Thermodynamics of manganese oxidzs: Effects of particle size and hydration on oxidation-reduction equilibria among hausmannite, bixbyite, and pyrolusite
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EXPERIMENT DETAILS

High temperature oxide melt solution calorimetry was performed to obtain a total heat effect using a series of synthesized nanophase manganese-oxide phases of different structure, water content, and surface area. Solution calorimetric studies of nanoparticles of varying size provide a direct measurement of the variation of enthalpy with surface area; a linear relation implies a constant surface enthalpy (energy) (McHale et al., 1997a, 1997b; Ranade et al., 2002; Pitcher, 2005; Navrotsky et al., 2010). The measured enthalpy, called the heat of drop solution ΔH_{ds}, contains several contributions: the heat content of the sample, its enthalpy of dissolution at calorimetric temperature, and any enthalpy of oxidation-reduction or gas evolution associated with the process. To interpret the data properly, both the initial state (chemical composition, structural state, surface area of the solid sample) and the final state (complete dissolution, changes in oxidation state, evolution of gases) must be characterized. Additionally, surface water contributes to the total heat effect and must be accounted for, as previously published. (Mazeina and Navrotsky, 2007; Mazeina et al., 2006; Castro et al., 2006; Ushakov and Navrotsky, 2005)

The total heat effect was then corrected for total water content, which was calculated as bulk water, to produce a corrected enthalpy of drop solution. These data were plotted with respect to molar surface area. The slope for this line gave the surface energy (J / m^2) for the hydrous surface. Water adsorption experiments were done to obtain the integral enthalpy of chemisorbed water to provide an additional correction for the measured drop solution enthalpy, which produced a surface energy of the anhydrous surface for each of the nanophase oxides. The measurement of the differential heat of water adsorption as a function of dose is now done routinely using a combination of a conventional gas dosing system such as that developed for surface area measurement by the Brunauer-Emmett-Teller (BET) gas adsorption method (Brunauer et al., 1938) and a commercial Calvet microcalorimeter operating at room temperature (Ushakov and Navrotsky, 2005).

PREPARATION AND CHARACTERIZATION

Sample preparation

Hausmannite, bixbyite, and pyrolusite were synthesized using minor modifications of previously published methods (McKenzie, 1971). The overall procedures for handling the synthesized Mn-oxide samples were the same for all samples. They were centrifuge-washed at 2,800 rpm (digital) with 18 MΩ/cm ULTRApure® H_2O until the conductivity of the washes equaled 0.14 mS, after which the samples were oven dried at 65-70 °C overnight. The samples were then stored at room temperature until analysis. After synthesis, a portion of the samples was placed in small open vials, transferred into the calorimetry laboratory to be stored for 1 month under constant temperature (25 °C) and humidity (50 %) to equilibrate the hydration state prior to calorimetry measurements.

Powder X–ray diffraction

All phases were confirmed by powder X-Ray diffraction using a Bruker diffractometer (Cu K_α radiation, 1.540596 Å) operated at 45 kV and 40 mA. The XRD patterns were collected with a 0.02^o step size and 10 seconds dwell time, and analyzed by Jade software (version 6.11, 2002; Materials Data Inc., Livermore, CA) to evaluate the mineral phase and size of the nanoparticles. All samples showed X-ray diffraction patterns appropriate to a single phase, with peak broadening consistent with the small particle size. The samples of Mn_3O_4 were identified as hausmannite PDF# 64-0519. The samples of Mn_2O_3 were identified as bixbyite PDF# 62-7926. The samples of MnO_2 were identified as pyrolusite PDF# 63-8208.

Specific surface area analysis using the BET nitrogen adsorption method

Specific surface areas were measured by N_2 adsorption at -196 °C using a five-point Brunauer–Emmett–Teller (BET) technique (Brunauer et al., 1938) on a Micromeritics ASAP

2020 in the P / P_0 range 0.05 to 0.3. Prior to analysis, the samples were made into 20 mg pellets as previously described (Navrotsky et al., 2010) and degassed under nitrogen gas at 300 °C for 4 h (MnO_2), 350 °C for 4 h (Mn_2O_3), and 450 °C for 4 h for (Mn_3O_4).

