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Measurements of the formation enthalpy of Mo_6S_{8-y} clusters[1]

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Abstract

The combustion enthalpies of Mo_6S_{8-y} clusters ($7.8 \leq 8 - y \leq 8.0$) were measured at 773 K in flowing oxygen using a Calvet-type twin calorimeter. There was a maximum value at the sulfur composition $8 - y = 7.9$. Evaporated gas ratios of SO_3/SO_2 for each sulfur composition were calculated using the results of quantitative chemical analysis of SO_2. From the data of the combustion enthalpy combined with the values of the formation enthalpies of MoO_3, SO_2 and SO_3, the formation enthalpy of Mo_6S_{8-y} clusters was determined. The standard formation enthalpies of Mo_6S_{8-y} clusters were also determined by measuring the heat content for clusters with various compositions in the temperature range from 298 to 773 K.

Keywords: Calorimeter; Combustion; Formation enthalpy; Mo_6S_{8-y} cluster

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1. Introduction

From both the basic and applied standpoints, ternary molybdenum sulfides of formula $M_xMo_6S_{8-y}$ (M is metal), the so-called Chevrel phase sulfides, have been studied intensively since the discovery of their unique crystal structure [1], high superconducting transition temperature (for $PbMo_6S_8$, $T_c \approx 15$ K [2]), high critical field (for $PbMo_6S_8$, $H_{c2} \approx 60$ T [3]), and their potential application as cathode material for high-energy-density lithium secondary batteries [4–6].

Atoms of the third component M enter into sites produced by the arrangement of Mo_6S_{8-y} clusters and stabilize the whole crystal structure [7]. In fact, the crystal structure can be considered as containing two types of building blocks, one being an

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[1] Dedicated to Takeo Ozawa on the Occasion of his 65th Birthday.

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Mo_6S_8 unit which consists of a distorted Mo_6 octahedron with faces bridged by S atoms, and the other being a "cloud" of M atoms which separates the adjacent Mo_6S_8 units. If M is a "small" atom, e.g. Fe, Co, Ni or Cu, it occupies statistically a network of 12 (6 inner and 6 outer) small tetrahedron-shaped interstices which result from a compression of the large hole at the origin along the hexagonal c-axis. If M is a "big" atom, e.g. Ag, In, Sn or Pb, it occupies a large hole at the origin of the unit cell surrounded by 8 S atoms which belong to 8 different Mo_6S_8 units [8].

The thermal oxidation of copper Chevrel phase $Cu_xMo_6S_{8-y}$ has been reported by Takei et al. [9] and Taniguchi et al. [10]; and the oxidation mechanisms of Mo_6S_{8-y} clusters have been investigated by Pisarska and Wakihara [11]. However, there are not enough literature data concerning the thermal oxidation and thermodynamics of Chevrel phase compounds $M_xMo_6S_{8-y}$, expecially the Mo_6S_{8-y} cluster building blocks.

In this paper, we have synthesized Mo_6S_{8-y} clusters with various nonstoichiometric compositions for sulfur and measured the combustion enthalpies of these clusters. By analyzing the gas after the combustion, the standard formation enthalpies of Mo_6S_{8-y} have been obtained.

2. Experimental

2.1. Sample preparation

The Mo_6S_{8-y} samples were prepared by leaching out copper from the Chevrel phase sulfides $Cu_xMo_6S_{8-y}$ which were synthesized preliminarily using a single-phase region

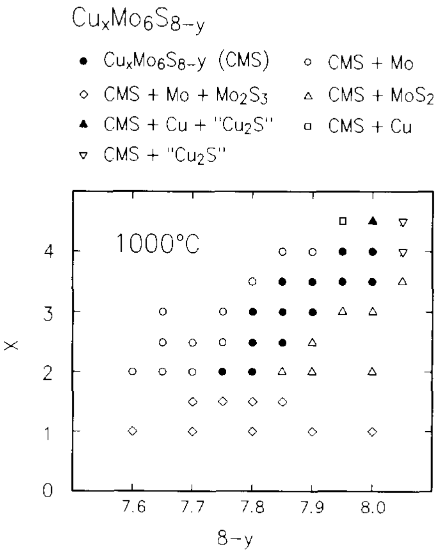

Fig. 1. Single-phase region of $Cu_xMo_6S_{8-y}$ at 1273 K.

