Thermal Behavior of the Potassium-Sulfur Electrolyte

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ABSTRACT

Enthalpy of fusion and heat capacity data are reported for the compositions: di-, tri-, tetra-, penta-, and hexa-polysulfides. Pronounced glass forming tendencies on cooling from the molten state are observed in the region of \( \sim 62 \) to \( \sim 67 \) wt% sulfur; this composition range is also characterized by inverse crystallization phenomena, much as observed in the closely related sodium-sulfur system. The calorimetric studies were extended to compositions in the region of liquid-liquid immiscibility, and the behavioral aspects are also reported.

Introduction

High-temperature thermodynamic data have recently been reported for the \( \text{Na}_2\text{S} \)-sulfur system as part of investigations of energy-related candidate salt systems for the molten sulfur electrode. In the present communication we report the results of an extension of these studies to the \( \text{K}_2\text{S} \)-sulfur system. Interest in this system has been re-stimulated through two recent developments in advanced battery concepts, namely the reports by Tsang (1) of potassium permeable hollow glass fibre techniques and by Crosbie and Tennenhouse (2) and Crosbie (3) of potassium beta"-alumina membranes. The potassium-sulfur system differs from the sodium-sulfur system in at least two aspects of practical interest; the open-circuit voltage (OCV) is higher in the potassium system, (2.414 V and 2.08 V, respectively) and the solidus-liquidus fields in the potassium system enable operation of the molten sulfur electrode at temperatures significantly lower than in the corresponding sodium system. For additional information, see ref. 3.

Investigations of the thermal properties appear limited to the work of Bousquet et al. (drop calorimetry; differential thermal analysis) (4). Markedly different values for the enthalpy of fusion were reported for two of the potassium polysulfides, viz: \( \text{K}_2\text{S}_n \) and \( \text{K}_2\text{S}_5 \), the technique of DTA leading to values \( \sim 70-250\% \) larger than from drop calorimetry. Our principle effort, thus, was aimed at obtaining reliable values for the thermal properties. The measurements were extended to the
characterization of the melting-crystallization behavior of compositions lying in the liquid-liquid immiscible region of the K$_2$S-sulfur system, and these results are also reported.

**Experimental**

The differential scanning calorimetry facility in this laboratory centers around a Perkin Elmer DSC-Model 2 calorimeter, together with an LMS system of microprocessor components and software (5) for computer-assisted data acquisition, base-line corrections, and data analysis in enthalpy and heat capacity measurements. A Cahn equipment for quantitative and accurate small mass measurements completes the assembly. The latter was kept in a dry N$_2$ atmosphere together with the sample capsules and seal-press so that all steps in the sample transfers and encapsulations were carried out in an inert environment.

Energy calibrations were made with three metals, indium, tin, and lead, and two salt systems, KNO$_3$ and LiCl-KCl eutectic (6-8). The accuracy limits of the measurements thus established were as follows: temperatures, ±0.5°C; heats of fusion, ±2%; heat capacities, ±2%.

For the enthalpy and heat capacity measurements, the compositions were prepared "in-capsule" i.e., the reactant materials were directly weighed into the DSC sample pans in milligram amounts and in the exact stoichiometries required for the desired compositions. Contamination through trace impurities, such as moisture and oxygen, is thus minimized, if not completely by-passed.

The K$_2$S$_3$ was prepared from metallic potassium (Purified Grade; Baker Chemical Co., Inc.) and highly refined sulfur (9) using the ethanolic technique of Pearson and Robinson (10). The analytical procedures of Feher and Berthold (11) were used to establish the exact composition of the K$_2$S$_3$ (±2%). The tetra-, penta-, and hexa-sulfide compositions were prepared by the "in-capsule" DSC technique using K$_2$S$_3$ and the highly refined sulfur in the required (weighed) amounts. For K$_2$S$_2$, the "in-capsule" technique was also used, but with K$_2$S (99.9% purity; Cerac/Pure Chemicals Co., Inc.) and K$_2$S$_3$ as reactant materials. The use of K$_2$S and sulfur as starting materials for the preparation of the above polysulfides via the "in-capsule" technique was explored but was not successful. The events during the above processes are illustrated in Fig. 1 and the values are given in Table 1. Completion of the reaction was taken as disappearance of
the K_2S_3 or the sulfur endotherms (via repetitive scans). The DSC scans for the melting process for the polysulfides thus prepared are also in Figure 1, together with the results for elemental sulfur. Melting temperatures were determined from the leading edge of the melting endotherms (12,13).

