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THERMAL DECOMPOSITION OF HYDRATED SODIUM SULPHIDE

R. C. KERBY AND M. R. HUGHSON

EXTRACTION METALLURGY DIVISION

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SODIUM SULPHIDE

by

R.C. Kerby* and M.R. Hughson**

ABSTRACT

The thermal decomposition of $Na_2S \cdot 9H_2O$ to Na_2S resulted in the formation of several intermediate hydrates. The stabilities of $Na_2S \cdot H_2O$, $Na_2S \cdot 2H_2O$ and $Na_2S \cdot 3H_2O$ were determined as a function of water vapour partial pressure and temperature. The heats and free energies associated with the dehydration reactions were estimated from this data. The monohydrate $Na_2S \cdot H_2O$ was shown to exist over a wide range of temperatures and water vapour partial pressures.

*Research Scientist and **Physical Scientist, Extraction Metallurgy Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada. K1A 0G1.

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LA DÉCOMPOSITION THERMIQUE DE SULFURE DE SODIUM HYDRATÉ

par

R. C. Kerby* et M. R. Hughson**

RÉSUMÉ

Les auteurs ont trouvé que la décomposition thermique de $Na_2S \cdot 9H_2O$ à Na_2S a mené à la formation de plusieurs hydrates intermédiaires. Ils ont déterminé les stabilités de $Na_2S \cdot H_2O$, $Na_2S \cdot 2H_2O$ et $Na_2S \cdot 3H_2O$ en fonction de la pression partielle de vapeur d'eau et de la température. Ils ont pu estimer les chaleurs et les énergies libres associées aux réactions de déshydratation de ces données. Les auteurs ont montré que le monohydrate $Na_2S \cdot H_2O$ existait à travers de très grandes intervalles de température et de pressions partielles de vapeur d'eau.

*Chercheur scientifique et **Scientifique en sciences physiques, Division de la métallurgie extractive, Direction des mines, ministère de l'Énergie, des Mines et des Ressources, Ottawa, Canada. K1A 0G1

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INTRODUCTION

In two previous reports[1,2], a process was outlined for the recovery of sodium sulphite solution from waste sulphite pulping liquors. The reports also contained a detailed study of the kinetics of the solid state carbonation of sodium sulphide smelts. The study indicated that the state of hydration of the sodium sulphide smelts had a substantial effect on their rate of carbonation. In particular, sodium sulphide monohydrate was found to undergo carbonation much faster than either the higher hydrates or anhydrous sodium sulphide. It was necessary, therefore, to characterize the conditions of temperature and water vapour partial pressure under which the various hydrates and the anhydrous form of sodium sulphide were formed.

The literature contains but little information on the thermal stability of hydrated sodium sulphide. Five hydrates ($Na_2S \cdot 9H_2O$, $Na_2S \cdot 6H_2O$, $Na_2S \cdot 5\frac{1}{2}H_2O$, $Na_2S \cdot 5H_2O$, $Na_2S \cdot H_2O$) have been reported, the four higher hydrates decomposing at less than 200°C and the monohydrate decomposing at 700°C under hydrogen[3,4,5]. Crystal structures have been determined for $Na_2S \cdot 9H_2O$[6], $Na_2S \cdot 5H_2O$[7], and Na_2S[8].

EXPERIMENTAL

Materials

Reagent-grade hydrated sodium sulphide ($Na_2S \cdot 9H_2O$)
supplied by three companies and special-grade (99.9% pure)
anhydrous sodium sulphide supplied by two companies were used
in the experiments. Excess water was removed from the
hydrated sodium sulphides by pressing crushed crystals
between sheets of filter paper. $Na_2S \cdot 5H_2O$ was prepared from
$Na_2S \cdot 9H_2O$ by dehydration under a partial vacuum of one Torr
at room temperature for six hours. $Na_2S \cdot 3H_2O$ was prepared
from $Na_2S \cdot 5H_2O$ by dehydration under a partial vacuum of one
Torr at 50°C for thirty minutes. $Na_2S \cdot H_2O$ was prepared from
$Na_2S \cdot 5H_2O$ by dehydration under a vacuum of 10^{-2} Torr at
150°C for six hours. The hydrates and anhydrous sodium
sulphide were handled under dry nitrogen conditions at all
times. The material was ground to minus 100 mesh for all
experiments. The nitrogen and hydrogen used were high-
purity cylinder grades further purified by passing over hot
copper strips to remove oxygen and by passing through
Ascarite to remove carbon dioxide.

