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THERMOCHEMICAL AND THERMODYNAMICAL PROPERTIES OF SOME COMPOUNDS IN THE SYSTEM Ga–Sb–S

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Abstract

With help of literature data and some empirical methods the main thermochemical and thermodynamical properties were estimated for condensed GaSb, GaS, Ga_2S, Ga_2S_3, Ga_4S_5, Sb_2S_3 and for gaseous Ga_2S and SbS phases.

Keywords: Ga–Sb–S system, thermoanalytical properties, thermodynamic properties

Introduction

In the system Ga–Sb–S some semiconductor phases can be formed. For thermodynamical analysis of opportunities of their production and behaviour it is necessary to know for compounds of this system the thermochemical and thermodynamical properties (TTP). In present paper on a base of critical review of literature data and by using various empirical dependencies [1–12] the values $\Delta_f H^\circ_{298}$, S°_{298}, $H^\circ_{298} - H^\circ_0$ T and $\Delta H_{\text{melting (decomposition)}}$, $C_p(T)$ for condensed GaSb, GaS, Ga_2S, Ga_2S_3, Ga_4S_5, Sb_2S_3 and gaseous Ga_2S, and SbS has been found and taken as reliable.

The definition and calculation of TTP

Standard enthalpy of formation, $\Delta_f H^\circ_{298}$

The average arithmetic values are taken as reliable data for condensed phases GaSb [1–5], GaS [1–5, 8], Sb_2S_3 [3–5], Ga_2S_3 [2–5, 8] and for gaseous SbS [3, 8] and Ga_2S [3, 5]. Values of $\Delta_f H^\circ_{298}$ for condensed Ga_4S_5 and Ga_2S are taken from work [8].

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Standard entropy of formation S°_{298}

The average arithmetic values are taken as reliable date for condensed GaSb [1–5], GaS [1–5, 8] Sb_2S_3 [3–5, 8], Ga_2S_3 [3–5] and for gaseous SbS [3, 8] and Ga_2S [3, 5].

The values S°_{298} for Ga_4S_5 and Ga_2S were calculated by following way. The standard entropy of Ga_2S_3(cd) and GaS(cd) recalculated on one g-atom of compounds (cal/(K·g-atom)) were used as the basic values. Than we calculated the linear dependencies of those values from a number of atoms in molecule of compounds (m) and from a molecular mass of compounds (M):

$$S^\circ_{298} = 3.1251 + 0.7185 \cdot m \quad \text{cal}\cdot\text{K}^{-1}\cdot\text{g–atom}^{-1} \tag{1}$$

$$S^\circ_{298} = 2.9232 + 0.0161 \cdot M \quad \text{cal}\cdot\text{K}^{-1}\cdot\text{g–atom}^{-1} \tag{2}$$

At the supposition, that Eqs (1) and (2) can be realised for Ga_2S_3 and GaS, we calculated for them the standard entropy of formation correspondingly to Eqs (1) and (2): for Ga_4S_5 is equal 86.32 and 89.975 cal/(K·mol) and for Ga_2S is equal 15.842 and 17.05 cal/(K·mol). The average arithmetic values, equal 88.148 (Ga_4S_5) and 15.842 cal/(K·mol) (Ga_2S), are taken as reliable date of S°_{298}.

Enthalpy increment, $H^\circ_{298}-H^\circ_o$

We used for condensed GaSb and GaS the data according to Ref. [1]. For other condensed phases the enthalpy increments are calculated by using the dependence [6]:

$$H^\circ_{298}-H^\circ_o = 204 \cdot S^\circ_{298} \cdot \exp\left(-\frac{S^\circ_{298}}{23.5}\right) \quad \text{cal}\cdot\text{K}^{-1}\cdot\text{g–atom}^{-1} \tag{3}$$

were values of S°_{298} are recalculated to one g-atom of compounds.

The verification of Eq. (3) for phases GaSb and GaS give us mere disagreements with the experimental date [1] equal correspondingly –0.3 and +6.0%.

For SbS(g) the enthalpy increment taken from [11]; for Ga_2S(g) the value has been calculated with help of empirical equation [10]:

$$H^\circ_{298}-H^\circ_o = 1410 + 420 \cdot m \quad \text{cal}\cdot\text{mol}^{-1} \tag{4}$$

were m is the number of atoms in molecule of compounds.

The comparison of enthalpy increments for SbS(g), calculated by Eq. (4), with the date [11] shows the difference of 4.5%.

Temperature of melting (decomposition)

The average arithmetic values are taken as reliable data for GaSb [1–3, 5], GaS [1–5], Sb_2S_3 [3–5, 8] and Ga_2S_3 [2, 3, 5, 8]. For phase Ga_4S_5 and Ga_2S the date from the work [8] are taken as reliable.

Heat of melting (decomposition)

The average arithmetic values are taken as reliable data for GaSb [1–3] and for Sb_2S_3 [3, 8]. For the compounds $\Delta H_{\text{melting (decomposition)}}$ are calculated with help of the method, described in the work [9].

Temperature dependence of heat capacity of crystalline compounds

The average arithmetic values of coefficients a, b and c in equation

$$C_p = a+b\cdot10^{-3}\cdot T-c\cdot10^{5}\cdot T^{-2} \quad \text{cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \tag{5}$$

are taken as reliable date for GaSb [1–5], Sb_2S_3 [3–5, 8] and Ga_2S_3 [3, 5, 8].

