

ser
622(a1)
ca12rr



DEPARTMENT OF
ENERGY, MINES AND RESOURCES
MINES BRANCH
OTTAWA

*THERMAL DECOMPOSITION OF HYDRATED
SODIUM SULPHIDE*

R. C. KERBY AND M. R. HUGHSON

EXTRACTION METALLURGY DIVISION

APRIL 1973

© Crown Copyrights reserved

Available by mail from Information Canada, Ottawa,
and at the following Information Canada bookshops:

HALIFAX
1687 Barrington Street

MONTREAL
640 St. Catherine Street West

OTTAWA
171 Slater Street

TORONTO
221 Yonge Street

WINNIPEG
393 Portage Avenue

VANCOUVER
800 Granville Street

or through your bookseller

Price 50 cents Catalogue No. M38-1/262

Price subject to change without notice

Information Canada
Ottawa, 1973

Mines Branch Research Report R 262

THERMAL DECOMPOSITION OF HYDRATED
SODIUM SULPHIDE

by

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

ABSTRACT

The thermal decomposition of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ to Na_2S resulted in the formation of several intermediate hydrates. The stabilities of $\text{Na}_2\text{S}\cdot \text{H}_2\text{O}$, $\text{Na}_2\text{S}\cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{S}\cdot 3\text{H}_2\text{O}$ 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 $\text{Na}_2\text{S}\cdot \text{H}_2\text{O}$ 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.

Direction des mines
Rapport de recherches R 262

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 $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ à Na_2S a mené à la formation de plusieurs hydrates intermédiaires. Ils ont déterminé les stabilités de $\text{Na}_2\text{S} \cdot \text{H}_2\text{O}$, $\text{Na}_2\text{S} \cdot 2\text{H}_2\text{O}$ et $\text{Na}_2\text{S} \cdot 3\text{H}_2\text{O}$ 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 $\text{Na}_2\text{S} \cdot \text{H}_2\text{O}$ 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

CONTENTS

	<u>Page</u>
ABSTRACT.....	i
INTRODUCTION.....	1
EXPERIMENTAL.....	2
Materials.....	2
Apparatus and Method.....	2
RESULTS.....	4
DISCUSSION.....	12
CONCLUSIONS.....	14
ACKNOWLEDGEMENTS.....	15
REFERENCES.....	15

FIGURES

<u>No.</u>	<u>Page</u>
1 Thermal Dissociation of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ as Measured by Thermogravimetric (TGA), Differential Thermal (DTA), and Effluent Gas Analysis (EGA).....	6
2. Log Pressure Versus Reciprocal Temperature Relationships for the Dehydration of $\text{Na}_2\text{S}\cdot \text{H}_2\text{O}$, $\text{Na}_2\text{S}\cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{S}\cdot 3\text{H}_2\text{O}$	11

TABLES

<u>No.</u>		<u>Page</u>
1	Thermal Dissociation of Hydrated Sodium Sulphide.....	7
2.	Powder Diffraction Data - Compounds "A" and "B".....	8
3.	Decomposition Pressures over $\text{Na}_2\text{S}\cdot\text{H}_2\text{O}$, $\text{Na}_2\text{S}\cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{S}\cdot 3\text{H}_2\text{O}$	10
4.	Reaction Sequences for the Thermal Dissociation of Hydrated Sodium Sulphide.....	13

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 ($\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$, $\text{Na}_2\text{S}\cdot 6\text{H}_2\text{O}$, $\text{Na}_2\text{S}\cdot 5\frac{1}{2}\text{H}_2\text{O}$, $\text{Na}_2\text{S}\cdot 5\text{H}_2\text{O}$, $\text{Na}_2\text{S}\cdot \text{H}_2\text{O}$) 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 $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ ⁽⁶⁾, $\text{Na}_2\text{S}\cdot 5\text{H}_2\text{O}$ ⁽⁷⁾, and Na_2S ⁽⁸⁾.