Apparatus and Method

The dehydration of $Na_2S \cdot 9H_2O$ as a function of
temperature was determined by several techniques, including

differential thermal analysis (DTA), effluent gas analysis
(EGA) using a mass spectrometer, thermogravimetric analysis
(TGA), high-temperature X-ray diffraction analysis, and
decomposition pressure measurements.

The DTA experiments were done in a Fisher DTA
controlled atmosphere system using minus 100-mesh samples
and heating rates of $1.0°C$ min^{-1}. Flushing gases of either
90 vol % nitrogen and 10 vol % hydrogen or nitrogen were
passed through the samples at flows of 50 cc min^{-1}. The
effluent gas was analysed using a MS-10 mass spectrometer
connected to the effluent gas line. The TGA experiments
were done using a Cahn electrobalance system. Powdered
samples contained in gold crucibles were heated at $1.0°C$
min^{-1} in a 50 cc min^{-1} stream of 90% nitrogen and 10%
hydrogen. The weight changes and temperature were recorded
on a strip chart recorder and in a digital print-out system.
The reaction temperature was measured by a thermocouple
located within 1 cm of the sample.

The high-temperature X-ray diffraction analyses
were done with a Rigaku Continuous High-Temperature X-Ray
Diffraction Camera (90-mm-diam). With this camera, a sequence
of eight pictures was taken during an experiment, each
picture being taken at a different sample temperature. During
each experiment, a 50-cc min^{-1} flow of 90% nitrogen and 10%

hydrogen was passed through the camera. The sample specimens were mounted in unsealed, 0.3-mm-ID, quartz capillaries and were heated at the set temperatures for approximately twenty-four hours before an X-ray diffraction exposure was made.

The apparatus used to measure the water vapour pressure resulting from the decomposition of hydrated sodium sulphide with increasing temperature has been described previously[9]. Pressure was measured using a Statham strain-gauge absolute-pressure transducer. The signal from the transducer and the emf from a thermocouple inbedded in the sample, which was contained in an alumina boat, were recorded on an Infotronics Digital Readout System.

RESULTS

Initial experiments indicated that the sodium sulphide hydrates were reactive towards oxygen and carbon dioxide, forming sulphites and carbonates respectively, and were hygroscopic. No noticeable sulphidation or carbonation occurred when the hydrated sodium sulphide samples were heated under an atmosphere of 90% nitrogen and 10% hydrogen or in the presence of purified nitrogen at a partial vacuum of one Torr. The reactivity of the sodium sulphide hydrates and their hygroscopic nature made chemical and X-ray powder

diffraction analysis difficult. The most reproducible X-ray powder diffraction analyses were obtained from the high-temperature X-ray powder diffraction camera because the hydrates could be maintained at the temperature at which they were stable in relation to a H_2/N_2 atmosphere.

