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The Sodium-Sulfur System. I. Differential Thermal Analysis[1]

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Attempts to gain a better understanding of the reactive species in the sodium-sulfur battery system developed at Ford Motor Co. have led us to reexamine the sodium-sulfur phase diagram published by Pearson and Robinson in 1930. A modified phase diagram was constructed based on dta studies. In addition, dta revealed that when a mixture of Na_2S and Na_2S_2 or Na_2S_4 and S_8 is heated, a reaction takes place around the melting point of sulfur, with the formation of the pentasulfide, Na_2S_5, as the initial step. Unless the sulfur:sodium ratio in the mixture is 5:2 or higher, further interaction between the sulfides can be observed by dta, until at equilibrium only those species are observed corresponding to the given stoichiometric Na:S ratio. The highest sulfide is Na_2S_5, whereas the trisulfide, Na_2S_3, does not exist at the melting point, and the mixture with the same stoichiometry was found to be a 1:1 Na_2S_2-Na_2S_4 eutectic.

Introduction

The discovery of the sodium-sulfur battery as a potentially high-energy density power source by Weber and Kummer[2] has regenerated interest in the sodium-sulfur system. The first sodium-sulfur phase diagram was published by Friedrich,[3] who postulated the existence of tetrasodium polysulfides such as Na_4S_3, Na_4S_5, Na_4S_7, and Na_4S_9. Although Bloxam[4] claimed to have isolated $Na_4S_9 \cdot 14H_2O$, subsequent investigations by Rule and Thomas[5] showed that only the disodium polysulfides could be established as definite compounds. Pearson and Robinson[6] not only confirmed the findings of Rule and Thomas but also presented an improved sodium-sulfur phase diagram. For the next 40 years this diagram was the only one available in the literature, although scattered reports were published concerning various aspects of the sodium-sulfur system. In addition to Feher's work,[7,8] the publications of Pauling[9] concerning the structure of S_8 and of Foss[10] dealing with the chain structure of the polysulfides constitute an indirect, yet valuable, contribution to a better understanding of the sodium-sulfur system.

In an effort to obtain information concerning the polysulfide species that are present in the sodium-sulfur melt in the battery, it was deemed necessary to restudy the sodium-sulfur phase diagram. The resurging interest in differential thermal analysis (dta) during the past decade and the advances made in dta equipment render this technique particularly suitable for restudying the sodium-sulfur phase diagram. Therefore, the primary objectives of this investigation are the study of the sodium-sulfur phase diagram and the thermal behavior of the individual sodium polysulfides and sulfur as deduced from dta.

Experimental Section

Apparatus. The bulk of the dta data was obtained from a Du Pont 900 differential thermal analyzer. At least triplicate runs were made both with the micro and macro sample tubes. Trial runs with temperature rates varying from 10 to 30°/min were conducted, and in terms of both the resolution of the dta curves and expedience of the experiments a rate of 20°/min was chosen as the most desirable rate for all the experiments. The heating compartment was flushed with N_2 (rate 1 l./min).

Sulfur and the polysulfides exhibit a marked tendency to supercool. This necessitates the occasional use of provisions to rotate the sample tube and using the thermocouple as a stirrer. The differential thermal signal from the sample and reference thermocouples was recorded by a Hewlett-Packard Type 419A dc null voltmeter, which acted as a preamplifier. The amplified signal from the voltmeter is fed into one channel of a dual channel strip chart recorder (HP Moseley Type 7100B). The second channel of the recorder is connected to the temperature-sensing device.

Materials. Sulfur was obtained as spectral grade sulfur from American Smelting and Refining Co. and was used without additional purification. The dta curve is identical with that of the Du Pont reference standard sulfur (Figure 1A). Anhydrous Na_2S was prepared from $Na_2S \cdot 9H_2O$ (Allied Chemical Code 2297), according to Brauer,[11] by drying in an evacuated desiccator at 40–70°C for 2 weeks and final dehydration in a furnace at 700° under a stream of H_2 (Figure 1B).

The polysulfides α-Na_2S_2, β-Na_2S_2, Na_2S_4, and Na_2S_5 were synthesized following Brauer's methods.

