Oxide melt solution calorimetry of sulfides: Enthalpy of formation of sphalerite, galena, greenockite, and hawleyite

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Abstract

Oxidative drop solution calorimetry is being developed as a general method for sulfide thermochemistry. The samples are dropped from room temperature into molten $3Na_2O \cdot 4MoO_3$ solvent at 975 K, with oxygen bubbling through the melt to ensure rapid and complete conversion of sulfide to dissolved sulfate. Complete dissolution of sulfides and retention of sulfur in the solvent is documented by furnace tests and visual observation, consistent determination of enthalpy of drop solution, and comparison with previous data for the heat of formation of ZnS, PbS, and CdS. Enthalpies of formation (kJ/mol) from the elements (ΔH_f^0) are determined for sphalerite (ZnS) (–206.53 ± 4.03 kJ/mol), galena (PbS) (–98.12 ± 4.37 kJ/mol), greenockite (hexagonal CdS) (–148.79 ± 4.13 kJ/mol), and hawleyite (cubic CdS) (–147.65 ± 4.28 kJ/mol). Thus, hawleyite appears to be energetically very similar to greenockite but possibly slightly metastable by about 1 kJ/mol. The results confirm that oxidative drop solution calorimetry in molten sodium molybdate is a viable method for sulfide thermochemistry. It will be most useful for sulfides with moderate heats of oxidation (e.g., the Fe-S, Co-S, and Ni-S systems), and should be applicable to ternary compounds, e.g., the Fe-Ni-S and Ni-Co-S systems, and systems showing large homogeneity ranges, as well as to other chalcogenides and pnictides.

Keywords: Sulfides, oxide melt solution calorimetry, enthalpy of formation, sphalerite, galena, greenockite, hawleyite
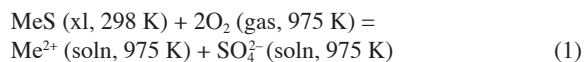
Introduction

Sulfides and other chalcogenides form important classes of minerals as well as semiconductors and other technological materials. Both binary and ternary sulfides show complexities in crystal structures, significant homogeneity ranges, and variations in the nominal oxidation state of the metals (Kim et al. 1987; Cheung and Steele 1980). There is recent interest in sulfide, chalcogenide, and pnictide nanoparticles (e.g., ZnS, Walker et al. 2003; CdSe, Walker et al. 2003; and GaAs, Malik et al. 2003) as quantum dot electronic materials (Li et al. 1999) and sensors. Nanoparticle sulfides with properties different from bulk may be important for ore deposits, bacterial degradation of sulfides, and environmental science (Watson et al. 2001). Sulfide minerals are the major ores of metals such as Pb, Fe, Co, Ni, Cu, Zn, and Ag (Kapustinsky and Korshunov 1939). Oxidation of exposed ore deposits is a major source of acid mine drainage and heavy metal pollution (Magombedze and Brattli 2003).

Despite this interest, thermochemical data for sulfides and related materials are quite incomplete. Determining their enthalpies of formation presents challenges of sample characterization and of slow kinetics of reaction. Thus, many different thermodynamic methods have been tried, but few are of general applicability. These include direct ignition of reaction mixtures (Kapustinsky and Korshunov 1939), electrochemical determination (Schaefer 1978), bromine reaction calorimetry (Stuve 1981), HCl acid solution calorimetry (Adami and King 1964), high-temperature direct-synthesis calorimetry (Bryndzia

and Kleppa 1988), and high-temperature solution calorimetry (Cemic and Kleppa 1986).