of $Cu_xMo_6S_{8-y}$ as described by our group [12] (Fig. 1). A brief description is as follows. $Cu_xMo_6S_{8-y}$ phases were prepared by mixing Cu powder (Soekawa Chemicals, purity 99.9%), MoS_2 powder (Soekawa Chemicals, purity 99.9%) and metallic Mo powder (Soekawa Chemicals, purity 99.99%) in appropriate ratios. The MoS_2 powder was dried in vacuum at 393 K for 12 h before use in order to remove gaseous impurities [13], and the composition $MoS_{2.00}$ was determined by oxidation to MoO_3 [14]. First, mixtures for obtaining $Cu_xMo_6S_{8-y}$ were heated in vacuum sealed ampoules at 673 K for 24 h, and then at 1273 K for 48 h, followed by quenching. After grinding the samples, they were again sealed under vacuum and heated at 1273 K for 48 h.

The Mo_6S_{8-y} clusters were prepared using a leaching technique in reaction with I_2 in acetonitrile medium. The same molar ratio of I_2 to Cu (Cu/I = 2) was used [15]. The leaching reactions in the liquid were run over 24 h at room temperature under atmospheric pressure using a magnetic stirrer. The Mo_6S_{8-y} samples were filtered off, washed with acetonitrile, and dried in vacuo at 383 K for 15 h.

The absence of copper in the sample was confirmed by ICP analysis. Neither impurity phases nor unreacted ingredients were found in the X-ray powder diffraction pattern (Cu K_α) of the prepared samples. The hexagonal and/or rhombohedral lattice parameters evaluated for both $Cu_xMo_6S_{8-y}$ and Mo_6S_{8-y} are listed in Table 1.

2.2. Apparatus and procedure

The Calvet-type twin calorimeter designed for operation at temperatures up to 923 K [16,17] was used to determine both the combustion and the heat content of the Mo_6S_{8-y} cluster sulfides. In this calorimeter, the thermal effect is detected as an electrical output with a 158 + 158 junction Pt-platinel thermopile. The output of the thermopile is amplified by means of a microvolt amplifier and integrated to obtain the enthalpy change using an on-line computer.

Table 1
The hexagonal and rhombohedral lattice parameters for $Cu_xMo_6S_{8-y}$ and Mo_6S_{8-y}

	Hexagonal		Rhombohedral	
	a_H/Å	c_H/Å	a_R/Å	α_R/deg
$Cu_2Mo_6S_{7.8}$	9.64	10.21	6.52	95.25
$Mo_6S_{7.8}$	9.20	10.88	6.43	91.33
$Cu_3Mo_6S_{7.85}$	9.74	10.23	6.58	95.55
$Mo_6S_{7.85}$	9.20	10.90	6.43	91.28
$Cu_3Mo_6S_{7.90}$	9.74	10.25	6.58	95.50
$Mo_6S_{7.9}$	9.20	10.90	6.43	91.28
$Cu_{3.5}Mo_6S_{7.95}$	9.75	10.24	6.59	95.59
$Mo_6S_{7.95}$	9.21	10.90	6.44	91.28
$Cu_4Mo_6S_{8.00}$	9.75	10.25	6.59	95.52
$Mo_6S_{8.00}$	9.20	10.88	6.43	91.31

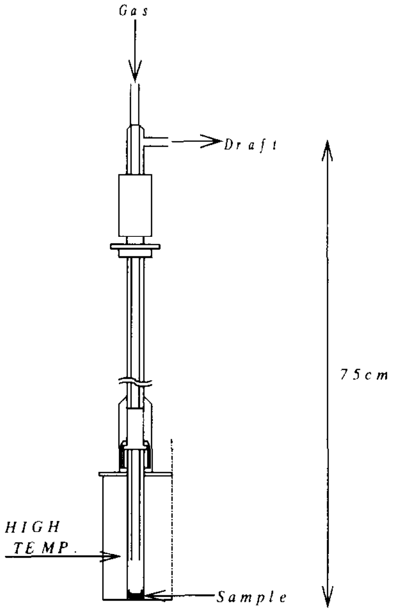

Fig. 2. Schematic figure of the sample side of the calorimeter.

