlayer cation (the data are most complete for $M = \text{K}$). The layer structure appears most stabilized. However, as is discussed below, the degree of hydration must be considered.

In fact, in the case of manganese dioxides, it has not yet been possible to prepare OMS materials that do not have tunnel cations. It has been proposed that such

cations act as templates during crystallization,² and studies suggest that OMS-1 prefers divalent cations, whereas OMS-2 prefers monovalent cations.^{1,3}

Another factor that can affect the energetics of the tetravalent manganese oxides is the oxidation state of the manganese cations. To separate possible effects of the reduction reaction (O_2 involved in the reaction, see reaction 14), a second thermodynamic cycle was used. Another way to write the formation reaction is to consider Mn_2O_3 and MnO_2 rather than Mn_2O_3 and gaseous O_2 (see reaction 14). In this case, the thermodynamic cycle used for the same synthetic oxide ($K_{0.3}\text{Mn}_{1.00}\text{O}_2 \cdot 1.55\text{H}_2\text{O}$) is the following:



where ΔH_{15} , ΔH_{16} , ΔH_{17} , and ΔH_{18} are the measured enthalpies, ΔH_{19} is the heat content of water,³² and ΔH_{20} ($=\Delta H_{15} + \Delta H_{16} + \Delta H_{17} + \Delta H_{18} + \Delta H_{19}$) is the enthalpy of formation (from the oxides), without incorporation of O_2 , at 298 K of $K_{0.3}\text{Mn}_{1.00}\text{O}_2 \cdot 1.55\text{H}_2\text{O}$.

The corresponding enthalpies of formation are reported in Table 5 and in Figure 2. The enthalpies of formation are shifted to more positive values when no oxidation is considered (reaction 20). However the energetic trends are similar. The enthalpy of formation (ΔH_{14}) as a function of the average oxidation state of manganese ($\text{Mn}^{4+}/\text{total Mn}$) is shown in Figure 3. The oxidation state of manganese does not seem to play a major role in the energetics. At this point, we believe that it is the tunnel cations that influence the structure stability.

Comparison of different polymorphs containing the same tunnel cation (K in this case) reveals more negative values of the enthalpy of formation (ΔH_f) with increasing K content for both the layer and the octahedral 2×2 tunnel structures. However, the natural cryptomelane (2×2 tunnel) has a more negative enthalpy than the corresponding synthetic one (for the same K content). The natural cryptomelane also contains Sr, Ba, and Na in the tunnels, which probably

(33) Navrotsky, A.; Petrovic, I.; Hu, Y.; Chen, C. Y.; Davis, M. E. *J. Non-Crystalline Solids* Submitted.

Table 4. Measured and Calculated Enthalpies of Drop Solutions of Simple Oxides, in 3Na₂O·4MoO₃, at 977 K

oxide	origin and purity	heat treatment before experiment	FW (g/mol)	ΔH drop sol. (kJ/mol)
MgO	Johnson Matthey, 99.95 %		40.30	13.5 ± 1.4(7)
PbO	Johnson Matthey, 99.9995 %		223.19	-20.3 ± 1.9(6)
ZnO	Aldrich, 99.99 %	15 h, 900 °C	81.38	18.6 ± 0.6(4) ^a
Fe ₂ O ₃	Johnson Matthey, 99.999 %		159.69	113.3 ± 1.7(8)
V ₂ O ₅	Johnson Matthey, 99.9 %		181.88	140.0 ± 2.1(8)
Mn ₂ O ₃	Prepared by heating MnO ₂ (see below)		157.87	168.2 ± 2.6(8)
MnO ₂	Johnson Matthey, 99.999 %		86.94	126.3 ± 1.2(5)
BaO ^a			153.33	-178.5 ± 1.3(5)
Na ₂ O ^a			61.98	-204.7 ± 1.4(8)
K ₂ O ^a			94.20	-300.1 ± 2.7(8)
SrO ^b			103.62	-130.8 ± 2.6(8)

^a Values calculated from measured enthalpies of the corresponding carbonates (see Table 3). ^b Values obtained from the work of McHale.²⁷

Table 5. Enthalpy of Formation from the Oxides at 298 K of Complex Manganese Oxides

phase	tunnel size	composition	Mn ⁴⁺ /total Mn	ΔH_f ,298K (kJ/mol)	
				c	d
pyrolusite	1 × 1 tunnel	MnO ₂	100	0 ^a	
ramsdellite	1 × 2 tunnel	MnO ₂	100	5.4 ^a	
hollandite	2 × 2 tunnel	K _{0.12} Mn _{1.00} O ₂ ·1.55H ₂ O	88.0	10.2 ^b	42.5
		K _{0.3} Mn _{1.00} O ₂ ·1.55H ₂ O	55.8	-34.5	-11.5
		Na _{0.0125} Al _{0.029} Si _{0.01} K _{0.005} Mn _{0.82} Fe _{0.165} - Ba _{0.09} Pb _{0.02} O ₂ ·0.099H ₂ O	83.0	-39.9	-14.9
		Na _{0.03} Al _{0.02} K _{0.12} Mn _{0.94} Fe _{0.0375} Sr _{0.016} - Ba _{0.012} O ₂ ·0.0375H ₂ O	85.1	-58.2	-28.9
		Pb _{0.175} Mn _{0.99} Al _{0.006} Zn _{0.006} O ₂ ·0.19H ₂ O	65.6	-27.4	-3.5
romanechite	2 × 3 tunnel	Ba _{0.132} Mn _{1.00} O ₂ ·0.268H ₂ O	87.7	-55.0	-24.1
todorokite	3 × 3 tunnel	Mg _{0.19} Mn _{1.00} O ₂ ·0.75H ₂ O	41.0	-39.0	-22.8
birnessite	layer structure	K _{0.125} Mn _{1.00} O ₂ ·0.19H ₂ O	87.5	-68.8	-36.7
		K _{0.29} Mn _{1.00} O ₂ ·0.19H ₂ O	63.7	-93.5	-69.6

^a Previously determined.²⁵ ^b Average of two samples (same composition but different preparation methods). ^c O₂ involved in the thermodynamic cycle (eq 14). ^d O₂ not involved in the thermodynamic cycle (eq 20).