The results obtained by thermogravimetric (TGA), differential thermal (DTA), and effluent gas analysis (EGA) for $Na_2S \cdot 9H_2O$ samples heated at $1°C/min$ in a flowing H_2/N_2 atmosphere are shown in Figure 1. Analysis of the effluent gas indicated that the observed endothermic effects were associated with the evolution of water vapour. Only trace amounts of hydrogen sulphide were found in the effluent gas. The probable dehydration reactions which gave rise to the thermal effects are listed in Table 1. The DTA and TGA results indicate that $Na_2S \cdot 8H_2O$ is stable from $70°C$ to $100°C$, $Na_2S \cdot 3H_2O$ is stable from $165°C$ to $175°C$, and $Na_2S \cdot H_2O$ is stable from $220°C$ to $640°C$ under these conditions. High-temperature X-ray powder diffraction analysis indicated that $Na_2S \cdot 5H_2O$ (ASTM pattern 18-1249) was present between $120°$ and $180°C$, whereas anhydrous Na_2S (ASTM pattern 3-0933) was present at temperatures above $800°C$. Two previously unreported spectra were found and are identified as compound "A" (stable from $70°$ to $100°C$) and compound "B" (stable from $250°$ to $700°C$) in Table 2. These stability regions corres-
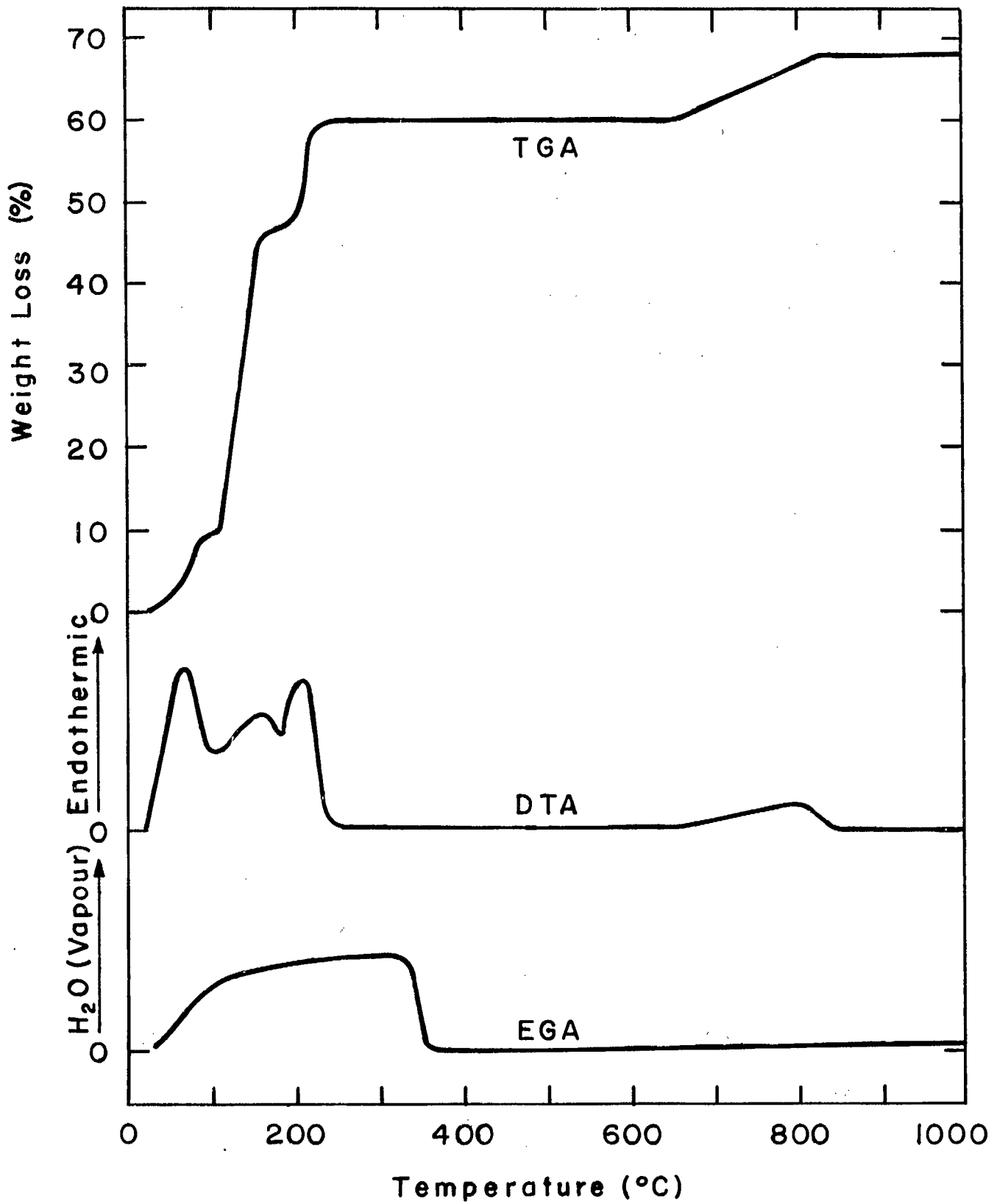
Figure 1: Thermal Dissociation of $Na_2S \cdot 9H_2O$ as Measured by Thermogravimetric (TGA), Differential Thermal (DTA), and Effluent Gas Analysis (EGA).

TABLE 1

THERMAL DISSOCIATION OF HYDRATED SODIUM SULPHIDE

DTA Endothermic Peaks (°C)	TGA Weight Loss (%)	Reaction Products*	Reaction
25 - 70	8	Compound "A"	$Na_2S \cdot 9H_2O \rightarrow Na_2S \cdot 8H_2O$
100 - 165	38	Compound "A" $Na_2S \cdot 5H_2O$	$Na_2S \cdot 8H_2O \rightarrow Na_2S \cdot 5H_2O$ $Na_2S \cdot 5H_2O \rightarrow Na_2S \cdot 3H_2O$
175 - 220	14	Compound "B"	$Na_2S \cdot 3H_2O \rightarrow Na_2S \cdot H_2O$
640 - 830	7.5	Na_2S	$Na_2S \cdot H_2O \rightarrow Na_2S$

*identified by high-temperature X-ray diffraction analysis.