The sample, accurately weighed to 20 ± 0.01 mg, was put in a quartz crucible, and set in the sample holder, and argon gas was passed into the sample holder for about 2 h to replace the atmosphere in the holder. Purification of the argon gas was carried out by the following two methods; (a) water was removed by passing over P_2O_5, and (b) oxygen impurity was removed by an oxygen pump using a calcia-stabilized zirconia oxide ion conductor [18,19], operated at 1073 K. The sample holder was set at the correct position in the apparatus as shown in Fig. 2. After attaining thermal equilibrium, dried oxygen gas was introduced to initiate the combustion reaction. The sample was completely oxidized to MoO_3 after the experimental run. The general scheme for this experiment is shown in Fig. 3.

The TG–DTA experiment showed that the oxidation of Mo_6S_{8-y} starts at about 630 K in air [11]. In order to determine the optimum experimental conditions, the combustion experiments were performed from 630 to 873 K. It was found that the detected combustion peak was broad in shape and that the unreacted sulfide was also detected by X-ray powder diffraction at temperatures below 723 K. For investigating the stability of Mo_6S_{8-y} in an argon atmosphere while attaining thermal equilibrium, the samples were heated at 773 and 873 K for 2 h and their X-ray powder diffraction patterns recorded. Peaks belonging to MoS_2 phase were found in the sample heated at 873 K as shown in Fig. 4. The optimum experimental conditions determined for the present study are summarized in Table 2.

Calibration of the calorimeter was performed by the following two methods.

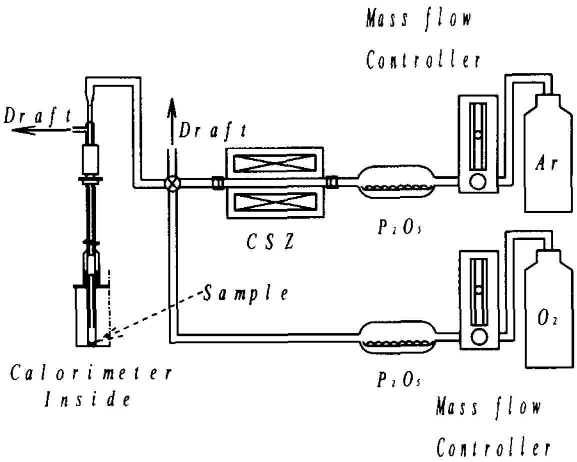

Fig. 3. Schematic diagram of the gas flow system.

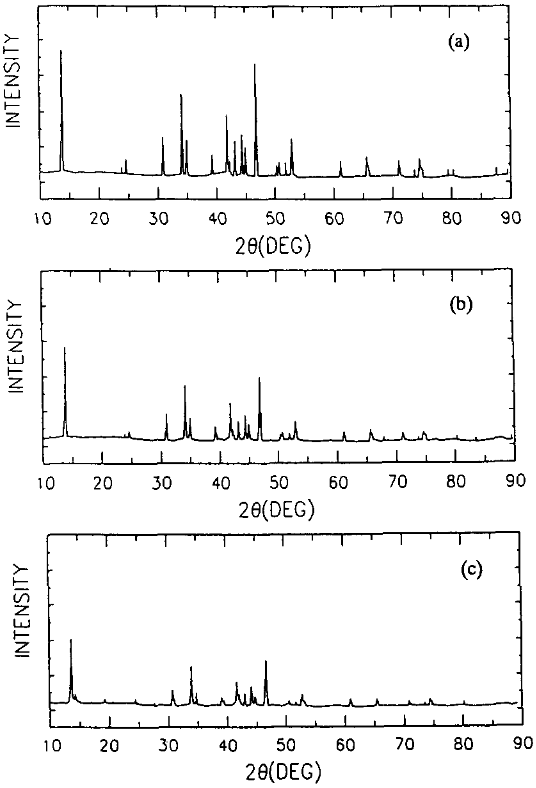

Fig. 4. Typical X-ray diffraction patterns of (a) $Mo_6S_{7.9}$, (b) $Mo_6S_{7.9}$ heated at 773 K, and (c) $Mo_6S_{7.9}$ heated at 873 K for 2 h in Ar gas.