High-temperature oxide melt solution calorimetry has recently been extended to two classes of materials potentially relevant to sulfide thermochemistry. In this method, small pellets of sample are dropped into a molten oxide solvent. In addition to extensive work on oxides (see Navrotsky 1977, 1997 for reviews), calorimetry of sulfates ($CaSO_4$, $PbSO_4$, and $BaSO_4$) (Majzlan et al. 2002) and nitrides (Elder et al. 1993; Navrotsky 2001) have been developed. Both sulfate and nitride calorimetry use $3Na_2O \cdot 4MoO_3$ near 975 K as the solvent of choice. The studies show that both anhydrous (Majzlan et al. 2002) and hydrated (Drouet and Navrotsky 2003) sulfates dissolve readily, and that the SO_4^{2-} ion remains dissolved in the solvent. Oxidative drop solution calorimetry of nitrides converts them quantitatively to dissolved oxides, with the evolution of N_2 gas (Elder et al. 1993). The molybdate in the solvent appears to take part catalytically in the oxidation; Mo^{6+} species are converted to lower oxidation states, turning the solvent blue, and then reoxidized to a light yellow melt by oxygen gas bubbling through the solvent. This process enhances the rate of oxidative dissolution of the nitrides, and has been applied to a variety of nitrides, including GaN and InN (Ranade et al. 2000; Ranade 2001).
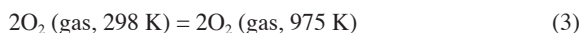
The proposed calorimetric scheme for sulfides is illustrated for a binary sulfide, MeS, as follows:

$$MeS \text{ (xl, 298 K)} + 2O_2 \text{ (gas, 975 K)} =$$
$$Me^{2+} \text{ (soln, 975 K)} + SO_4^{2-} \text{ (soln, 975 K)} \quad (1)$$

"xl" means crystalline solid and "soln" means dissolved oxides

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at low concentration in the molten salt solvent.

$$MeSO_4 \text{ (xl, 298 K)} = Me^{2+} \text{ (soln, 975 K)} + SO_4^{2-} \text{ (soln, 975 K)} \quad (2)$$

$$2O_2 \text{ (gas, 298 K)} = 2O_2 \text{ (gas, 975 K)} \quad (3)$$

This leads to

$$MeS \text{ (xl, 298 K)} + 2O_2 \text{ (gas, 298 K)} = MeSO_4 \text{ (xl, 298 K)} \quad (4)$$

with $\Delta H_4 = \Delta H_1 - \Delta H_2 + \Delta H_3$

If the enthalpy of formation of the sulfate is known or can be measured, the heat of formation of the sulfide can be calculated. If the anhydrous sulfate is not available, alternative thermochemical cycles using the oxides can be formulated, see below.

To test the feasibility of this method, the following questions must be addressed: (1) does oxidation occur rapidly and reproducibly, leaving all sulfur dissolved as sulfate species? (2) Is there any evolution of gaseous sulfur species from the calorimetric solvent? (3) Because the enthalpy of oxidation (reaction 1) is large and exothermic, can both the composition of the sulfide (moles of sulfur) and the calorimetric measurement be controlled well enough to obtain enthalpies of formation with useful accuracy (better than ±5 kJ/mol of sulfur)?

The present work tests the feasibility of this calorimetric approach by applying it to these sulfides with known thermodynamic properties: sphalerite (ZnS), galena (PbS), and greenockite (hexagonal CdS). In addition, hawleyite (cubic CdS), whose thermodynamic properties are unknown, was studied by calorimetry.

EXPERIMENTAL PROCEDURES

The samples for thermodynamic experiments should be phase pure, crystalline, and without chemical impurities. The chemicals used in this study, their purity and sources are listed in Table 1. All sulfides were washed two to three times with benzene to remove residual sulfur (Day 2004). They were cleaned in an ultrasonic cleaner with a solution of sodium acetate and were then washed consecutively with alcohol and distilled water. ZnO and PbO were prepared by heating ZnS and PbS in a furnace at 1173 K for 24 hours. The oxides were ground and washed with ethanol before drying at room temperature. CdO and anhydrous PbSO$_4$ were used without any treatment. Hawleyite (CdS) was prepared by microwave heating of a solution of cadmium acetate and thiourea, analogous to the synthesis process described by Ding and Zhu (2003).