Total water content analysis using thermogravimetry

H_2O content was determined from the weight difference before and after annealing (300 °C for MnO_2, 600 °C for Mn_2O_3, and 1100 °C for Mn_3O_4) the samples. A microbalance was used to maximize the weight-loss measurement accuracy.

CALORIMETRIC TECHNIQUES

High temperature oxide melt solution calorimetry

Because oxides are generally poorly soluble in aqueous solvents, the well established technique of high temperature oxide melt calorimetry (Navrotsky, 1997a; Navrotsky, 1997b) was used. Mn_3O_4, Mn_2O_3, and MnO_2 sample pellets (~5 mg) were dropped into sodium molybdate ($3Na_2O_4$-MoO_3) melt (20 g) at 700 °C with oxygen flushing through the calorimeter at 30 mL / min and also bubbling though the solvent at 5 mL / min. Flushing and bubbling maintains oxidizing conditions, removes the evolving moisture, and aids dissolution. The custom built

Calvet twin calorimeter and techniques have been described previously (Navrotsky, 1997a, 1997b). Hydrated nanoparticles were reacted in a molten oxide solvent at 700 °C, dissolving the oxide and liberating water vapor. Subsequently, to account for the heat effect of chemically bound surface water, use was made of the established technique (Ushakov and Navrotsky, 2005) for measurement of the enthalpy of water adsorption.

Surface water adsorption micro-calorimetry

H_2O content of metal oxide nanoparticles can be as high as 10 wt % and its contribution to the drop solution enthalpy was measured by water adsorption calorimetry at room temperature using a Calvet microcalorimeter, coupled with a Micromeritics ASAP 2020 analysis system as described previously (Ushakov and Navrotsky, 2005). Sample pellets were placed in one side of a forked silica gas tube and degassed under a static vacuum ($<10^{-3}$ Pa) at elevated temperatures to remove most of the water without coarsening the sample. After BET measurement of the surface area of the sample and the free space of the tube, the system was re-evacuated. Then, a series of precisely controlled small doses of gaseous water were released into the system at room temperature until P / P_0 reached 0.35. The adsorption heat of each dose generated an exothermic calorimetric peak. The simultaneous record of the amount of adsorbed water and the adsorption enthalpy provided a higher resolution measurement of differential heat of adsorption as a function of surface coverage. Water adsorption experiments gave an integral heat of adsorption, which was used for calculation of anhydrous surface energy.

THERMOCHEMICAL CYCLES AND CALCULATIONS

Enthalpies of bulk phase redox reactions

The consistency of the high temperature oxide-melt calorimetry method was validated by using the measured values of enthalpy (enthalpy of drop solution and enthalpy of formation) for Mn_2O_3 along with the formation enthalpy of Mn_3O_4 and the heat capacity of oxygen gas to calculate the enthalpy of drop solution for Mn_3O_4 using the appropriate thermochemical redox-reaction cycle.

$1.5\ Mn_2O_3\ (s, 25\ °C) \rightarrow 1.5\ Mn_2O_3\ (sln, 700\ °C)$ (ΔH_1)

$Mn_3O_4\ (s, 25\ °C) + 0.25\ O_2\ (g, 25\ °C) \rightarrow 1.5\ Mn_2O_3\ (s, 25\ °C)$ (ΔH_2)

$0.25\ O_2\ (g, 25\ °C) \rightarrow 0.25\ O_2\ (g, 700\ °C)$ (ΔH_3)

$Mn_3O_4\ (s, 25\ °C) + 0.25\ O_2\ (g, 700\ °C) \rightarrow 1.5\ Mn_2O_3\ (s, 700\ °C)$ (ΔH_4)

Here, ΔH_1 = 1.5* the enthalpy of drop solution of Mn_2O_3 = 1.5*154.79 = 232.18 kJ / mol. ΔH_2 = enthalpy of oxidation of Mn_3O_4 to Mn_2O_3 = $1.5*(\Delta H_{f,el})Mn_2O_3 - (\Delta H_{f,el})Mn_3O_4$ = -54.0 kJ