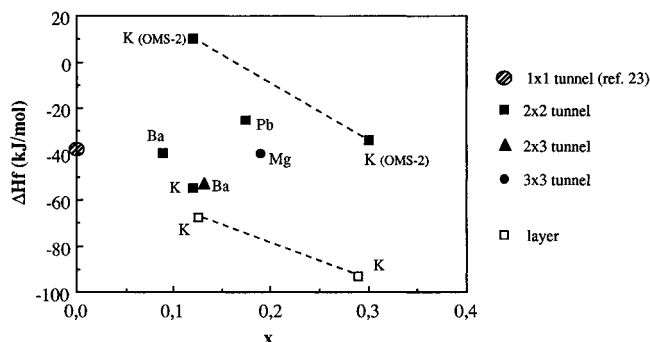


Figure 1. Enthalpy of formation, at 298 K, of manganese dioxides from Mn₂O₃ and M₂O or MO as a function of tunnel-cation content. Because the incorporation of extraframework cations reduces Mn⁴⁺ to Mn³⁺, the reaction consumes a variable amount of oxygen, which decreases with tunnel cation content.

affect the energetics. The layer structure is also more stable than the framework one.

Thermal analysis has shown that the effect of tunnel cations on OMS-1 oxides stability may be related to the nature of such cations.³⁴ Moreover, temperature-programmed desorption experiments made on OMS-2 samples have shown a decreasing thermal stability with decreasing ionic radius of the tunnel cation.³⁵ Similar trends have been seen between the stability of AMnO₃ perovskites and the ionic radii of A cations. However,

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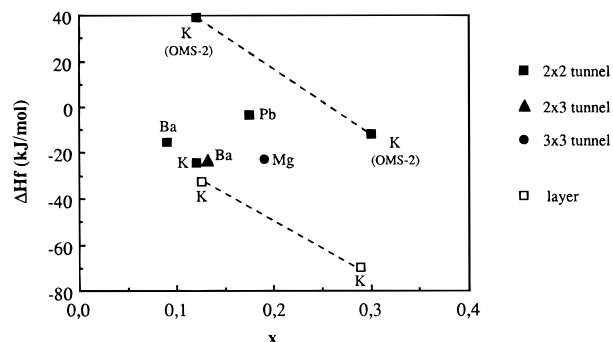


Figure 2. Enthalpy of formation, at 298 K, of manganese dioxides from MnO₂, Mn₂O₃, and M₂O or MO as a function of tunnel-cation content. No gaseous O₂ is involved in this thermodynamic cycle.

thermal decomposition reactions are sensitive to kinetic factors (including grain size), so additional studies are needed to separate thermodynamic and kinetic parameters.

The degree of hydration probably also contributes to the energetics. Previous thermochemistry studies made on calcium zeolites^{28,29} have shown that the enthalpy of dehydration of different tunnel or cage cations depends on the size and charge. Furthermore, water molecules are bonded in different ways to the structure, and consequently, the dehydration process can be accompanied by different energy effects. Since we do not have enough information on where the water is located in the structure, it is impossible to predict the energy of hydration. Further work characterizing the hydration state and its thermal evolution is needed.

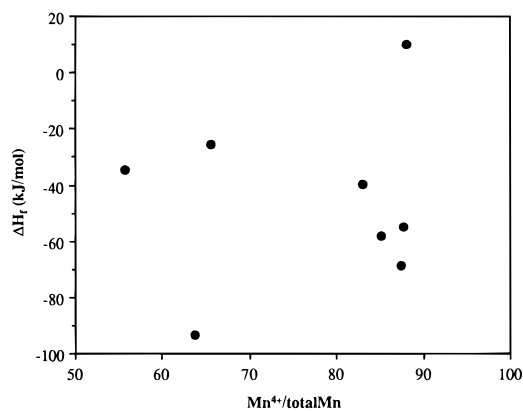


Figure 3. Enthalpy of formation, at 298 K, of manganese dioxides, for all structure types, as a function of manganese average oxidation state (Mn⁴⁺/total Mn).

Conclusion

High-temperature solution calorimetry experiments permit the determination of the energetics of natural and synthetic framework and layer manganese dioxides.

The enthalpy of formation depends on the nature and the amount of the cation located in the tunnel (or between the layers) on the water content, but not strongly on the tunnel size nor the average manganese oxidation state. The synthesis of different microporous materials should be possible by varying these parameters. The trends seen for various structure types suggest that, for manganese oxides, like for zeolites, the synthesis of a given structure depends on finding an appropriate mechanistic and kinetic pathway, rather than being limited by large energetic differences between different possible framework topologies.

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