The phase purity of the samples was checked by X-ray (XRD) analysis with an INEL XRG 3000 using Cu$K\alpha$ radiation and a CPS 120 detector. Phase identification was done using Jade 6.1 (Materials Data Inc. 2001) software and the PDF file version 3.0 (ICDD 1999). The lattice parameters determined by Rietveld refinement using Materials Studio 3.0.1 software (Accelrys Inc. 2003) are presented in Table 2. Atomic positions, occupancies, and strain were not refined.

High temperature oxide melt drop solution calorimetry was performed in a custom-built Calvet twin microcalorimeter described previously (Navrotsky 1977, 1997). The samples (~5 mg sulfide pellets and ~15 mg oxide pellets) were dropped from room temperature and dissolved in the calorimetric solvent 3Na$_2$O·4MoO$_3$ at 975 K. The different sizes of sample pellets were chosen to optimize the heat effect obtained for different samples. The pellets were prepared by hand-pressing the desired weight of sample in a die. Calibration was done using the heat content

TABLE 1. Chemicals used; their purity and sources

Sample	Purity (metals basis) (%)	Source
ZnS	99.990	Cerac Inc.
PbS	99.999	Alfa Aesar
CdS	99.999	Alfa Aesar
PbSO$_4$	99.999	Alfa Aesar
CdO	99.999	Alfa Aesar

of ~5 mg α-Al$_2$O$_3$ pellets (for oxide samples) and of 200–250 mg platinum rods, corrected for heat pickup by samples during drop from room temperature to 975 K, for the sulfides. The rationale for these calibrations, particularly when large exothermic oxidation enthalpies are obtained, has been discussed previously in the context of nitride calorimetry (Ranade et al. 2000). An oxidizing atmosphere was maintained by flushing the calorimeter with oxygen (75 mL/min) and by bubbling oxygen through the solvent (8.5 mL/min). Bubbling both oxidizes the sample and disperses it in the solvent for quicker dissolution.

The dissolution of sulfides in the calorimetric solvent produced a large heat effect ΔH_{dsol}. This meant that a small error in weighing the sample resulted in a large error in the observed heat effect. For example, an error of 0.01 mg corresponds to an error of ~1.3 to 1.9 kJ/mol in the measured heat effect. These errors were minimized by using a Mettler Toledo MT5 microbalance with a reproducibility of 0.8 μg.

The return of the calorimetric signal to its original baseline within 50–60 min and the normal shape of the calorimetric peak suggested rapid oxidative dissolution of the sulfide samples. To check further whether the samples dissolve fast enough for accurate calorimetry, furnace tests were performed in 3Na$_2$O·4MoO$_3$ at 975 K; a pellet was dissolved in the solvent in a furnace outside of the calorimeter without any oxygen bubbling. The dissolution of the sulfide samples in the solvent was checked visually. The pellets disappeared within 20–30 min. Furnace tests were also used to check for evolution of gaseous sulfur species from the solvent. Moist lead acetate paper was held over the solvent while MeS samples were dropped into the solvent at 975 K. No change in the color of the paper was observed, indicating that no H$_2$S was evolved. No odor was detected.

TABLE 2. Lattice parameters, R_{wp} and R_p values from Rietveld refinement of samples

Sample name	Crystal system	Unit-cell parameter a (Å) This work	Unit-cell parameter a (Å) Reference*	R_{wp} (%)	R_p (%)
PbS	Cubic $Fm3m$	5.9400 ± 0.0001	5.9315†	7.0	5.6
ZnS	Cubic $F43m$	5.4071 ± 0.0002	5.4340‡	10.0	14.6
CdS	Cubic $F43m$	5.8196 ± 0.0314	5.8304*	7.76	6.14
		a (Å)	c (Å)	a (Å)	c (Å)
CdS	Hexagonal $P63mc$	4.1186 6.6847 ±0.0002	4.1370§ 6.7144§ ±0.0004	23.4	16.1

* FIZ/NIST Inorganic Crystal Structure Database 2004.
† Noda et al. (1987).
‡ Rabadanov et al. (1997).
§ Xu and Ching (1993).