/ mol, and $\Delta H_3 = 0.25*(\Delta H_{25\ °C} - \Delta H_{700\ °C})O_2 = 0.25*21.84 = 5.5$ kJ / mol. $\Delta H_{f,el}$ = enthalpy of formation from the elements. The equation for ΔH_3 accounts for the heat content of the oxygen (Robie and Hemingway, 1995) going from room temperature to the calorimeter temperature. The enthalpy of oxidation and heat content of oxygen were both obtained from Robie and Hemingway (1995). The final enthalpy then is simply a summation of the steps from the cycle, as follows: $\Delta H_4 = \Delta H_1 + \Delta H_2 - \Delta H_3$ = 232.18 kJ / mol – 54.0 kJ / mol – 5.5 kJ / mol = 172.68 kJ / mol. Thus, by using the measured enthalpy of drop solution of Mn_2O_3 and then calculating from this an enthalpy of drop solution for Mn_3O_4, the consistency of drop solution method was verified.

Likewise, the validation of the experimentally obtained values for the enthalpies MnO_2 reduction to Mn_2O_3, according to the balanced redox reaction equation for the reduction, 4 MnO_2 (s) → 2 Mn_2O_3 (s) + O_2 (g), was calculated using a corresponding thermochemical cycle.

2 Mn_2O_3 (s, 25 °C) → 2 Mn_2O_3 (sln, 700 °C) (ΔH_1)

4 MnO_2 (s, 25 °C) → 2 Mn_2O_3 (s, 25 °C) + O_2 (g, 25 °C) (ΔH_2)

O_2 (g, 25 °C) → O_2 (g, 700 °C) (ΔH_3)

4 MnO_2 (s, 25 °C) → 2 Mn_2O_3 (s, 700 °C) + O_2 (g, 700 °C) (ΔH_4)

Here, ΔH_1 = 0.5*(the enthalpy of drop solution of Mn_2O_3) = -0.5*(154.79) = -77.39 kJ / mol.

ΔH_2 = enthalpy of reduction = $0.5*(\Delta H_{f,el})Mn_2O_3 - (\Delta H_{f,el})\ MnO_2 = 0.5*(-959.0) - (-520.0) = 40.5$ kJ / mol. $\Delta H_3 = 0.25*(\Delta H_{25\ °C} - \Delta H_{700\ °C})\ O_2 = 5.5$ kJ / mol. $\Delta H_4 = -\Delta H_1 + \Delta H_2 + \Delta H_3 = 77.39 + 40.5 + 5.5 = 123.39$ kJ / mol. Thus, by comparing the measured results of enthalpy Mn_2O_3 and then calculating from this an enthalpy of drop solution for MnO_2, the consistency of drop solution method was verified.

The calculated enthalpy of drop solution for bulk Mn_3O_4, 172.68 kJ / mol, agrees well with our measured enthalpy of drop solution for bulk Mn_3O_4, 172.27±0.99 kJ / mol. The calculated enthalpy of drop solution for bulk MnO_2, 123.39 kJ / mol, agrees well with our measured enthalpy of drop solution for bulk phase MnO_2, 124.92±1.03 kJ / mol. The results are summarized in Table 2.

Formation enthalpies of the oxides were used to calculate the enthalpies for the redox equilibria. The enthalpy of oxidation and heat content of oxygen were both obtained from Robie and Hemingway (1995). The ΔH_f^0 at 25 °C for MnO_2 (pyrolusite) -520.0±0.7 kJ / mol, Mn_2O_3 (bixbyite) -959.0±1.0 kJ / mol, and Mn_3O_4 (hausmannite) -1384.5±1.4 kJ / mol along with the heat capacity of oxygen gas $\int_{25°C}^{700°C} C_p(O_2)dT = 21.84$ kJ / mol were used to calculate the redox enthalpy as:

Mn_3O_4 (s, 25 °C) + 0.25 O_2 (g, 25 °C) = 1.5 Mn_2O_3 (s, 25 °C)

ΔH = 1.5*(-959.0) - (-1384.5) = -54±1.8 kJ / mol

MnO_2 (s, 25 °C) = 0.5 Mn_2O_3 (s, 25 °C) + 0.25 O_2 (g, 25 °C)

ΔH = 0.5*(-959.0) - (-520.0) = 40.5±0.99 kJ / mol

Mn_3O_4 (s, 25 °C) + O_2 (g, 25 °C) = 3 MnO_2 (s, 25 °C)

ΔH = -1384.5 – 3*(-520.0) = 175.5±1.7 kJ / mol.