Na_2S_5 was prepared from a mixture of anhydrous Na_2S and sulfur which was present in slight excess of the stoichiometric ratio. The mixture was heated in an evacuated and sealed Vycor tube for 1–2 hr at 550°. The excess sulfur was removed from the powdered product by washing with toluene, and its purity was checked by dta (Figure 1E). Na_2S_5 is a greenish-yellowish brown solid, mp 258°. Na_2S_4 was synthesized from an anhydrous ethanolic solution of NaHS by adding the proper amount of sulfur: $2NaHS + 3S \rightarrow Na_2S_4 + H_2S(g)$.[12] Disodium tetrasulfide supplied by Alfa Inorganics turned out to be contaminated with excess sulfur. This can be removed by washing with toluene (Figure 1D). Na_2S_4 is a yellow to orange solid, mp 285°.

α-Na_2S_2 was prepared by adding the proper amount of sodium metal to the ethanolic solution of Na_2S_4 prepared previously: $Na_2S_4 + 2Na \rightarrow 2\alpha$-$Na_2S_2$. It is a bright yellow solid, mp 475°. On heating it changes gradually and irreversibly into β-Na_2S_2, commencing around 150° (Figure 1C).

β-Na_2S_2 can be made from α-Na_2S_2, or it can be made directly from the high-temperature synthesis of anhydrous Na_2S and the required amount of sulfur. It is a dark brown solid, mp 475°.

Mixtures of sodium polysulfides (1:2 Na_2S-Na_2S_5, etc.) and of sodium polysulfide and sulfur (1:1, 1:2, etc., Na_2S_2-S),[12] having various integral mole ratios, were prepared by weighing and mixing the appropriate amounts of the components of the mixture.

Results and Discussion

The data obtained from dta are tabulated in Table I. The preweighed amounts of the components in the mixture are given in mole ratio rather than in grams, and the weight per cent of sulfur is calculated from this mole ratio. Figure 2 is the sodium-sulfur phase diagram constructed from these data. A direct comparison of the present result with that of Pearson and Robinson,[6] indicated by the broken curves, is shown in the figure. The data shown in full black circles

(1) Presented at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., April 1971.

(2) N. Weber and J. T. Kummer, *Proc. Annu. Power Sources Conf.*, 21, 37 (1967).
(3) K. Friedrich, *Metall. Erz*, 88 (1914).
(4) W. P. Bloxam, *Z. Anorg. Chem.*, **60**, 113 (1908).
(5) A. Rule and J. S. Thomas, *J. Chem. Soc.*, **105**, 177 (1914).
(6) T. G. Pearson and P. L. Robinson, *J. Chem. Soc.*, 1473 (1930).
(7) F. Feher and H. J. Berthold, *Z. Anorg. Allg. Chem.*, **273**, 140 (1953).
(8) F. Feher and E. Heuer, *Z. Anorg. Chem.*, **255**, 185 (1947).
(9) L. Pauling, *Proc. Nat. Acad. Sci. U. S.*, **35**, 495 (1949).
(10) O. Foss, *Advan. Inorg. Chem. Radiochem.*, **2**, 237 (1960).
(11) G. Brauer, "Handbuch der praparativen anorganischem Chemie," Ferdinand Enke Verlag, Stuttgart, 1960.

(12) When 1 S, 2 S, etc., are indicated, we actually mean the more proper symbols $^1/_8$ S_8, $^1/_4$ S_8, etc.