TABLE 3. Enthalpies of drop solution (ΔH_{dsol}) of sulfide samples

Mass of pellet (mg)	ΔH_{dsol} (kJ/mol)*	Mass of pellet (mg)	ΔH_{dsol} (kJ/mol)
PbS (galena)		**ZnS (sphalerite)**	
4.77	−773.32	4.705	−768.79
4.65	−775.51	4.657	−773.81
4.42	−778.26	4.532	−769.94
4.22	−772.08	3.939	−770.47
4.19	−774.24	5.870	−772.53
3.76	−777.49	4.999	−768.30
Mean value	−775.15 ± 1.96 (6)†	4.541	−772.41
		3.858	−768.57
		5.066	−773.06
		5.050	−769.24
		6.004	−767.00
		Mean value	−770.37 ± 1.36 (11)
CdS (greenockite)		**CdS (hawleyite)**	
5.226	−758.20	4.151	−760.68
6.318	−760.43	5.065	−760.30
5.963	−759.28	4.593	−761.75
5.362	−760.28	5.552	−761.06
3.744	−762.88	5.600	−763.78
5.406	−760.50	4.206	−766.83
6.13	−758.19	4.975	−760.10
5.946	−756.19	5.342	−758.12
5.859	−758.54	4.578	−757.06
8.281	−764.92	Mean value	−761.08 ± 1.94 (9)
Mean value	−759.94 ± 1.59 (10)		

* The associated error of ΔH_{dsol} measurements represents two standard deviations (2σ) of the mean.
† The value in parentheses represents the number of experiments.

RESULTS AND DISCUSSION

All samples produced sharp XRD patterns. Only the peaks for the desired phases were discernible. The lattice parameters for the sulfide samples are in good agreement with the lattice parameters in the ICSD database (FIZ/NIST 2004) (Table 2).

According to Majzlan et al. (2002), the sulfur in metal sulfate (MeSO$_4$) samples dissolves to form SO$_4^{2-}$ species as shown in Equation 2. The metal sulfide samples (MeS) are thought to oxidize and dissolve similarly as shown in Equation 1.

Table 3 shows the ΔH_{dsol} values for all sulfide samples and Table 4 shows data for the oxide and sulfate samples. The thermochemical cycle used for determining ΔH_f^0 of MeS by using anhydrous MeSO$_4$ as the reference phase is simple. A representative experiment using lead (PbS and anhydrous PbSO$_4$) was performed and Table 5 shows the thermochemical cycle. The ΔH_f^0 of PbS, calculated using the cycle (Table 7), is -99.44 ± 4.00 kJ/mol and compares well with the tabulated value of -98.30 ± 2.00 kJ/mol (Robie and Hemingway 1995).

The ΔH_f^0 of other sulfides (ZnS, PbS, and CdS) is calculated from the ΔH_{dsol} by a thermochemical cycle (Table 6) with MeO as

TABLE 4. Enthalpies of drop solution (ΔH_{dsol}) of oxide and sulfate samples

Sample	ΔH_{dsol} (kJ/mol)*
anglesite (PbSO$_4$)	78.9 ± 0.8 (6)†
litharge (PbO)	−10.9 ± 0.3 (12)
zincite (ZnO)	18.7 ± 0.4 (8)
monteponite (CdO)	−5.2 ± 0.5 (10)

* The associated error of ΔH_{dsol} measurements represents two standard deviations (2σ) of the mean.
†The value in parentheseas represents the number of experiments.