The enthalpies of solid-solid transitions and melting, and the heat capacities of the polysulfides as crystalline solids and as glasses and molten liquids are summarized in Tables 2-5. For these measurements, the heating and cooling rates were set at 10°/min, with a N_2 sweep of ~20 cm^3/min throughout the assembly. The heat capacity data were acquired in overlapping 50° temperature increments over the total temperature range spanned.

Results and Discussion

The data of the Phase-Rule studies (3,10,15, and present work) are summarized in Figure 1. Inspection shows the existence of five maxima and three eutectics. For the di-, tri-, penta-, and hexa-polysulfides the maxima are well defined; for the tetra- the maximum appears to be slightly hidden (i.e., incongruently melting composition). At compositions of 71.8 wt% sulfur and greater, there is a separation into two layers (3), one consisting of a saturated solution of sulfur in the hexasulfide and the other, a saturated solution of the polysulfides in sulfur. The proposal by Pearson and Robinson (10), that the di- and tri-polysulfides do not melt congruently is not supported by the present melting-crystallization studies. In a related communication from this laboratory concerning structural studies (14), the macroscopic preparative synthesis and the characterization of this polysulfide series are reported (melting points, elemental analyses, X-ray powder diffraction data). The results from the present DSC measurements (Table 2, mpts) are in close accord with the earlier observations (~±3°C); for the disulfide the limits are somewhat larger, (~±5°C). The Na_2S-sulfur system is also shown in Figure 1. Inspection shows the lower range of temperature available for the molten sulfur electrode in the K_2S-sulfur system.

Melting-crystallization behaviors are illustrated in Figure 3 for the five stoichiometric compositions, and Figure 4 for the two additional compositions of higher sulfur content. The partial crystallization exhibited by some compositions (e.g., K_2S_5, Fig. 3), the pronounced supercooling effects, and the onset of the crystallization
exotherms on reheating the materials (i.e., "inverse"
crystallization, K₂S₄; K₂S₅; Fig. 3) indicate clearly the
difficulties that would be encountered in obtaining trust-
worthy transition point data (m.p.t.s., enthalpies, heat
capacities) with techniques such as drop calorimetry
and/or DTA (differential thermal analyses). It is of
interest to examine the enthalpies of fusion from the
various calorimetric techniques, viz:

| ΔH (kJ mol⁻¹) | K₂S₂ | K₂S₃ | K₂S₄ | K₂S₅ | K₂S₆ |
|---------------|------|------|------|------|------|
| Drop cal. (4)  | 11.150 | 16.150 | 8.305 | 7.196 | 25.941 |
| DTA (4)        | -    | 14.64 | 14.23 | 25.10 | 26.36 |
| DSC (this work)| 18.28 | 24.94 | 11.63 | 26.99 | 27.61 |

Inspection shows that the results from all three
techniques for K₂S₆ are in close accord and for K₂S₅ the
agreement is moderately good from two (for DTA and DSC).
For K₂S₅ the difference between the drop and the differ-
tential calorimetric techniques is in the direction pre-
dicted for partial crystallization effects.

The differing results from the DTA (4) and the
present DSC measurements are not as readily understood.
Some of the differences may be due, in part, to the
thermal history of the materials prior to the measure-
ments. In the present work an "in-capsule" preparative
technique, with K₂S, K₂S₃, and sulfur as reactants, was
used to gain the various polysulfides as polycrystalline
materials.

For the two compositions that fall in the region of
liquid-liquid immiscibility, the melting behavior is
summarized in Table 2 and in Figure 4, respectively. The
melting point data (Table 2) indicate very sparing solu-
bilities of the second components. Quantitative solubil-
ity estimates, however, were not undertaken in the present
work. Relative to the enthalpies of fusion and the heat
capacities it is found that these can be predicted quanti-
tatively from the known stoichiometries of these samples,
and the data for sulfur (9,12) and for the hexa-sulfide
(Tables 2-5), using the principles of mol-fractions and
state-functions additivity. Thus using heat capacity as
illustration the results are: K₂S₇₀₈₃, Cₚ (J deg⁻¹ mol⁻¹):
obsv'd, 169.4; calc'd, 173.0 at 300°C; and for K₂S₁₉₈₄₄,
Cₚ (J deg⁻¹ mol⁻¹): obsv'd, 86.9; calc'd, 84.7 at 250°C.
The agreement leaves little to be desired, and offers
additional support for this as a region of liquid-liquid
immiscibility.
Comparison of the composition ranges over which the glass-forming tendencies are greatest in the Na$_2$S-sulfur system and in the K$_2$S-sulfur system is of interest. In the sodium system it was found to be most pronounced in the tri-sulfide composition range (10, 12, 15, 16); by contrast, in the potassium system, the tri-sulfide composition shows sharp crystallization exotherms, with virtually no supercooling (present work), i.e., the same behavioral aspects as shown by well-defined crystalline materials such as NaCl, KCl, ...). The tendency to glass formation in the potassium system is greatest in the tetra- to penta-polysulfide composition range. The glass transition temperature (Tg) from the present measurements, for K$_2$S$_4$ and K$_2$S$_5$ are respectively 46.9°C and 49.4°C. For the tetrasulfide, Cleaver (16) reported a value of 42°C; no value was reported for K$_2$S$_5$.