TABLE 2

POWDER DIFFRACTION DATA - COMPOUNDS "A" AND "B"

Pattern No. 157-2*, Compound "A"		Pattern No. 157-4*, Compound "B"	
I**	d Å (meas)	I**	d Å (meas)
10	3.01	5	3.77
2	2.57	5	3.03
3	2.42	4	2.56
9	2.12	4	2.42
1	1.98	10	2.32
2	1.89	5	1.97
3	1.78	4	1.88
< 1	1.44	5	1.75
3	1.41	3	1.64
		1	1.50
		3	1.42
		4	1.33

*Copper radiation.

**estimated

ponded to the formation of $Na_2S \cdot 8H_2O$ (70° to 100°C) and

$Na_2S \cdot H_2O$ (250° to 700°C) in TGA experiments, indicating a

close correlation between the compounds and the spectra.

In the presence of flowing nitrogen held at a

partial vacuum of one Torr, $Na_2S \cdot 9H_2O$ was found by TGA to

dehydrate to $Na_2S \cdot 5H_2O$ at room temperature. The $Na_2S \cdot 5H_2O$

was stable to 40°C, then dehydrated by 100°C to form

$Na_2S \cdot H_2O$. No experiments were done above 300°C. When a

flow of nitrogen saturated with water vapour was passed over

$Na_2S \cdot 9H_2O$ during heating, $Na_2S \cdot 8H_2O$ was stable from 70° to

110°C, $Na_2S \cdot 5H_2O$ from 130°C to 150°C, $Na_2S \cdot 3H_2O$ from 175°C

to 250°C, $Na_2S \cdot 2H_2O$ from 300°C to 320°C, and $Na_2S \cdot H_2O$ from

400°C to 800°C.

The decomposition pressures over $Na_2S \cdot H_2O$, $Na_2S \cdot 2H_2O$

and $Na_2S \cdot 3H_2O$ as a function of temperature are listed in

Table 3. One to three hours were required for equilibrium to

be attained at each temperature. The logarithmic pressure

versus reciprocal temperature relationships for the three

hydrates are shown in Figure 2. The logarithmic relationships

and the corresponding free-energy relationships (calculated

assuming unit activity for the components) for the hydration

reactions are:

TABLE 3

a. <u>Decomposition Pressures Over $Na_2S \cdot H_2O$</u>

<u>Temperature (°C)</u>	<u>Pressure (atm)</u>
375.4	0.00171
387.7	0.00255
399.3	0.00312
411.3	0.00447
425.2	0.00516
501.0	0.0121
578.5	0.0446
596.6	0.0571
616.4	0.0665
650.3	0.0794
724.6	0.1884

b. <u>Decomposition Pressures Over $Na_2S \cdot 2H_2O$</u>

<u>Temperature (°C)</u>	<u>Pressure (atm)</u>
305.0	0.334
323.8	0.391
339.0	0.434
346.9	0.455
356.2	0.486
367.0	0.575
373.2	0.601
386.6	0.650
397.7	0.695
402.2	0.780
417.3	0.861