TABLE 5. Thermochemical cycle for the calculation of enthalpy of formation of PbS from drop solution data using PbSO$_4$ as the reference state

Reaction number and reaction	Enthalpy change
(1) PbS (xl, 298 K) + 2O$_2$ (gas,975 K) → Pb^{2+} (soln, 975 K) + SO$_4^{2-}$ (soln, 975 K)	$\Delta H_1 = \Delta H_{ds}$(PbS)*
(2) O$_2$ (gas, 298 K) → O$_2$ (gas, 975 K)	$\Delta H_2 = \Delta H_{hc}$(O$_2$)†
(3) PbSO$_4$ (xl, 298 K) → Pb^{2+} (soln, 975 K) + SO$_4^{2-}$ (soln, 975 K) $\Delta H_3 = \Delta H_{ds}$(PbSO$_4$) §	
(4) Pb (xl, 298 K) + 2 O$_2$ (gas, 298 K) + S (xl, 298 K) → PbSO4 (xl, 298 K)	$\Delta H_4 = \Delta H_f^0$(PbSO$_4$)†
(5) Pb (xl, 298 K) + S (xl, 298 K) → PbS (xl, 298 K)	$\Delta H_5 = \Delta H_f^0$(PbS)

Notes: $\Delta H_5 = \Delta H_f^0$(PbS) $= -\Delta H_1 - 2\Delta H_2 + \Delta H_3 + \Delta H_4$.
* Experimental data in Table 3.
† Taken or calculated from Robie and Hemingway (1995).
§ Experimental data from Table 4.

the reference phase (see below). Table 7 lists the ΔH_f^0 for sulfides along with the associated error. They agree with reported values within experimental errors.

The ΔH_f^0 of hawleyite, for which no previous thermodynamic data are available, was determined to be -147.65 ± 4.28 kJ/mol. The ΔH_t^0 for CdS (greenockite → hawleyite), based on differences in drop solution enthalpies, is 1.14 ± 2.51 kJ/mol.

DISCUSSION

The high temperature of the solvent and the agitation provided by oxygen bubbling results in rapid dissolution of the sulfide and oxide samples. A major advantage of this method is that the dissolution time of samples (20–30 min) is far shorter than that encountered for incomplete dissolution in acid solution calorimetry (Adami and King 1964) or bromine reaction calorimetry (Stuve 1981).

Since MeS and MeSO$_4$ reach the same final state, as shown in Equations 1 and 2, MeSO$_4$ would be an ideal reference phase. But many sulfates have multiple hydrated states, which makes sample characterization difficult. This problem can be solved by using MeO as the reference state. Most metal oxides are anhydrous, thermodynamically stable, and dissolve quickly in the calorimetric solvent, according to Equation 5:

$$\text{MeO (xl, 298 K)} \rightarrow \text{Me}^{2+} \text{ (soln, 975 K)} + \text{O}^{2-} \text{ (soln, 975 K) (5)}$$
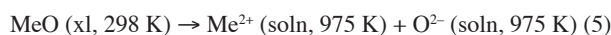
To use MeO as a reference state, the ΔH_{dsol}^0 of SO$_3$ needs to be accounted for in the thermochemical cycle (Table 5). SO$_3$ gas is predicted to dissolve in the melt as a sulfate species:

$$\text{SO}_3 \text{ (gas, 298 K)} + \text{O}^{2-} \text{ (soln, 975 K)} \rightarrow \text{SO}_4^{2-} \text{ (soln, 975 K) (6)}$$
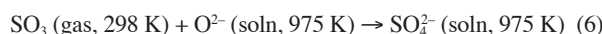
The average value for ΔH_{dsol}^0 of SO$_3$ was determined by Majzlan et al. (2002), using high-temperature oxide melt calorimetry in the same solvent, by dissolving various MeSO$_4$ samples (anhydrite, barite, celestine, and anglesite). This value of ΔH_{dsol}^0, -205.80 ± 3.70 kJ/mol, is used in the calculation of ΔH_f^0 of MeS (Table 5).

The ΔH_f^0 of PbS, calculated using PbSO$_4$ and PbO (litharge) as reference phases, is -99.44 ± 4.00 kJ/mol and -98.12 ± 4.37 kJ/mol respectively. The values are the same within their uncertainties, thus confirming that PbO is a valid reference state when used in combination with SO$_3$ in the thermochemical cycle.