EXPERIMENTAL

Materials

Reagent-grade hydrated sodium sulphide ($\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$) 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. $\text{Na}_2\text{S}\cdot 5\text{H}_2\text{O}$ was prepared from $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ by dehydration under a partial vacuum of one Torr at room temperature for six hours. $\text{Na}_2\text{S}\cdot 3\text{H}_2\text{O}$ was prepared from $\text{Na}_2\text{S}\cdot 5\text{H}_2\text{O}$ by dehydration under a partial vacuum of one Torr at 50°C for thirty minutes. $\text{Na}_2\text{S}\cdot \text{H}_2\text{O}$ was prepared from $\text{Na}_2\text{S}\cdot 5\text{H}_2\text{O}$ 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 $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ 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 $1.0^{\circ}\text{C min}^{-1}$. 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 $1.0^{\circ}\text{C min}^{-1}$ 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 $1^\circ C/min$ 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 $70^\circ C$ to $100^\circ C$, $Na_2S \cdot 3H_2O$ is stable from $165^\circ C$ to $175^\circ C$, and $Na_2S \cdot H_2O$ is stable from $220^\circ C$ to $640^\circ C$ 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 $180^\circ C$, whereas anhydrous Na_2S (ASTM pattern 3-0933) was present at temperatures above $800^\circ C$. Two previously unreported spectra were found and are identified as compound "A" (stable from 70° to $100^\circ C$) and compound "B" (stable from 250° to $700^\circ C$) in Table 2. These stability regions corres-

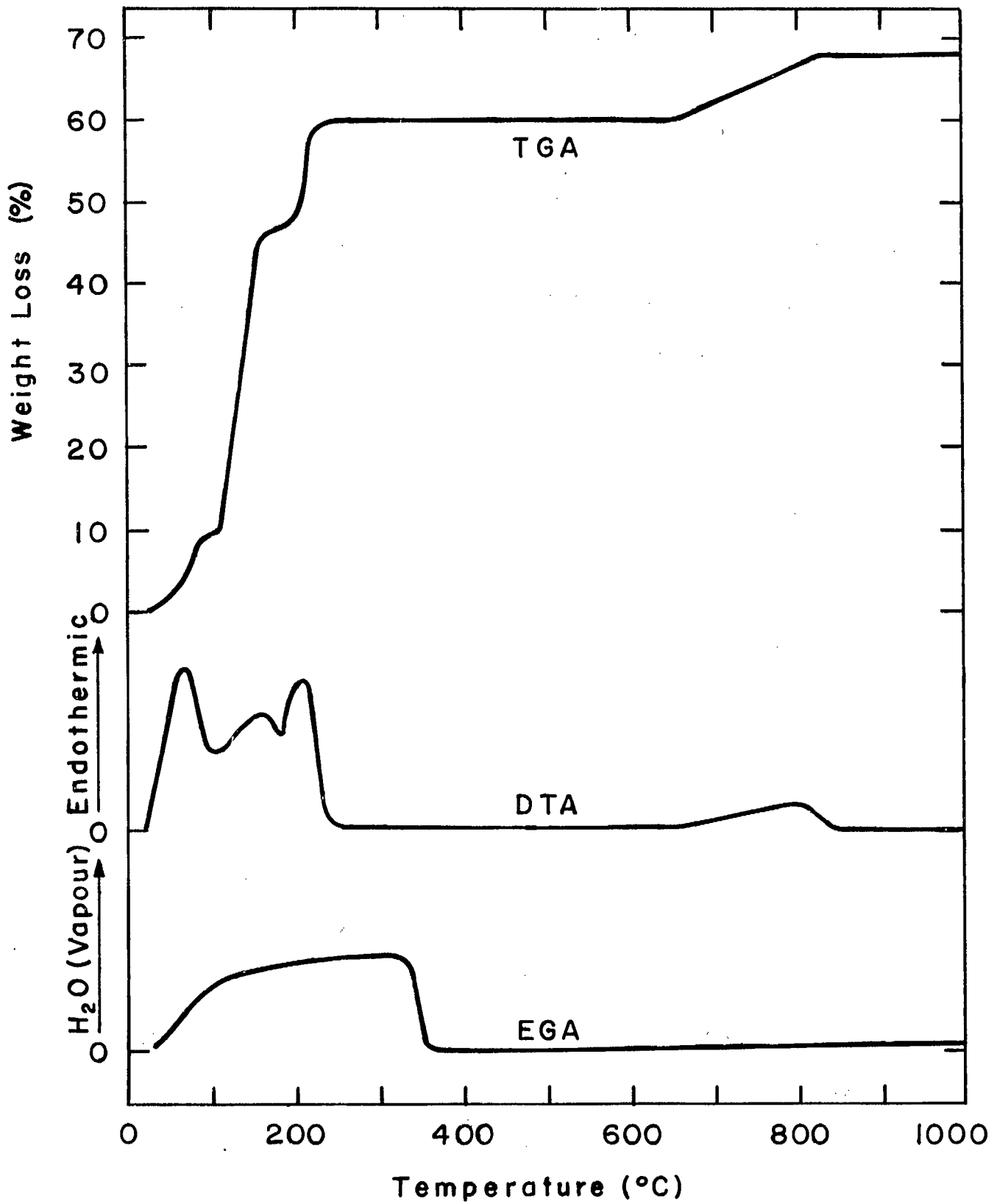


Figure 1: Thermal Dissociation of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ as Measured by Thermogravimetric (TGA), Differential Thermal (DTA), and Effluent Gas Analysis (EGA).