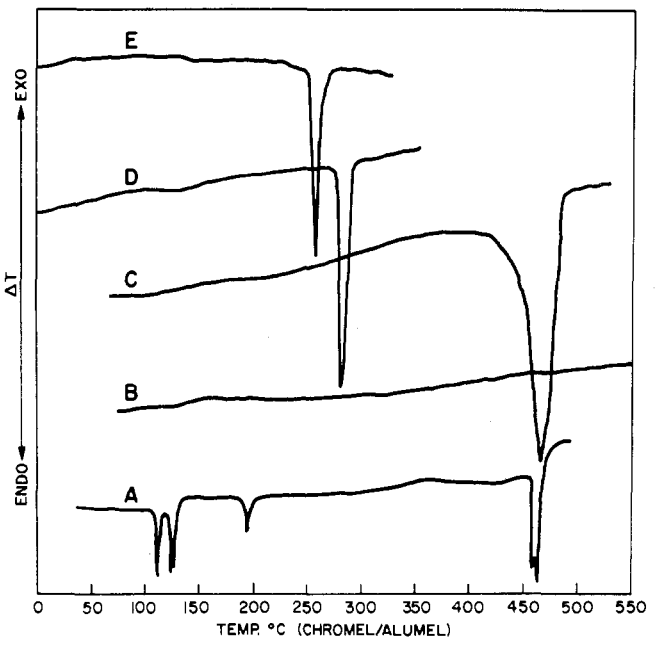

Figure 1. Dta curves for (A) pure sulfur, (B) Na_2S, anhydrous, (C) Na_2S_2, (D) Na_2S_4, and (E) Na_2S_5.

Table I. Transition Temperatures from Dta of Mixtures of Sodium Polysulfides

Mole ratio of polysulfides				Transition temp,
% of Na_2S_2	% of Na_2S_4	% of Na_2S_5	Wt % of S	°C
100			58.3	475
10	1		60.3	465-468
6	1		61.4	461-463
4	1		62.5	428-430
3	1		63.5	398-400
5	2		64.1	368-370
2	1		65.0	325-329
5	3		65.7	303-305
1	1		67.6	240-238
1	2		69.8	255-258
1	3		70.9	268-270
1	4		71.4	270-273
	100		73.6	285
	4	1	74.4	273-275
	2	1	75.1	265-269
	1	1	75.8	247-250
	1	2	76.4	235-238
	3	4	76.6	242-244
	1	4	77.0	249-247
	1	6	77.2	252-254
		100	77.7	258

were obtained by a completely independent method, namely, emf measurements by Gupta and Tischer[13] of this laboratory. There is substantial agreement between the data obtained by dta and emf measurements. The major difference between our results and the Pearson-Robinson phase diagram is the absence of the arrest in temperature *vs.* composition in the range Na_2S_2 to 2:3 Na-S. The slight discrepancies in the older data might be due to contamination of the starting materials. Two impurities which are not easily detected by older analytical methods, namely, H_2O and S_8, play a major role in the result of the experiment. The presence of any trace of water in the polysulfides causes hydrolysis with formation of H_2S and S_8, altering the melting point of the system considerably. Therefore, materials synthesized from aqueous solutions were excluded in this work. Pearson and Robinson[6] employed polysulfides synthesized by both the

(13) N. K. Gupta and R. P. Tischer, *J. Electrochem. Soc.*, 119, 1033 (1972).

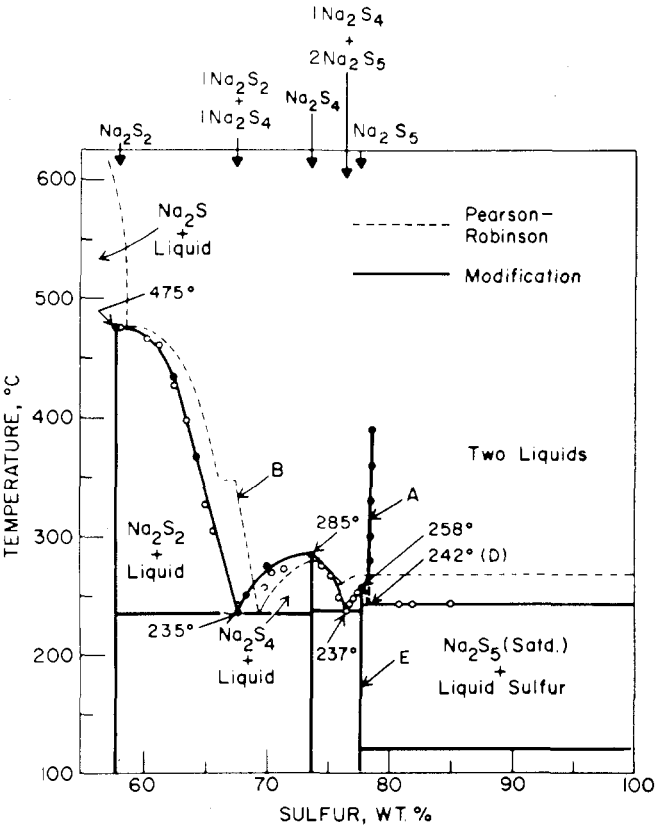

Figure 2. Phase diagram of the Na-S system between the compositions Na_2S_2 and 100% S.