Table 2
Conditions for the experiment on Mo_6S_{8-y} cluster compounds

Temperature of calorimeter	773 K
Particle size of samples	< 74 μm
Amount of samples	20 mg
Flow rate of reaction gas	2 ml s^{-1}
Time of measurement	50–60 min

(1) For calibration of the combustion enthalpy, the following reaction for the oxidation of Nb metal to stoichiometric Nb_2O_5 phase was adopted. The combustion enthalpy of the reaction

$$2Nb + \frac{5}{2}O_2 \rightarrow Nb_2O_5$$

was determined as $\Delta H = -1888.29\,kJ\,mol^{-1}$ at 773 K by using a database [20].
(2) For obtaining the heat content of Mo_6S_{8-y} clusters, the enthalpy increment, $H_T - H_{298K}$, of quartz [21] at $T = 773\,K$ was also measured. The heat pick-up correction for quartz between room temperature and 773 K was negligibly small, so it was unnecessary to correct our enthalpy increment data.

2.3. Gas analysis

To determine the formation enthalpy, the ratio of SO_3/SO_2 in the outlet gas after combustion was analyzed as follows.

The combustion experiment was performed as described before, and in this case oxygen was passed through for 1.5 h for complete removal of the reacted gases. The outlet gas was passed through the terminal U-tube cooled with ice water to condense SO_3, and then through a column packed with NaOH granules to take up SO_2. The amount of SO_2 was calculated by the weight change of the column. However, the amount of SO_3 deposited in the U-tube was so low that the amount of SO_3 had to be calculated from the amount of SO_2 obtained and the sulfur composition in the sample.

3. Results and discussion

3.1. The combustion enthalpy of Mo_6S_{8-y}

Mo_6S_{8-y} clusters cannot be synthesized directly from the elements. Therefore, measurement of the formation enthalpy is impossible by direct reaction of metallic Mo and sulfur in the calorimeter. We measured the combustion enthalpy of Mo_6S_{8-y} and calculated the formation enthalpy using thermodynamic data of the element Mo and S.

The combustion reaction is

$$\mathrm{Mo_6S_{8-y}(s)} + \frac{18 + (3-\alpha)(8-y)}{2}\mathrm{O_2} \rightarrow$$

$$6\,\mathrm{MoO_3(s)} + \alpha(8-y)\mathrm{SO_2(g)} + (1-\alpha)(8-y)\,\mathrm{SO_3(g)} \tag{1}$$

$$\alpha = \frac{\mathrm{SO_2(mol)}}{\mathrm{SO_2(mol)} + \mathrm{SO_3(mol)}} \tag{2}$$

The enthalpies of combustion ΔH_c of Mo_6S_{8-y} obtained in the present study are summarized with their precision in Table 3 and plotted graphically in Fig. 5. The deviation is shown as error bars at each point in Fig. 5.

The enthalpy is defined as

$$\Delta H = \Delta U + p\Delta V \tag{3}$$

Since the sulfides are solid in the present study, ΔV, in Eq. (3) is almost zero. The internal energy ΔU is approximately equal to the cohesion energy U_0 and, accordingly, the relation $\Delta H = U_0$ is obtained. The energy levels of the oxidation of sulfides can be estimated from a diagram of energy states as shown in Fig. 6. A transition-metal sulphide MS_x separates into a metal atom M(g) and a sulfur atom S(g), which are able to react with oxygen. The term U_0 for Mo_6S_{8-y} corresponds to the reaction

$$\mathrm{Mo_6S_{8-y}} \rightarrow 6\,\mathrm{Mo(g)} + (8-y)\mathrm{S(g)} \tag{4}$$