From the drop solution enthalpies of the present work we calculated:

Mn_3O_4 (s, 25 °C) + 0.25 O_2 (g, 25 °C) = 1.5 Mn_2O_3 (s, 25 °C)

ΔH = 172.27 + 0.25*21.84 – 1.5*154.79 = -54.5±0.9 kJ / mol

MnO_2 (s, 25 °C) = 0.5 Mn_2O_3 (s, 25 °C) + 0.25 O_2 (g, 25 °C)

ΔH = 124.92 - 0.5*154.87 - 0.25*21.84 = 42.0±1.6 kJ / mol

Mn_3O_4 (s, 25 °C) + O_2 (g, 25 °C) = 3 MnO_2 (s, 25 °C)

ΔH = 3*124.92 - 21.84 - 172.27 = 180.7±1.4 kJ / mol

From earlier drop solution experiments (Fritsch and Navrotsky, 1996) we calculated:

Mn_3O_4 (s, 25 °C) + 0.25 O_2 (g, 25 °C) = 1.5 Mn_2O_3 (s, 25 °C)

ΔH = 170.6 + 0.25*21.84 – 1.5*151.7 = -51.5±0.9 kJ / mol

MnO_2 (s, 25 °C) = 0.5 Mn_2O_3 (s, 25 °C) + 0.25 O_2 (g, 25 °C)

ΔH = 126.3 – 0.5*151.7 – 0.25*21.84 = 45.0±1.7 kJ / mol

Mn_3O_4 (s, 25 °C) + O_2 (g, 25 °C) = 3 MnO_2 (s, 25 °C)

ΔH = 3*126.3 - 21.84 - 170.6 = 186.5±1.5 kJ / mol

Calculations were performed using drop solution values obtained from additional prior experiments (Guillemet-Fritsch et al., 2005):

Mn_3O_4 (s, 25 °C) + 0.25 O_2 (g, 25 °C) = 1.5 Mn_2O_3 (s, 25 °C)

ΔH = 170.56 + 0.25*21.84 - 1.5*155.45 = -57.2±1.0 kJ / mol

MnO_2 (s, 25 °C) = 0.5 Mn_2O_3 (s, 25 °C) + 0.25 O_2 (g, 25 °C)

ΔH = 123.77 – 0.5*155.45 – 0.25*21.84 = 40.6±1.4 kJ / mol

Mn_3O_4 (s, 25 °C) + O_2 (g, 25 °C) = 3 MnO_2 (s, 25 °C)

ΔH = 3*123.77 - 21.84 - 170.56 = 178.9±1.7 kJ / mol.

Surface Enthalpy Calculations

Thermochemical cycle for water correction for manganese oxide phases $Mn_xO_y{\cdot}nH_2O$. Here, x and y are (3, 4), (2, 3), and (1, 2), for Mn_3O_4, Mn_2O_3, and MnO_2 phases respectively.

$Mn_xO_y \cdot nH_2O_{\text{(nano, 25 °C)}} \rightarrow Mn_xO_{y\text{ (soln, 700 °C)}} + nH_2O_{\text{(gas, 700 °C)}}$ $\Delta H_1 = \Delta H_{ds}$

$H_2O_{\text{(gas, 700 °C)}} \rightarrow H_2O_{\text{(gas, 25 °C)}}$ ΔH_2 = (-25 ± 0.1 kJ / mol)

$H_2O_{\text{(gas, 25 °C)}} \rightarrow H_2O_{\text{(liq, 25 °C)}}$ ΔH_3 = (-44 ± 0.1 kJ / mol)

$x\mathrm{H_2O}_{\text{(gas, 25 °C)}} \rightarrow x\mathrm{H_2O}_{\text{(liq, 25 °C)}}$ $\Delta H_4 = x(\Delta H_{\text{ads}})$

$\mathrm{Mn_xO_y}_{\text{(nano, 25 °C)}} \rightarrow \mathrm{Mn_xO_y}_{\text{(soln, 700 °C)}}$ $\Delta H_5 = \Delta H$ hydrous surface

$\Delta H_5 = \Delta H_1 + n\Delta H_2 + n\Delta H_3$

$\mathrm{Mn_xO_y}_{\text{(nano, 25 °C)}} \rightarrow \mathrm{Mn_xO_y}_{\text{(soln, 700 °C)}}$ $\Delta H_6 = \Delta H$ anhydrous surface

