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Thermodynamic assessment of the Mo-S system and its application in thermal decomposition of MoS_2

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ABSTRACT

The Mo-S system is crucial to extractive metallurgy, tribology, and various possible applications in design and fabrication of novel two-dimensional (2D) materials. First-principles calculations were utilized to compute the enthalpies of formation of molybdenum sulfides at 0 K and the heat capacity of Mo_2S_3 up to 960 K. A critical evaluation of the thermodynamic properties, phase equilibria, and phase diagram information in the literature was carried out to facilitate the thermodynamic optimization of the Mo-S system. The obtained thermodynamic description of the Mo-S system can satisfactorily represent most of the reliable thermodynamic and phase diagram information. Pressure-temperature (*P-T*), pressure-composition (*P-x*), and temperature-composition (*T-x*) diagrams of the Mo-S system were utilized to study the thermal decomposition of MoS_2 for raw Mo production. Reduced pressure and high temperature are thermodynamically favorable conditions for the MoS_2 reduction process.

1. Introduction

The Mo-S system is very attractive due to its importance in extractive metallurgy, tribology, and various possible applications in design and fabrication of novel two-dimensional (2D) materials. MoS_2 (molybdenum disulfide) mineral is the major resource for the extraction of Mo and rare metal Re [1–4] which have important applications in aerospace industry [2,4]. MoS_2 has a lamellar structure which is formed by van der Waals force bonding of many stacked layers [5]. The high strength covalent bonds within the layer make it easy to slide rather than be destroyed. MoS_2 is therefore well-known as solid lubricant with a lubricity comparable to graphite [5–8] and as nanoscale additive of lubricating oil [9]. Besides, MoS_2 as a 2D material exhibits excellent optoelectronic [8,10–14], piezoelectronic [15], and valleytronic [10] properties. In addition, the possibility of tuning structural phase within MoS_2 lattice offers wider space and more flexibility for manipulating properties [16–19]. Thus, there are great potential applications of MoS_2 in solar energy harvesting and conversion [8,10,13], photon detectors [10,13], photon catalysis [13], transistor [8,11,20,21], light emitter [14,20], modular [20], etc.

Another layer crystal structured [22] molybdenum sulfide phase Mo_2S_3 (molybdenum sesquisulfide) was utilized to synthesis nanorods [23]. The nanostructured Mo_2S_3 is of interest in the applications as catalysis, electrodes, and intercalation hosts. In addition, the metastable Mo_3S_4 (molybdenum tetrasulfide) phase has potential applications as superconductor [24].

During the synthesis or fabrication of nanostructured molybdenum sulfide material or 2-D layered device, the methods like solid/gas reaction [23], chemical vapor deposition (CVD) [12,20], low pressure CVD [20], plasma enhanced CVD [20], etc., may be utilized. Thermodynamic and kinetic information of the Mo-S system is of fundamental importance in controlling the rate of chemical reactions involved, and the thickness and homogeneity of the layer of 2D material [25] as well as in understanding the gas/solid interaction during the fabrication process. Furthermore, the traditional Mo production process has unsolved problems such as long production cycle, complex purification procedure, low yield, and pollution due to H_2S and SO_2 [26]. The eco-friendly, low energy consumption, and high resource utilization Mo extraction processes such as vacuum thermal decomposition of MoS_2 are under further development [26,27]. Pressure and temperature are

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Table 1
Summary of thermodynamic studies in the Mo-S system.