"wet" or aqueous method and the "dry" or nonaqueous method. However, their "dry method" refers to the synthesis of polysulfides from the elements in toluene. Feher and Berthold[7] showed from X-ray diffraction patterns that the result of such a synthesis was generally a mixture of polysulfides. Wet analysis of the sodium polysulfides, upon which Pearson and Robinson relied, yields total sulfur content only, and no distinction is possible between the results obtained from a mixture consisting of 1:1 Na_2S_4-S or from pure Na_2S_5. For this reason the purity of the polysulfides used in this work is judged by their dta curves.

Additional results of interest are the presence of the eutectics corresponding to the composition 1:1 Na_2S_2-Na_2S_4 at 235° and 1:2 Na_2S_4-Na_2S_5 at 237°. It is quite clear from Feher and Berthold's work[6] that sodium trisulfide, Na_2S_3, with the same Na:S ratio as the 1:1 eutectic Na_2S_2-Na_2S_4, does not exist in the melt; and our results are consistent with their conclusions.

The thermal kinetic behavior of the polysulfides mixed with sulfur can be studied by analyzing the dta curves when these mixtures are subjected to dta. Figure 3 shows such a curve for a 1:1 Na_2S-S mixture, when it is heated from 0 to 160° (curve A). A comparison of this dta curve with the curves for anhydrous Na_2S and S_8 (Figure 1, curves A and B) reveals that a reaction is taking place between these compounds around 110° as indicated by the exothermic peaks around this temperature region. If there were no interactions between the components of the mixture, we would expect the dta curve to be a superposition of the dta curves of the components. When the sample was cooled, powdered, and again subjected to dta, another curve (B) was obtained. The first endothermic peak corresponds to the melting point of S_8; the second, to the melting point of Na_2S_5. Although the Na:S stoichiometric ratio is not 1:5, apparently there is

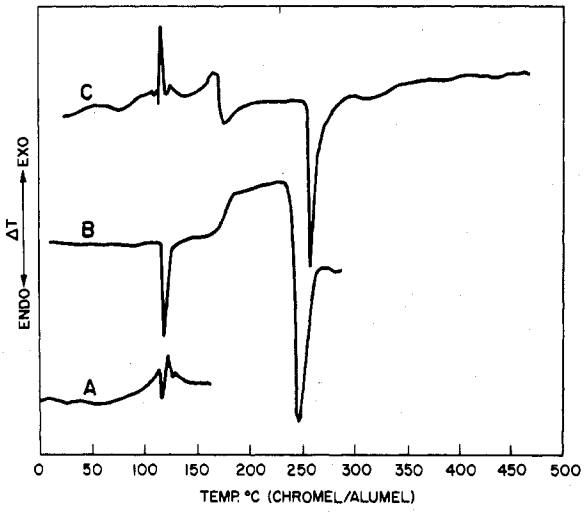

Figure 3. Dta curves for (A) the reaction between 1 Na_2S and 1 S; (B) the intermediate products from (A), and (C) the reaction between 1 Na_2S and 2 S.

formation of the pentasulfide. The same pattern is shown by the dta curve for the 1:2 Na_2S-S mixture (Figure 3C). Again we see a quite pronounced peak around 258° corresponding to the Na_2S_5 endotherm. Dta of mixtures of Na_2S or Na_2S_2 and sulfur show similar traits, and whatever the ratio of total Na to total S, the pentasulfide is always formed first. Therefore, assuming that the reaction between 1 Na_2S and 1 S is proceeding along the reaction path indicated by the dta curve, namely, with the formation of Na_2S_5, we could write (employing integral coefficients) the following equation: $4Na_2S + 4S \rightarrow 3Na_2S + Na_2S_5$.

