Thermochimica Acta, 37 (1980) 343—345

Note

COMMENTS ON THERMOCHEMICAL DATA AND FUSION TEMPERATURE FOR PURE SODIUM SULFIDE

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(Received 28 September 1979)

Sodium sulfide, Na_2S, is a compound of considerable industrial interest, particularly in the pulp and paper industry. In the recovery plant of a modern large chemical pulp mill (kraft or sodium bisulfite pulping), several tons of Na_2S/h are processed. Thus, due to its practical significance, as well as for obvious fundamental reasons, it is desirable that accurate physical and thermochemical data are available for this apparently simple alkali metal chalcogenide. The crystal structure (anti-fluorite) of solid Na_2S is known [1].

The major practical problem in accurate studies of this compound is the preparation of highly pure Na_2S. Sodium sulfide is usually prepared and available as $Na_2S \cdot 9\,H_2O$ (perhaps $NaHS \cdot NaOH \cdot 8\,H_2O$) or $Na_2S \cdot 5\,H_2O$. In the course of removal of this water, sulfide is very easily oxidized to thiosulfate or polysulfide; also, the rather stable compound $Na_2S \cdot NaOH$ [2,3] is very easily formed. However, a procedure for preparing >99.5% Na_2S exists [2] and has been used by us [4a,b] in a slightly modified form.

The use of impure sodium sulfide is evidently the cause of very incorrect figures for the melting point, T_m, of Na_2S. In fact, the data for this compound, listed in common standard reference books [5—9], are all ultimately based on dated erroneous results [10a,b] from early studies where highly impure Na_2S was used. In fact, the case of the thermochemical data for Na_2S, particularly its melting point, seems to be an almost classical example of the perpetuation of erroneous scientific information. The correct value for the melting point of Na_2S is 1170 ± 10°C [15—19] (Table 1), whereas refs. 5—10 quote 914—980°C.

The most reliable compilation of thermochemical data for common Na—S compounds is that by Rosén [11a,b]. We have accepted his data, with minor corrections, of heat content, $H^0_T - H^0_{298}$, due to a recent determination of the heat of fusion, ΔH_m [12]. The standard entropy, $S^0_{298} = 90.3$ J K^{-1} $mole^{-1}$ = 21.6 cal K^{-1} $mole^{-1}$ for $Na_2S(s)$ estimated by Voronin and Landiya [13a,b], is consistent with Rosén's log K_f values [11a,b] with ±0.2 log K_f units.

The anti-fluorite structure of $Na_2S(s)$ should show up as a secondary transition with an anomalous enthalpy increase at temperatures somewhat below the melting point; cf. K_2S enthalpy data [14]. However, no similar enthalpy data measurements for Na_2S are available, and no explicit allowance for secondary transition has been made in the heat content data of Table 1.

TABLE 1

Recommended thermochemical data for Na_2S and calculated log K_f values

$Na_2S(s)$: $\Delta H_{f298} = -386.6$ kJ mole^{-1} [11a]; $S^0_{298} = 90.3$ J K^{-1} mole^{-1} [13a,b]; T_m = 1170 ± 10°C = 1443 ± 10 K [15—19]; ΔH_m = 7.2 kcal mole^{-1} = 30.1 kJ mole^{-1} [12].

T (K)	$H_T - H^0_{298}$ (kJ mole^{-1})		log $K_{f(T)}$	
	$Na_2S(s)$	$Na_2S(l)$	$Na_2S(s)$	$Na_2S(l)$
1000	61.46	93.7	16.5	15.5
1100	70.64	102.9	14.3	13.8
1200	79.83	112.1	12.4	12.2
1300	89.16	121.8	10.4	10.2
1400	98.53	129.5	8.4	8.3

PHASE DIAGRAMS

Because of the difficulty of preparing highly pure Na_2S, there are few reasonably accurate studies on systems with Na_2S as a component. Those available are the phase diagrams of the systems Na_2S—Na_2SO_4 [15—17], Na_2S—Na_2CO_3 [18,19], Na_2S—S [2], Na_2S—NaOH [3,20] and very recently Na_2S--NaCl, and Na_2S—NaCl—Na_2CO_3 [4a,b,21]. In the systems involving Na_2CO_3 and NaCl there is evidence of mutual solid solubility to a limited extent [19]. A study of the system Na_2S—Na_2SO_4—Na_2CO_3 is in progress [4b]. In the Na_2S—S system there are, of course, stable polysulfides, viz. Na_2S_2, Na_2S_4 and Na_2S_5 [2]. In the system Na_2S—NaOH [3] there are two stable intermediate phases, $Na_2S \cdot NaOH$ and $Na_2S \cdot 2\,NaOH$. As hinted above, these compounds, not least the former, may cause complications when one tries to prepare pure anhydrous Na_2S from the commonly available starting material $Na_2S \cdot 9\,H_2O$, and hence complicates this preparation.

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