Table 3
Enthalpies of combustion of Mo_6S_{8-y}

$8-y$ in Mo_6S_{8-y}	w/mg	$-\Delta H_c$/kJ mol^{-1}	$-\Delta H_c$/kJ mol^{-1} mean ± SD
7.80	20.724	5484	
	19.329	5531	
	21.181	5644	
	19.464	5632	5573 ± 65
7.85	21.499	6049	
	20.879	6098	
	20.149	6195	
	20.750	6051	6098 ± 48
7.90	19.273	6389	
	19.832	6258	
	20.452	6318	
	20.960	6195	6290 ± 64
7.95	19.743	6189	
	19.711	6128	
	20.447	6145	
	19.920	6196	6165 ± 28
7.80	19.972	5922	
	20.161	5804	
	20.548	5860	
	20.545	5928	5879 ± 47

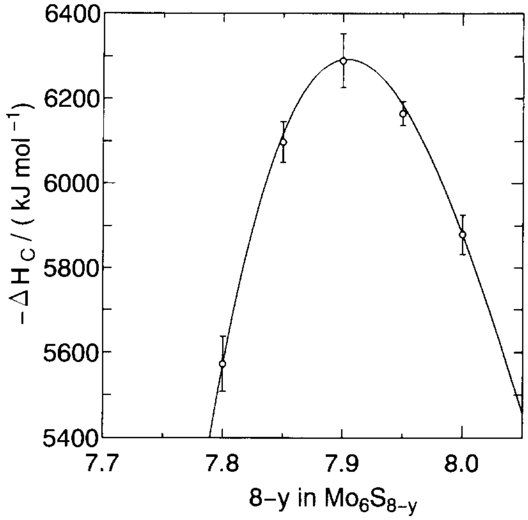

Fig. 5. Combustion enthalpy of Mo_6S_{8-y} clusters with the sulfur composition $(8-y)$.

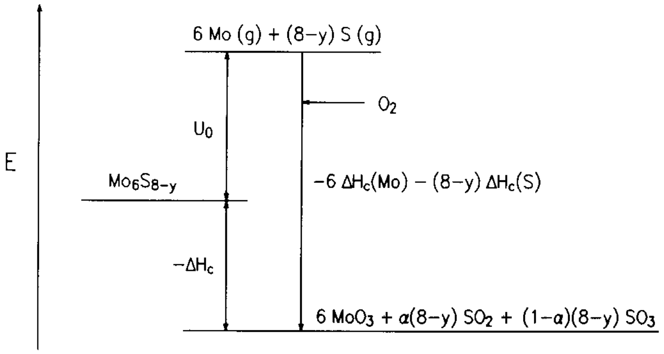

Fig. 6. Schematic diagram of the energy states.

Then, 6Mo(g) and $(8-y)$S(g) react with oxygen and form MoO_3. Therefore, $-\Delta H_c$ can be expressed as

$$-\Delta H_c = U_0 - \{6\Delta H_c^M + (8-y)\Delta H_c^S\} \tag{5}$$

where $-\Delta H_c^M$ and $-\Delta H_c^S$ are enthalpies of oxidation of the molybdenum and sulphur atoms, respectively. These schematic energy levels are shown in Fig. 6. If U_0 is large (sulphide is stable), the observed $-\Delta H_c$ will be small. If the enthalpy of combustion is proportional to the sulfur content $(8-y)$, the cohesion energy U_0 is governed only by the nonstoichiometry of sulfur. The resulting curve, however, has a maximum at $8-y=7.9$. So the stability of Mo_6S_{8-y} clusters would depend on other factors, e.g.,