Even though the error in the ΔH_{dsol} is less than 0.2%, as the error propagates through the thermochemical cycle, it becomes as large as 1.8–3% for ΔH_f^0. Nevertheless, these errors (Table

TABLE 6. Thermochemical cycle for the calculation of enthalpy of formation of metal sulfide (MeS, Me = Pb, Zn, Cd) from drop solution data using MeO as the reference state

	Reaction number and reaction	Enthalpy change
(1)	MeS (xl, 298 K) + 2O$_2$ (gas, 975 K) → Me^{2+} (soln, 975 K) + SO$_4^{2-}$ (soln, 975 K)	$\Delta H_1 = \Delta H_{ds}$(MeS)*
(2)	O$_2$ (gas, 298 K) → O$_2$ (gas, 975 K)	$\Delta H_2 = \Delta H_{hc}$(O$_2$)†
(3)	MeO (xl, 298 K) → Me^{2+} (soln, 975 K) + O^{2-} (soln, 975 K)	$\Delta H_3 = \Delta H_{ds}$(MeO)§
(4)	Me (xl, 298 K) + 1/2 O$_2$ (gas, 298 K) → MeO (xl, 298 K)	$\Delta H_4 = \Delta H_f^0$(MeO)†
(5)	SO$_3$ (gas, 298 K) + O^{2-} (soln, 975 K) → SO$_4^{2-}$ (soln, 975 K)	$\Delta H_5 = \Delta H_{ds}^0$(SO$_3$)‡
(6)	S (xl, 298 K) + 3/2 O$_2$ (gas, 298 K) → SO$_3$ (gas, 298 K)	$\Delta H_6 = \Delta H_f^0$(SO$_3$)†
(7)	Me (xl, 298 K) + S (xl, 298 K) → MeS (xl, 298 K)	$\Delta H_7 = \Delta H_f^0$(MeS)

Notes: $\Delta H_7 = \Delta H_f^0$(MeS) $= -\Delta H_1 - 2\Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6$.
* Experimental data in Table 3.
† Taken or calculated from Robie and Hemingway (1995).
‡ Majzlan et al. (2002).
§ Experimental data from Table 4.

Table 7. Enthalpy of formation of MeS (Me = Pb, Zn, Cd)

Sample	ΔH_f^0 (kJ/mol) (This work)	ΔH_f^0 (kJ/mol) (Robie and Hemingway 1995)
PbS	−98.12 ± 4.37	−98.3 ± 2.0*
ZnS	−206.53 ± 4.03	−204.1 ± 1.5†
CdS (greenockite)	−148.79 ± 4.13	−149.6 ± 1.3‡
CdS (hawleyite)	−147.65 ± 4.28	−

* Stubbles and Birchenall (1959).
† Schaefer and Gokcen (1982).
‡ Adami and King (1964).

6) are less than ±5 kJ/mol and the values of ΔH_f^0 are consistent with available data. Although this uncertainty is relatively large, the method should be applicable to a large number of different sulfide systems that cannot be studied by other calorimetric methods, e.g., transition metal sulfides. For sulfides with a less exothermic enthalpy of oxidation, the uncertainty is expected to be smaller.

The ΔH_f^0 of hawleyite is less negative than the ΔH_f^0 of greenockite by about 1 kJ/mol. Although this value is zero within experimental error, the drop solution data suggests that hawleyite is slightly metastable to greenockite. This difference is too small to explain the preference of greenockite or hawleyite in ore formations. A review of geological data (Augustithis 1982; Cerny 1957; Enikeev 1977; Genkin 1984) available for naturally occurring CdS also does not offer any thermodynamic insight into the presence of one polymorph of CdS over the other. The natural occurrence of hawleyite or greenockite may depend on other factors like the composition of the ore, the impurities, and the formation environment. The control may be kinetic rather than thermodynamic. What we have shown is that there is little, if any, thermodynamic driving force for the transformation. This is analogous to the case of ZnS, where the difference in enthalpy between wurtzite and sphalerite is only 0.30 ± 2.12 kJ/mol (wurtzite being unstable) (Robie and Hemingway 1995).

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