TABLE 1

THERMAL DISSOCIATION OF HYDRATED SODIUM SULPHIDE

DTA Endothermic Peaks (°C)	TGA Weight Loss (%)	Reaction Products*	Reaction
25 - 70	8	Compound "A"	$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O} \rightarrow \text{Na}_2\text{S} \cdot 8\text{H}_2\text{O}$
100 - 165	38	Compound "A" $\text{Na}_2\text{S} \cdot 5\text{H}_2\text{O}$	$\text{Na}_2\text{S} \cdot 8\text{H}_2\text{O} \rightarrow \text{Na}_2\text{S} \cdot 5\text{H}_2\text{O}$ $\text{Na}_2\text{S} \cdot 5\text{H}_2\text{O} \rightarrow \text{Na}_2\text{S} \cdot 3\text{H}_2\text{O}$
175 - 220	14	Compound "B"	$\text{Na}_2\text{S} \cdot 3\text{H}_2\text{O} \rightarrow \text{Na}_2\text{S} \cdot \text{H}_2\text{O}$
640 - 830	7.5	Na_2S	$\text{Na}_2\text{S} \cdot \text{H}_2\text{O} \rightarrow \text{Na}_2\text{S}$

*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 $\text{Na}_2\text{S}\cdot 8\text{H}_2\text{O}$ (70° to 100°C) and $\text{Na}_2\text{S}\cdot \text{H}_2\text{O}$ (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, $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ was found by TGA to dehydrate to $\text{Na}_2\text{S}\cdot 5\text{H}_2\text{O}$ at room temperature. The $\text{Na}_2\text{S}\cdot 5\text{H}_2\text{O}$ was stable to 40°C , then dehydrated by 100°C to form $\text{Na}_2\text{S}\cdot \text{H}_2\text{O}$. No experiments were done above 300°C . When a flow of nitrogen saturated with water vapour was passed over $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ during heating, $\text{Na}_2\text{S}\cdot 8\text{H}_2\text{O}$ was stable from 70° to 110°C , $\text{Na}_2\text{S}\cdot 5\text{H}_2\text{O}$ from 130°C to 150°C , $\text{Na}_2\text{S}\cdot 3\text{H}_2\text{O}$ from 175°C to 250°C , $\text{Na}_2\text{S}\cdot 2\text{H}_2\text{O}$ from 300°C to 320°C , and $\text{Na}_2\text{S}\cdot \text{H}_2\text{O}$ from 400°C to 800°C .

The decomposition pressures over $\text{Na}_2\text{S}\cdot \text{H}_2\text{O}$, $\text{Na}_2\text{S}\cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{S}\cdot 3\text{H}_2\text{O}$ 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. Decomposition Pressures Over $\text{Na}_2\text{S}\cdot\text{H}_2\text{O}$

<u>Temperature ($^{\circ}\text{C}$)</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. Decomposition Pressures Over $\text{Na}_2\text{S}\cdot 2\text{H}_2\text{O}$

<u>Temperature ($^{\circ}\text{C}$)</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. Decomposition Pressures Over $\text{Na}_2\text{S}\cdot 3\text{H}_2\text{O}$

<u>Temperature ($^{\circ}\text{C}$)</u>	<u>Pressure (atm)</u>
123.7	0.134
157.9	0.167
214.9	0.217
257.0	0.251