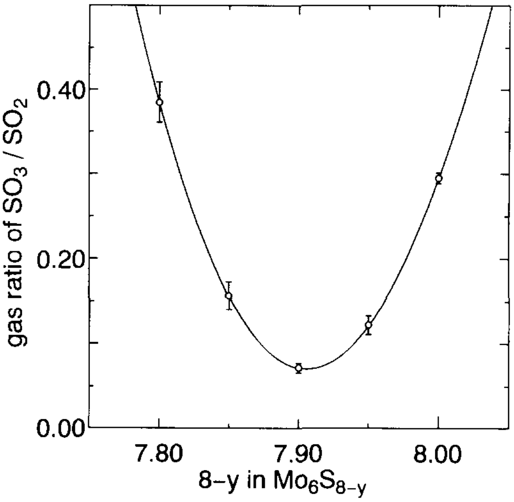

Fig. 7. Evaluated SO_3/SO_2 ratio for the sulfur composition $(8 - y)$.

defects in Mo_6S_{8-y}, interaction between atoms, etc. Structural analysis using neutron diffraction is now being planned.

The SO_3/SO_2 ratio in the outlet gas after the combustion of nonstoichiometric Mo_6S_{8-y} is shown in Fig. 7. In the equilibrium state, the ratio SO_3/SO_2 at 773 K was calculated from the thermodynamic data to be 57. So the content of SO_3 is much larger than that of SO_2. However, the reaction

$$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3 \qquad (3)$$

is only completed in the presence of catalyst (Pt or V_2O_5), and in the present experiment the oxygen gas was passed continuously, so the obtained ratio of SO_3/SO_2 was much smaller than the equilibrium value.

3.2. *The formation enthalpy of Mo_6S_{8-y}*

The formation reaction of Mo_6S_{8-y} is defined as

$$6Mo(s) + \frac{(8-y)}{2}S_2(g) \rightarrow Mo_6S_{8-y}(s) \qquad (7)$$

We first measured the combustion enthalpy of Mo_6S_{8-y}

$$Mo_6S_{8-y}(s) + \frac{18 + (3-\alpha)(8-y)}{2}O_2 = 6\,MoO_3(s) +$$

$$\alpha(8-y)SO_2(g) + (1-\alpha)(8-y)SO_3(g) - \Delta H_c(\text{kJ mol}^{-1}) \qquad (8)$$

$$\alpha = \frac{SO_2(\text{mol})}{SO_2(\text{mol}) + SO_3(\text{mol})}$$

Table 4
Thermal data for Mo_6S_{8-y} clusters

$8-y$ in Mo_6S_{8-y}	Combustion enthalpy $-\Delta H_c$/kJ mol^{-1} mean	Formation enthalpy $-\Delta H_f$/kJ mol^{-1} mean	Heat content $\Delta H(Mo_6S_{8-y})$/kJ mol^{-1}	Standard enthalpy of formation $-\Delta H_f$/kJ mol^{-1}
7.80	5573	1813	32.969	1254
7.85	6098	1197	32.162	635
7.90	6290	969	33.741	404
7.95	6165	1146	33.826	578
8.00	5879	1544	33.702	973

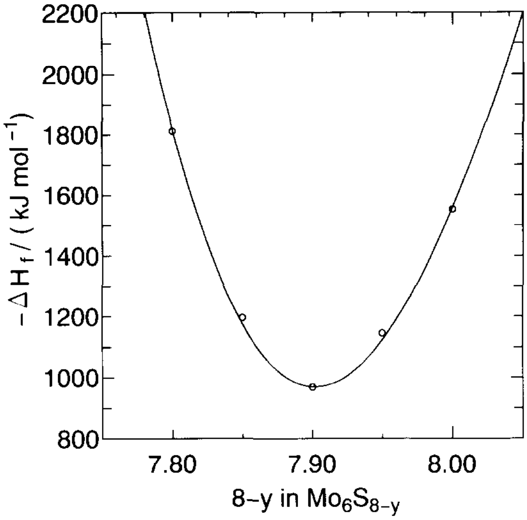

Fig. 8. Formation enthalpy of Mo_6S_{8-y} clusters at 773 K with the sulfur composition $(8-y)$.