$\Delta H_6 = \Delta H_1 + n\Delta H_2 + (n - x)_{\text{phys}}\, \Delta H_3 + x_{\text{chemi}}\, \Delta H4$

Here, soln = dissolved in $3\mathrm{Na_2O}$-$4\mathrm{MoO_3}$, 700 °C. $\Delta H_1 = \Delta H_{\text{ds}}$ denotes values obtained using high temperature oxide melt solution calorimetry. ΔH_2 is the heat content of water as it is changing temperature over the range 25 °C to 700 °C. ΔH_3 is the enthalpy of condensation. ΔH_2 and ΔH_3 are reference values obtained using the FactSage database (FactSage 2006). The resultant heat effect (heat of drop solution, ΔH_{ds}) includes the heat content of the oxide, the heat effect associated with desorbing and heating water (chemi- and physi-sorbed water), and the heat of dissolution of oxide in the high temperature solvent. Additionally, for $n = (n - x)_{\text{phys}} + x_{\text{chemi}}$, n denotes the total water, as measured by thermogravimetry. Both $(n - x)_{\text{phys}}$ and x_{chemi} were measured using water adsorption calorimetry.

Calculated Gibbs free energy shifts of nanophase equilibria

Surface energies and surface areas of the nanoparticles were used to calculate nanoscale phase diagrams, which showed a significant free energy shift from the values calculated for bulk phase assemblages. The calculated energy shifts in phase equilibria for the anhydrous- and hydrous-surfaces are shown in Table 4. The phase diagrams are presented in Figure 3.

Phase Diagram Calculations

Mn-O phase diagrams calculated for bulk phases:

I. MnO_2/Mn_2O_3 (bulk):

$2\ Mn_2O_3\ (s, bulk) + O_2\ (g) \rightarrow 4\ MnO_2\ (s, bulk)$ ....$K(I) = [P(O_2)]^{-1}$

Free energy of reaction = $\Delta G_r(I) = 4*\Delta G_f(MnO_2) - 2*\Delta G_f(Mn_2O_3) = -n*R*T*LnK(I)$

$\Delta G_r(I) = -n*R*T*Ln[P(O_2)]^{-1} = 1.0*R*T*Ln(P(O_2)/P_0) = 1.0*2.303*R*T*Log(P(O_2)/P_0)$

$Log(P(O_2)/P_0) = \Delta G_r(I)/(1.0*2.303*R*T)$

$Log(P(O_2)/P_0) = 4*\Delta G_f(MnO_2) - 2*\Delta G_f(Mn_2O_3)/(1.0*2.303*R*T)$

II. Mn_2O_3/Mn_3O_4 (bulk):

$4\ Mn_3O_4\ (s, bulk) + O_2\ (g) \rightarrow 6\ Mn_2O_3\ (s, bulk)$........$K(II) = [P(O_2)]^{-1}$

$\Delta G_r(II) = 6*\Delta G_f(Mn_2O_3) - 4*\Delta G_f(Mn_3O_4) = -n*R*T*LnK(II)$

$\Delta G_r(II) = -n*R*T*Ln[P(O_2)]^{-1} = 1.0*R*T*Ln(P(O_2)/P_0) = 1.0*2.303*R*T*Log(P(O_2)/P_0)$

$Log(P(O_2)/P_0) = \Delta G_r(II)/(1.0*2.303*R*T)$

$\mathrm{Log}(P(O_2)/P_0) = [6*\Delta G_f(Mn_2O_3) - 4*\Delta G_f(Mn_3O_4)]/(1.0*2.303*R*T)$

Calculations of Gibbs free energy shifts for the manganese oxide nanoparticles

III. MnO_2/Mn_2O_3 (nano):

$2\ Mn_2O_3$ (s, nano) + O_2 (g) → $4\ MnO_2$ (s, nano) ....$K(III) = [P(O_2)]^{-1}$

$\Delta G_r(III) = 4*\Delta G_f(MnO_2) + 4*\Delta H_{surface}(MnO_2) - 2*\Delta G_f(Mn_2O_3) - 2*\Delta H_{surface}(Mn_2O_3)$