c. <u>Decomposition Pressures Over $Na_2S \cdot 3H_2O$</u>

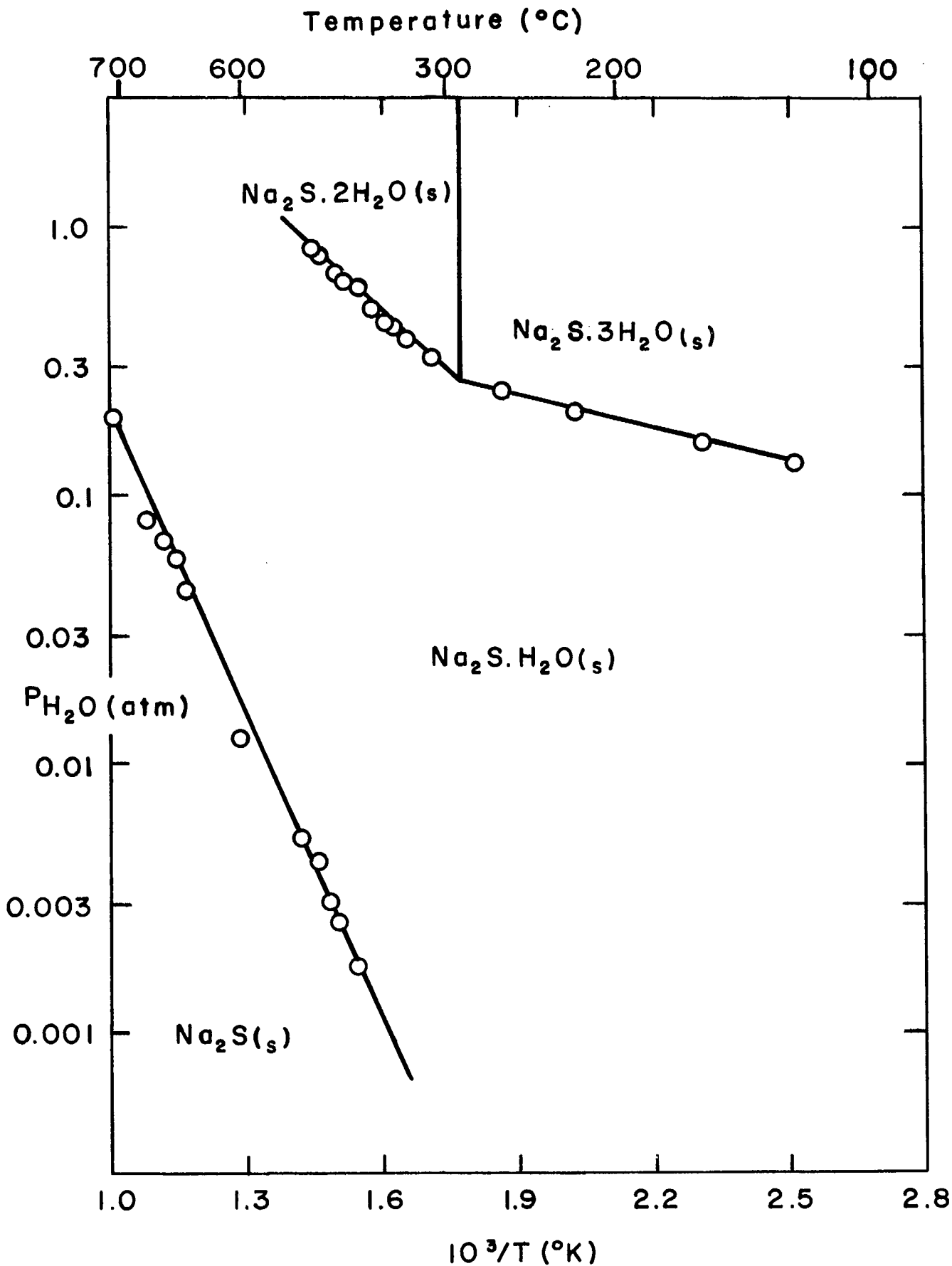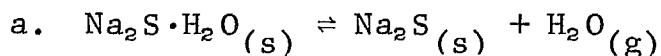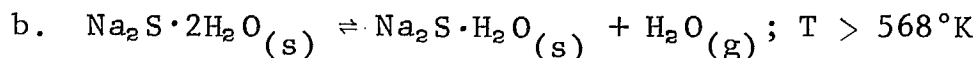| <u>Temperature (°C)</u>	<u>Pressure (atm)</u>
123.7	0.134
157.9	0.167
214.9	0.217
257.0	0.251

Figure 2: Log Pressure Versus Reciprocal Temperature
Relationships for the Dehydration of $Na_2S \cdot H_2O$,
$Na_2S \cdot 2H_2O$ and $Na_2S \cdot 3H_2O$.