The high-temperature synthesis of β-Na_2S_2, however, indicates that the end product of the reaction between 1 Na_2S and 1 S is the β-disulfide. Therefore, the previous equation only shows the first step of the reaction, which must be followed by another reaction between Na_2S and Na_2S_5, as shown in Figure 4. Curve A shows the dta curve for a mixture of Na_2S and Na_2S_5 in a 3:1 mole ratio when it is heated to 300°. The presence of the exotherms is again indicative of the reaction that is taking place between the components of the mixture. Curve B shows the dta curve for the final product of the reaction, which is β-Na_2S_2. Other mixtures of Na_2S with the other polysulfides or mixtures of polysulfides show similar interaction between components of the mixture (Figure 4C).

The results indicate that the synthesis of the polysulfides from Na_2S or lower polysulfides and sulfur does not proceed by a simple single-step reaction, but through an intermediate step with formation of Na_2S_5. If the pentasulfide is not the end product, then consecutive reactions between the pentasulfide and Na_2S or the other remaining lower polysulfides takes place, leading to the formation of a final product or products consistent with the phase diagram. Hence some of the reactions that were studied in this work—namely, $Na_2S + nS$, $Na_2S_2 + nS$, etc., or $Na_2S + qNa_2S_5$, etc.—could be described by the sequence

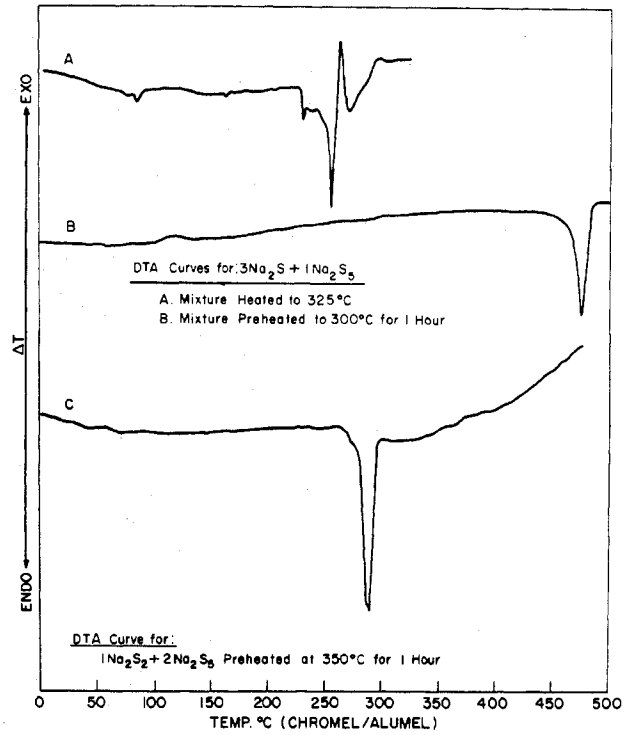

Figure 4. Dta curves for (A) the reaction between 3 Na_2S and 1 Na_2S_5; (B) the final product from (A); (C) the final product from the reaction 1 Na_2S_2 + 2 Na_2S_5.

$$2Na_2S + 4S \rightarrow Na_2S + Na_2S_5 \rightarrow Na_2S_2 + Na_2S_4$$
$$3Na_2S_2 + 6S \rightarrow 2Na_2S_5 + Na_2S_2 \rightarrow 3Na_2S_4$$

etc. The results also show that, although the sodium polysulfides with the exception of the trisulfide are individually rather stable compounds, on heating a mixture of these polysulfides, reactions may take place to form other polysulfide species. Which species is present at the end of the reaction is determined by the Na:S ratio and can be deduced from the phase diagram.

Conclusions

The following conclusions can be drawn from the dta study of the sodium-sulfur system.

1. A revised Na-S phase diagram is obtained showing the presence of eutectics with the compositions 1:1 Na_2S_2-Na_2S_4 at 235° and 1:2 Na_2S_4-Na_2S_5 at 237°.
2. The reaction between Na_2S or Na_2S_2 and sulfur proceeds with the formation of Na_2S_5 as an intermediate step. If the Na:S ratio is greater than 2:5, further reaction will take place as shown by the various examples.
3. The final product or mixture of products of the reaction among Na_2S, sodium polysulfides, and sulfur can be deduced from the Na:S ratio and the phase diagram.

Registry No. S, 7704-34-9; S_8, 10544-50-0; Na, 7440-23-5; Na_2S, 1313-82-2; Na_2S_2, 22868-13-9; Na_2S_4, 12034-39-8; Na_2S_5, 12034-40-1.