and the formation enthalpy is calculated using the thermodynamic data of MoO_3, SO_2, and SO_3, defined as follows

$$Mo(s) + \frac{3}{2}O_2(g) = MoO_3(s) - \Delta H_f(MoO_3)(kJ\,mol^{-1}) \tag{9}$$

$$\frac{1}{2}S_2(g) + O_2(g) = SO_2 - \Delta H_f(SO_2)(kJ\,mol^{-1}) \tag{10}$$

$$\frac{1}{2}S_2(g) + \frac{3}{2}O_2(g) = SO_3 - \Delta H_f(SO_3)(kJ\,mol^{-1}) \tag{11}$$

And then the formation enthalpy of Mo_6S_{8-y} is obtained from

$$-\Delta H_f = \Delta H_c - 6\,\Delta H_f(MoO_3) - \alpha(8-y)\Delta H_f(SO_2) - (1-\alpha)(8-y)\Delta H_f(SO_3) \tag{12}$$

The formation enthalpy of MoO_3, SO_2, and SO_3 in Eq. (12) can be cited from the thermodynamic database [20] as −737.802, −352.052, −450.509 kJ mol^{-1}, respectively. Using the ratio of SO_3/SO_2 and these values, we can obtain the formation enthalpy ΔH_f at 773 K. The results are summarized in Table 4 and plotted in Fig. 8.

3.3. *The standard formation enthalpy of Mo_6S_{8-y}*

The heat content of Mo_6S_{8-y} was measured in order to calculate the standard formation enthalpy. Each sample (about 100 mg) was sealed under vacuum in a quartz ampoule (2 mm diameter and 15 mm long). This ampoule was dropped into the calorimeter (773 K) at room temperature (298 K). The heat content of quartz was

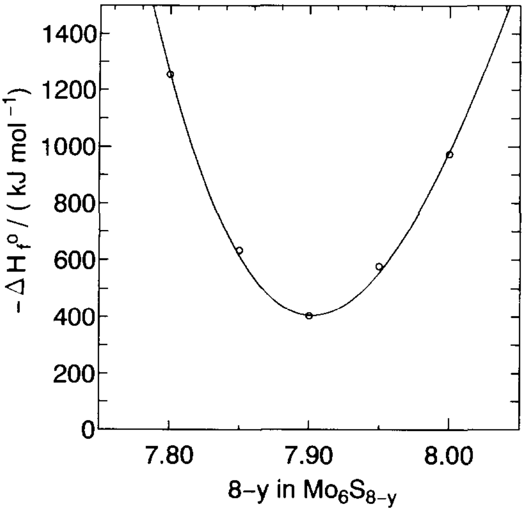

Fig. 9. Standard enthalpy of formation for Mo_6S_{8-y} clusters with the sulfur composition $(8-y)$.

subtracted using the literature data [21]. The result is also given in Table 4. The heat content was almost constant, and the sulfur content $8-y$ is thought to have no effect on the heat content. The average value of the heat content $\Delta H(Mo_6S_{8-y})$ was obtained as 33.280 kJ mol^{-1}.

The heat contents of Mo(s), S(s), S(l), and S(g) were calculated from the literature values of C_p [20]. The obtained standard formation enthalpies of Mo_6S_{8-y} are listed in Table 4 and are plotted in Fig. 9. It may be noted that there is a minimum at the sulfur composition $(8-y)=7.9$. This suggests that $Mo_6S_{7.9}$ is the most unstable of the Mo_6S_{8-y} clusters from the schematic energy diagram shown in Fig. 6. The non-stoichiometric end composition of $Mo_6S_{7.8}$ is thought to be the most stable. The large difference in formation enthalpy within a small difference in sulfur composition is responsible for the small single-phase region of Chevrel phase sulfides, $M_xMo_6S_{8-y}$; with M is Cu, $7.75 \leq 8-y \leq 8.0$ [12]; M is Pb, $7.5 \leq 8-y \leq 7.8$ [22]; M is Fe, $7.67 \leq 8-y \leq 8.12$ [23]; M is Sn, $6.75 \leq 8-y \leq 7.5$ [24]; M is Ni, $7.4 \leq 8-y \leq 7.7$ [25]; and M is Co, $7.65 < 8-y < 7.75$ [26].

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