a. $Na_2S \cdot H_2O_{(s)} \rightleftharpoons Na_2S_{(s)} + H_2O_{(g)}$

$$\log P_{H_2O} \text{ (atm)} = 2.897 - 3.639 \times 10^3 / T$$

$$\Delta G_T = 16,620 - 13.26T$$

$$\Delta H = 16,620 \text{ cal/mole}$$

b. $Na_2S \cdot 2H_2O_{(s)} \rightleftharpoons Na_2S \cdot H_2O_{(s)} + H_2O_{(g)}; \; T > 568°K$

$$\log P_{H_2O} \text{ (atm)} = 2.062 - 1.479 \times 10^3 / T$$

$$\Delta G_T = 6,760 - 9,449T$$

$$\Delta H = 6,760 \text{ cal/mole}$$

c. $Na_2S \cdot 3H_2O_{(s)} \rightleftharpoons Na_2S \cdot 2H_2O_{(s)} + H_2O_{(g)}; \; T < 568°K$
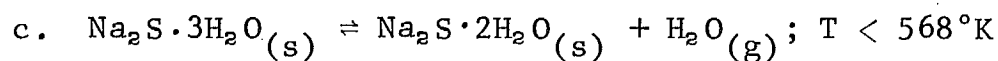
$$\log P_{H_2O} \text{ (atm)} = 0.213 - 0.429 \times 10^3 / T$$
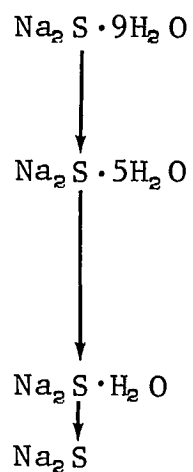
$$\Delta G_T = 1,962 - 0.975T$$

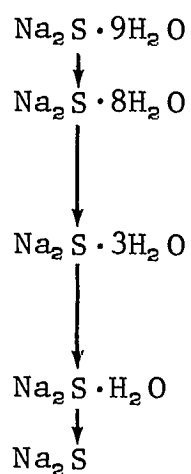$$\Delta H = 1,962 \text{ cal/mole}$$

DISCUSSION

Hydrated sodium sulphide was found to thermally dissociate by three different reaction sequences, depending on the partial pressure of water vapour in contact with the hydrates. These reaction sequences are shown in Table 4. Inert-gas flow rates over the dehydrating samples would substantially affect the dehydration sequence due to variations in partial pressure of water vapour.

TABLE 4

REACTION SEQUENCES FOR THE THERMAL DISSOCIATION
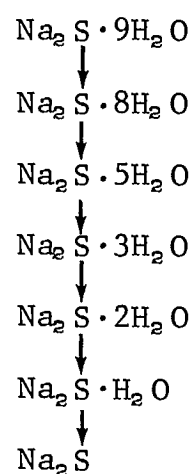
OF HYDRATED SODIUM SULPHIDE

$P_{H_2O} < 0.13$ atm	$P_{H_2O} = 0.13 - 0.27$ atm	$P_{H_2O} > 0.27$ atm
$Na_2S \cdot 9H_2O$	$Na_2S \cdot 9H_2O$	$Na_2S \cdot 9H_2O$
	$Na_2S \cdot 8H_2O$	$Na_2S \cdot 8H_2O$
$Na_2S \cdot 5H_2O$		$Na_2S \cdot 5H_2O$
	$Na_2S \cdot 3H_2O$	$Na_2S \cdot 3H_2O$
		$Na_2S \cdot 2H_2O$
$Na_2S \cdot H_2O$	$Na_2S \cdot H_2O$	$Na_2S \cdot H_2O$
Na_2S	Na_2S	Na_2S

Sodium sulphide monohydrate ($Na_2S \cdot H_2O$) was stable over large ranges of temperatures and water vapour pressures. The remarkable stability shown by this hydrate is probably an indication that the water molecule is intimately associated with, rather than loosely bound to, the sodium sulphide lattice. The X-ray powder diffraction pattern of compound "B", which is considered to represent the monohydrate, provides an indication of this because it is similar to the diffraction pattern found for anhydrous Na_2S, except for the addition of several lines. Thus, the addition of the water molecule does not appear to greatly perturb the Na_2S lattice. The large heat of hydration (16.62 kcal/mole) also indicates that the water molecule is strongly bonded to the sodium sulphide lattice

CONCLUSIONS

A number of intermediate hydrates are formed during the decomposition of $Na_2S \cdot 9H_2O$. The stabilities of these hydrates are governed by both temperatures and water vapour partial pressures. Of the hydrates, $Na_2S \cdot H_2O$ is stable over the largest pressure and temperature range. Heats of hydration were greatest for $Na_2S \cdot H_2O$ (16.62 kcal/mole), followed by $Na_2S \cdot 2H_2O$ (6.76 kcal/mole) and $Na_2S \cdot 3H_2O$ (1.96 kcal/mole).

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ACKNOWLEDGEMENTS

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