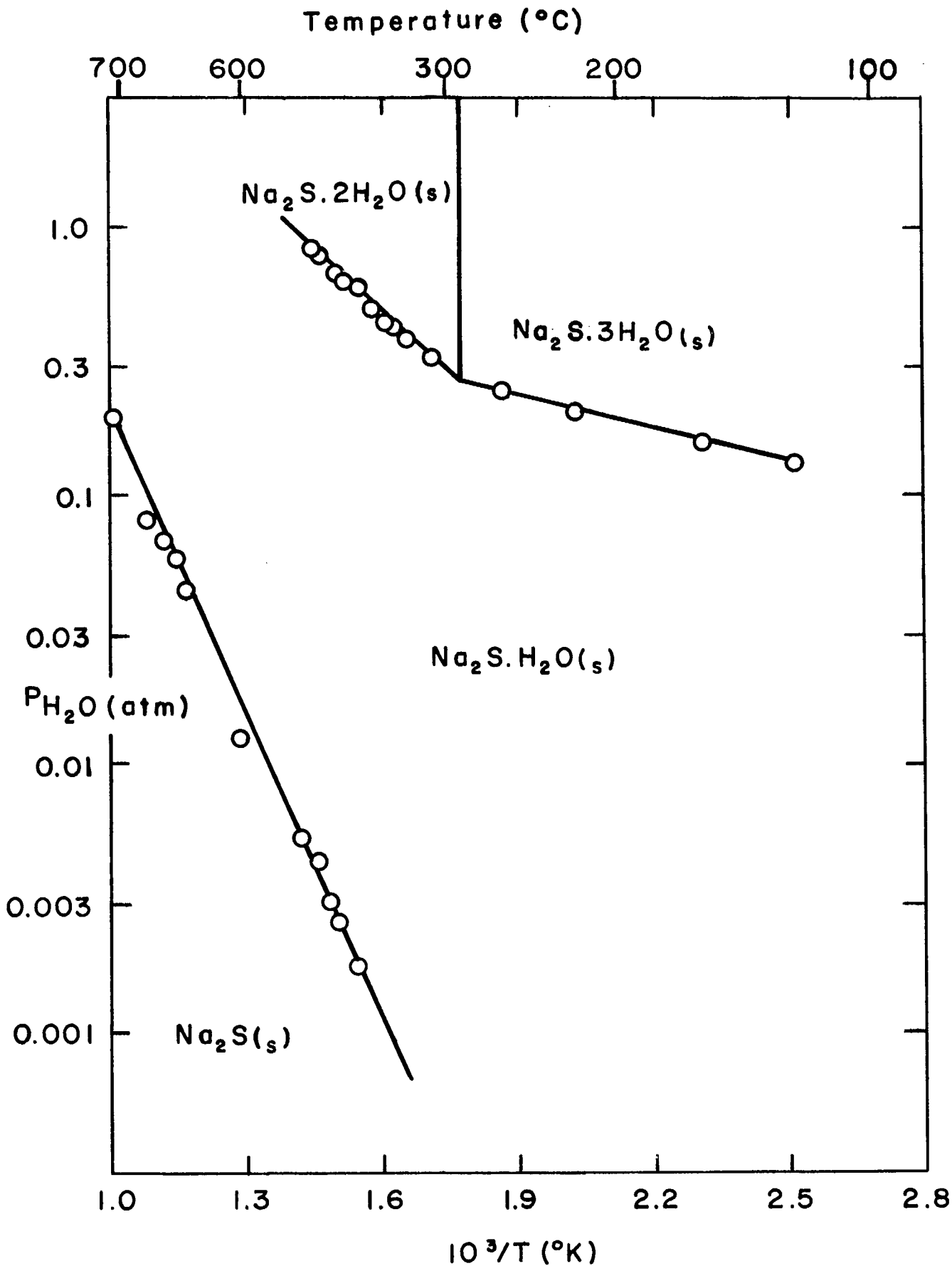
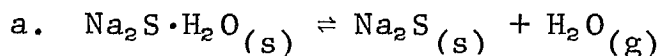


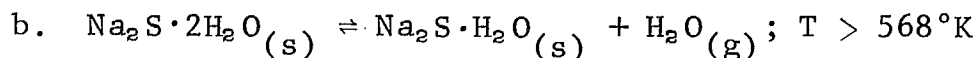
Figure 2: Log Pressure Versus Reciprocal Temperature Relationships for the Dehydration of $Na_2S \cdot H_2O$, $Na_2S \cdot 2H_2O$ and $Na_2S \cdot 3H_2O$.