Type of experimental data	Experimental details	Ref.
Heat capacity of 2H_MoS_2	56–292 K, adiabatic calorimetry	[45]
	20–100 K, low temperature adiabatic calorimetry	[46]
	6–212 K, adiabatic calorimetry	[47]
	5–350 K, adiabatic calorimetry	[48]
	525–1205 K, calorimetry	[49]
	773–1973 K, vacuum calorimetry	[50,51]
Heat content of 2H_MoS_2	525–1205 K, calorimetry	[49]
	773–1973 K, vacuum calorimetry	[50,51]
Entropy of 2H_MoS_2	298.15 K, 63.18 ± 0.84 J/mol-K, adiabatic calorimetry	[45]
	298.15 K, 65.04 J/mol-K, emf	[55]
	298.15 K, 62.43 ± 0.08 J/mol-K, adiabatic calorimetry	[54]
	298.15 K, 62.59 J/mol-K	[49]
	298.15 K, 62.59 ± 0.08 J/mol-K, adiabatic calorimetry	[48]
	298.15 K, 62.59 J/mol-K	[50,51]
Entropy	298.15 K, Mo_2S_3 (124.26 J/mol-K), MoS (52.72 J/mol-K), 2H_MoS_2 (71.54 J/mol-K), estimation	[56]
Entropy of α_Mo_2S_3	298.15 K, 115.53 J/mol-K, first-principles	This work
Formation enthalpy of 2H_MoS_2	298.15 K, −78003.71 J/g-atoms, emf at 15, 25, and 35 °C, Pt|H_2|KCl(0.01N)||KCl(0.01N)|H_2S|MoS_2	[55]
	298.15 K, −91266.67 ± 500 J/g-atoms, fluorine bomb calorimetry	[57,58]
	298.15 K, −92702.10 ± 697 J/g-atoms, estimation	[61,62]
	298.15 K, −91066.67 J/g-atoms, estimation	[60]
	298.15 K, −81966.67 ± 1667 J/g-atoms, evaluation	[59]
	0 K, −94529.85 J/g-atoms, first-principles; 298.15 K, −91699.42 J/g-atoms, CALPHAD	This work
Formation enthalpy of 2H_Mo_3	0 K, 137038.24 J/g-atoms, first-principles; 298.15 K, 24666.67 J/g-atoms, CALPHAD	This work
Formation enthalpy of 2H_S_3	0 K, 71112.47 J/g-atoms, first-principles; 298.15 K, 18333.33 J/g-atoms, CALPHAD	This work
Formation enthalpy of 2H_Mo_2S	0 K, 28421.14 J/g-atoms, first-principles; 298.15 K, 134699.42 J/g-atoms, CALPHAD	This work
Formation enthalpy of 3R_MoS_2	0 K, −94500.35 J/g-atoms, first-principles	This work
Formation enthalpy of α_Mo_2S_3	298.15 K, −81169.60 ± 2510 J/g-atoms, estimation	[57]
	0 K, −76317.17 J/g-atoms, first-principles; 298.15 K, −79423.68 J/g-atoms, CALPHAD [a]; 298.15 K, −76614.904 J/g-atoms, CALPHAD [b]	This work
Formation enthalpy of Mo_3S_4	0 K, −75601.84 J/g-atoms, first-principles	This work
Formation Gibbs energy of 2H_MoS_2	1073–1373 K, MoS_2-H_2-H_2S-Mo equilibrium	[69,70]
	1073–1373 K, MoS_2-H_2-H_2S-Mo equilibrium	[68]
	1119–1473 K, molybdenum sulphides-H_2-H_2S-Mo equilibrium, a radiochemical method, chemical analysis, X-ray diffraction analysis	[63]
	1738–1523 K, dissociation pressure measurements	[71]
	1123–1373 K, emf, MoO_2 (c), MoS_2 (c), Pt, P(SO_2) = 1 atm, PO_2|O^{2-}, $Zr_{0.85}Ca_{0.15}O_{1.85}$| P($O_2$) = 1 atm, Pt	[66]
	1033–1273 K, MoS_2-H_2S-H_2-Mo equilibrium	[65]
	867–1209 K, emf, Pt, MoS_2, MoO_2, SO_2 = 1 atm|ZrO_2|O_2 = 0.0112 atm, Pt	[61,62]
	1223 K, S (gas)-MoS_2-Mo equilibrium, MoS_2-H_2S-H_2-Mo equilibrium	[67]
	569.4–1276.8 K, MoS_2-H_2S-H_2-Mo equilibrium	[60]
	1100–1370 K, emf, Pt|Fe, $Fe_{0.95}O$|0.85ZrO_2-0.15Y_2O_3|$MoS_{1.457}$, MoS_2, MoO_2|Pt	[59]
Formation Gibbs energy of Mo_2S_3	1300–1425 K, Knudsen effusion method	[72]
	1119–1473 K, molybdenum sulphides-H_2-H_2S-Mo equilibrium, a radiochemical method, chemical analysis, X-ray diffraction analysis	[63]
	1365–1610 K, MoS_2-H_2S-H_2-Mo equilibrium	[56]
	1033–1273 K, MoS_2-H_2S-H_2-Mo equilibrium	[65]
	1223 K, S (gas)-MoS_2-Mo equilibrium, MoS_2-H_2S-H_2-Mo equilibrium	[67]
	1100–1373 K, evaluation	[59]

[a] heat capacity predicted from MoS_2 and Mo.
[b] heat capacity calculated from first-principles calculations.

among the determinant factors of the thermal decomposition process [26–29]. Thus, knowledge of phase equilibria in the Mo-S system under varying temperature, composition, and pressure is the prerequisite for the design and control of various related material fabrication and metallurgical processes.

The present study attempts to build the Mo-S phase diagram with the aid of CALPHAD (CALculation of PHAse Diagram) [30–35] approach, get a set of Gibbs energy functions that can represent the equilibrium state of the Mo-S system, and study the thermal decomposition process of MoS_2. A comprehensive literature review and critical evaluation is carried out for the thermodynamic, phase equilibria, and phase diagram measurements related to the Mo-S system. First-principles calculations are utilized to solve the controversial issues related to the phase stability and supplement the evaluation and optimization work. A set of thermodynamic parameters for the Mo-S system is obtained to describe the thermodynamic properties and phase diagram information. The thermal decomposition process of MoS_2 is studied based on the calculated pressure-temperature (*P-T*), pressure-composition (*P-x*), and temperature-composition (*T-x*) diagrams.

2. First–principles calculations

The highly efficient first-principles calculations method as implemented in the Vienna Ab initio Simulation Package (VASP) [36,37] was utilized to determine the ground-state enthalpies of formation and the heat capacity of the Mo-S intermetallics. The frozen-core Projector Augmented Wave method (PAW) [38,39] was adopted to depict the electron-ion interactions, and the exchange-correlation was described by the Generalized Gradient Approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) [40]. Plane wave cut-off energy was set to be 400 eV to make sure the total energy differences were less than 1 meV/atom for all the compounds. The integration of the Brillouin zone (BZ) was