$\Delta G_r(III) = -n*R*T*\mathrm{Ln}[P(O_2)]^{-1} = 1.0*R*T*\mathrm{Ln}(P(O_2)/P_0) = 1.0*2.303*R*T*\mathrm{Log}(P(O_2)/P_0)$

$\mathrm{Log}(P(O_2)/P_0) = \Delta G_r(III)/(1.0*2.303*R*T)$

$\mathrm{Log}(P(O_2)/P_0) = [4*\Delta G_f(MnO_2) + 4*\Delta H_{surface}(MnO_2) - 2*\Delta G_f(Mn_2O_3) -$

$2*\Delta H_{surface}(Mn_2O_3)]/(1.0*2.303*R*T)$

IV. Mn_2O_3/Mn_3O_4 (nano):

$4\ Mn_3O_4$ (s, nano) + O_2 (g) → $6\ Mn_2O_3$ (s, nano)........$K(IV) = [P(O_2)]^{-1}$

$\Delta G_r(IV) = 6*\Delta G_f(Mn_2O_3) + 6*\Delta H_{surface}(Mn_2O_3) - 4*\Delta G_f(Mn_3O_4) - 4*\Delta H_{surface}(Mn_3O_4)$

$\Delta G_r(IV) = -n*R*T*\mathrm{Ln}[P(O_2)]^{-1} = 1.0*R*T*\mathrm{Ln}(P(O_2)/P_0) = 1.0*2.303*R*T*\mathrm{Log}(P(O_2)/P_0)$

$\mathrm{Log}(P(O_2)/P_0) = \Delta G_r(IV)/(1.0*2.303*R*T)$

$\mathrm{Log}(P(O_2)/P_0) = [6*\Delta G_f(Mn_2O_3) + 6*\Delta H_{surface}(Mn_2O_3) - 4*\Delta G_f(Mn_3O_4) -$

$4*\Delta H_{surface}(Mn_3O_4)]/(1.0* 2.303*R*T)$

The Log($P(O_2)/P_0$) vs. 1/T curves were plotted by Origin Software, OriginLab Corporation, Version 8.5, 2010.

Formation free energy equations in kcal/mol (Pankratz, 1982)

MnO_2: Pyrolusite/Ramsdelite

25 °C – 527 °C, $\Delta G_f(MnO_2)$ = -126.453-4.062E-3*T*LnT+(1.302E-6)*T*T+159.200/T+72.195E-3*T

Mn_3O_4: Hausmannite

25 °C – 707 °C, $\Delta G_f(Mn_3O_4)$ = -333.592-(3.672E-3)*T*LnT+(0.331E-6)*T*T+123.300/T+(109.543E-3)*T

Mn_2O_3: Bixbyite

25 °C – 707 °C, $\Delta G_f(Mn_2O_3)$ = -230.513-2.449E-3*T*LnT-(0.095E-6)*T*T+85.700/T+79.830E-3*T

The units for calculated values were converted from kcal/mol to kJ/mol (1 kcal = 4.184 kJ).

ADDITIONAL FIGURES AND TABLES

Table 4. Calculated energy shifts for the phase equilibria involving hydrous and anhydrous surfaces.

Sample	Density (g / cm^3, 25 °C)	Standard molar mass (g / mol)	Particle diameter (nm)	SA (m^2 / g)	Molar Surface Area (m^2 / mol)*	† $\Delta H_{\text{Surface}}$ (kJ / mol) [hydrous]	† $\Delta H_{\text{Surface}}$ (kJ / mol) [anhydrous]
Mn_3O_4	4.84	228.81	100	12.397	2836.5	2.72	4.59
Mn_2O_3	4.94	157.88	100	12.133	1915.5	2.47	3.39
MnO_2	5.06	86.94	100	11.858	1030.9	1.69	2.11
Mn_3O_4	4.84	228.81	10	123.967	28364.9	27.23	45.95
Mn_2O_3	4.94	157.88	10	121.335	19156.3	24.71	33.90
MnO_2	5.06	86.94	10	118.577	10309.1	16.91	21.13

* Molar surface area is given by: molar mass / density / spherical volume * spherical surface area. † Total free energy shift arising from surface energy term (kJ / mol) is given by : molar surface area (m^2 / mol) * surface energy (J / m^2) / 1000.