For phase GaS we used the dependencies $C_p(T)$, given in [1–3]. For Ga_4S_5 the estimation of $C_p(T)$ was made with help of Neumann–Kopp method, described in [10]

$$C_p(T) = C_p(T)[Ga_2S_3] + 2C_p(T)[GaS] \tag{6}$$

For the determining of $C_p(T)[Ga_2S]$ the value of $C_p(298)$ was first estimated with help of the method [4]:

$$C_p(298) = 2\Delta C_p(Ga) + \Delta C_p(S) \tag{7}$$

and than $C_p(T)$ calculated with help of Ref. [12].

Heat capacity of compounds in liquid state

This values are calculated for all compounds according to the equation [7]:

$$C_p(l) = C_p(Cr)_{T_m} + \Delta S_m/4 \quad \text{cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \tag{8}$$

where T_m and ΔS_m are temperature of melting (decomposition) and changing of entropy at the melting (decomposition), respectively. For gaseous compounds SbS and Ga_2S the $C_p(T)$ are taken from [3].

Table 1 Thermodynamical and thermochemical properties of some compounds in the Ga–Sb–S system

No.	Compound	ΔH°_{298} /	S°_{298} /	$H^{\circ}_{298} - H^{\circ}_{o}$ /	T_{melt} / (decomp.)	ΔH_{melt} / (decomp.)	$C_p = a + b\cdot10^{-3}\cdot T - c\cdot10^{5}\cdot T^{-2}$ / cal·K^{-1}·mol^{-1}			$C_p(l)$ /
		kcal·mol^{-1}	cal·K^{-1}·mol^{-1}	cal·mol^{-1}	K	cal·mol^{-1}	*a*	*b*	*c*	cal·K^{-1}·mol^{-1}
1	GaSb(c)	–10.1	18.36	2542	985	15400	10.870	2.968	–	17.702
2	GaS(c)	–50.0	13.70	1968	1233	6493	9.880	3.75	–	15.820
3	Ga_2S(c)	–58.2	16.45	2657	1233(d)	11926	16.500	6.642	2.334	27.118
4	Ga_2S_3(c)	–122.68	33.60	5148	1371	17350	23.303	9.643	–	39.700
5	Ga_4S_5(c)	–214.60	88.15	11854	1213	26594	43.063	17.143	–	69.340
6	Ga_2S(g)	5.0	69.3	2670	–	–	13.385	0.275	2.210	–
7	Sb_2S_3(c)	–41.8	43.5	6126	821	15320	24.273	13.836	–	40.300
8	SbS(g)	44.43	59.7	2440	–	–	8.49	0.313	–	–

Table 2 Coefficients of Gibbs energy equation for some compounds in the Ga–Sb–S system

No.	Compound	$\Phi = \varphi_1 + \varphi_2 \cdot \ln x + \varphi_3 \cdot x^{-2} + \varphi_4 \cdot x^{-1} + \varphi_5 \cdot x + \varphi_6 \cdot x^2 + \varphi_7 \cdot x^3$ $(x = T \cdot 10^{-4})$ / $cal \cdot K^{-1} \cdot mol^{-1}$							Temperature range / K
		φ_1	φ_2	φ_3	φ_4	φ_5	φ_6	φ_7	
1	GaSb(c)	10.706	2.5981	0	0.01982	3.55	0	0	298–985
		12.3269	3.29745	0	0.05426	0	0	0	985–6000
2	GaS(c)	8.942	2.3615	0	0.02732	4.485	0	0	298–1233
		12.858	3.7813	0	–0.021	0	0	0	1233–6000
3	Ga_2S(c)	13.056	3.9437	–0.00028	0.07979	7.941	0	0	298–1233
		20.117	6.4816	0	–0.0176	0	0	0	1233–6000
4	Ga_2S_3(c)	21.341	5.5696	0	0.05318	11.527	0	0	298–1371
		31.394	9.4887	0	–0.04808	0	0	0	1371–6000
5	Ga_4S_5(c)	46.075	10.4358	0	0.04587	20.49	0	0	298–1213
		63.094	16.5729	0	–0.1468	0	0	0	1213–6000
6	Ga_2S(g)	24.554	3.1992	$-2.7 \cdot 10^{-5}$	0.03359	0.329	0	0	298–6000
7	Sb_2S_3(c)	23.992	5.8015	0	0.04116	16.54	0	0	298–821
		36.912	9.6321	0	–0.122	0	0	0	821–6000
8	SbS(g)	19.346	2.0293	0	0.00249	0.374	0	0	298–6000

Results

The recommended TTP of compounds are given in Table 1. With help of subprogram of the package ASTRA [13] there were calculated the coefficients of polynoms (Table 2) in order to approximate the temperature dependencies of reduced Gibbs energy

$$\Phi^*=\varphi_1+\varphi_2\cdot\ln x+\varphi_3\cdot x^{-2}+\varphi_4\cdot x^{-1}+\varphi_5\cdot x+\varphi_6\cdot x^2+\varphi_7\cdot x^3 \quad \text{cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \qquad (9)$$

were $x = T\cdot 10^{-4}$.

* * *

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Zusammenfassung — Mittels Literaturangaben und einiger empirischer Methoden wurden die wichtigsten thermochemischen und thermodynamischen Eigenschaften für kondensierte Phasen von GaSb, GaS, Ga_2S, Ga_2S_3, Ga_4S_5, Sb_2S_3 und für gasförmige Phasen von Ga_2S und SbS geschätzt.