$$\log P_{\text{H}_2\text{O}} \text{ (atm)} = 2.897 - 3.639 \times 10^3 / T$$

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

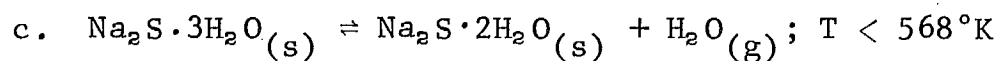
$$\Delta H = 16,620 \text{ cal/mole}$$



$$\log P_{\text{H}_2\text{O}} \text{ (atm)} = 2.062 - 1.479 \times 10^3 / T$$

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

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



$$\log P_{\text{H}_2\text{O}} \text{ (atm)} = 0.213 - 0.429 \times 10^3 / T$$

$$\Delta G_T = 1,962 - 0.975T$$

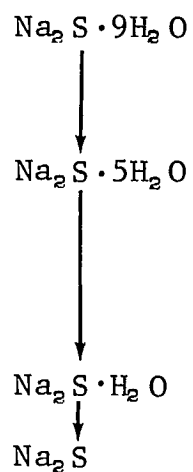
$$\Delta H = 1,962 \text{ cal/mole}$$

DISCUSSION

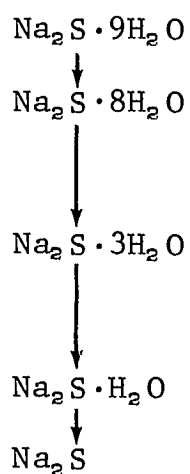
Hydrated sodium sulphide was found to thermally dissociate by three different reaction sequences, depending on the partial pressure of water vapour in contact with the hydrates. These reaction sequences are shown in Table 4. Inert-gas flow rates over the dehydrating samples would substantially affect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

TABLE 4
REACTION SEQUENCES FOR THE THERMAL DISSOCIATION
OF HYDRATED SODIUM SULPHIDE

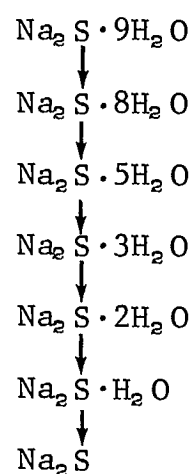
$P_{\text{H}_2\text{O}} < 0.13 \text{ atm}$



$P_{\text{H}_2\text{O}} = 0.13 - 0.27 \text{ atm}$



$P_{\text{H}_2\text{O}} > 0.27 \text{ atm}$



Sodium sulphide monohydrate ($\text{Na}_2\text{S}\cdot\text{H}_2\text{O}$) 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 $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$. The stabilities of these hydrates are governed by both temperatures and water vapour partial pressures. Of the hydrates, $\text{Na}_2\text{S}\cdot\text{H}_2\text{O}$ is stable over the largest pressure and temperature range. Heats of hydration were greatest for $\text{Na}_2\text{S}\cdot\text{H}_2\text{O}$ (16.62 kcal/mole), followed by $\text{Na}_2\text{S}\cdot 2\text{H}_2\text{O}$ (6.76 kcal/mole) and $\text{Na}_2\text{S}\cdot 3\text{H}_2\text{O}$ (1.96 kcal/mole).

ACKNOWLEDGEMENTS

Y. Lavoie assisted with the static pressure measurements and P. Carriere assisted with the high temperature X-ray powder diffraction measurements. Discussions with Dr. T.R. Ingraham are gratefully acknowledged.

REFERENCES

1. Kerby, R.C., and Ingraham, T.R., "Recycling of Waste Sulphite Liquors for Canadian International Paper Co., Hawkesbury, Ont.", Can. Mines Branch Investigation Report IR 71-67 (1971).
2. Kerby, R.C., and Ingraham, T.R., "An Evaluation of the Solid State Carbonation Process for the Recovery of Sodium Sulphite from Waste Sulphite Pulp Liquors", Can. Mines Branch Investigation Report IR 72-47 (1972).
3. Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. II, Supplement II, (1961), p. 981.
4. Kirk-Othmer Encyclopedia of Chemical Technology, 2nd ed., Interscience Pub., Vol. 18 (1969), p. 510.
5. Fukui, S., Ono, M., and Nakaburi, T., "Mitsubishi MRC Pulping Liquor Recovery Process", Tech. Rev., Mitsubishi Heavy Ind., 4(1), 60-67 (1967).

6. Bedlivy, D., and Preisinger, A., "Structure of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ and $\text{Na}_2\text{Se}\cdot 9\text{H}_2\text{O}$ ", Z. Krist. 121(2-4), 114-130 (1965).
7. Bedlivy, D., and Preisinger, A., "Crystal Structure of $\text{Na}_2\text{S}\cdot 5\text{H}_2\text{O}$, $\text{Na}_2\text{Se}\cdot 5\text{H}_2\text{O}$ and $\text{Na}_2\text{Te}\cdot 5\text{H}_2\text{O}$ ", Z. Krist. 121(2-4), 135-144 (1965).
8. Zintl, E., Harder, A., and Dauth, B., "Crystal Structure of the Oxides, Sulphides, Selenides and Tellurides of Lithium, Sodium and Calcium", Z. Electrochem. 40(8), 588, (1934).
9. Ingraham, T.R., and Hotz, M.C.B., "Equilibria in the Sodium Oxide - Sulphur Trioxide - Water System", Can. Met. Quart. 7(3), 139-145 (1968).