The melting-crystallization measurements of "aged" melts were limited to two compositions in this glass-forming range, namely the tetra- and the penta-polysulfide compositions. Samples of each, after "aging" in the molten state for ~800 hrs at 315°C were re-examined by the DSC technique by repeated thermal cycling, much as for the freshly prepared systems. The properties for the penta- were virtually unchanged from those prior to this aging treatment, i.e., the DSC thermal spectra were unchanged from those in Fig. 3, and the m.pt.s. and ΔH$_{rus}$ were as in Table 2. The tetra- samples, however, showed differences in the melting-crystallization pattern after this "aging" in the molten state. The tendency to formation of amorphous glassy masses on cooling was retained, but on reheating, the on-set of crystallization was no longer reproducible. When crystallization did occur, the on-set of this event now had shifted to higher temperatures (see Fig. 3, K$_2$S$_5$). Thus at the tetrasulfide composition, "aging" in the molten state induces structural changes that favor a complete "loss-of-memory" of crystallinity in the amorphous material gained by cooling the melts. Measurements are in progress to characterize the range of compositions for this, and further discussion is deferred until additional results are on-hand.

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Table 1. Thermicities of events during preparative reactions

| Temperature Range (°C) | Event | thermicity | ΔH (joule mol⁻¹) |
|------------------------|-------|------------|-----------------|
|                        | $K_2S_3 + K_2S + 2K_2S_2$ |            |                 |
| 265° - 293°            | endothermic | 2,610 | (per mole $K_2S_2$) |
| 293° - 340°            | exothermic  | 9,880 | (per mole $K_2S_2$) |
|                        | $K_2S_3 + S + K_2S_4$ |            |                 |
| 100° - 121°            | endothermic | 15,930 | (per mole sulfur) |
| 127° - 260°            | ***       | 6,380 | (per mole $K_2S_4$) |
|                        | $K_2S_3 + 2S + K_2S_5$ |            |                 |
| 100° - 121°            | endothermic | 15,590 | (per mole sulfur) |
| 129° - 177°            | endothermic | 1,372 | (per mole $K_2S_5$) |
| 177° - 197°            | endothermic | 2,778 | (per mole $K_2S_5$) * |
| 177° - 217°            | exothermic  | 1,058 | (per mole $K_2S_5$) ** |
|                        | $K_2S_3 + 3S + K_2S_6$ |            |                 |
| 100° - 121°            | endothermic | 15,000 | (per mole sulfur) |
| 132° - 177°            | endothermic | 4,100 | (per mole $K_2S_6$) |
| 177° - 200°            | exothermic  | 460 | (per mol $K_2S_6$) * |
|                        | endothermic | 2,340 | (per mol $K_2S_6$) * |

* integrated for all the exotherms and endotherms in this temp. range
+ prior to enthalpy of fusion

*** integrated over both the endo- and exo- therms

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Table 2. Enthalpies of Fusion and Solid-Solid Transitions (a)

| Composition | t (°C) | ΔH (J g⁻¹) | ΔH (J mol⁻¹) |
|-------------|-------|-------------|--------------|
| sulfur      |       |             |              |
| formula     |       |             |              |
| (wt %)      |       |             |              |
| solid state |       |             |              |
| transition  |       |             |              |
| 45.1 K₂S₂  | 146°  | 1.05        | 150          |
|            |       |             |              |
| solid       |       |             |              |
| melt (fusion)|      |             |              |
| 45.1 K₂S₂  | 487°  | 128         | 18,280       |
| 55.2 K₂S₃  | 302°  | 143         | 24,940       |
| 62.1 K₂S₄  | 154°  | 56.1        | 11,630       |
| 67.2 K₂S₅  | 205°  | 113         | 26,990       |
| 71.1 K₂S₆  | 189°  | 102         | 27,610       |
| 74.3 K₂S₇₆ | 81.6  |             |              |
| formula     |       |             |              |
| sulfur sat'd |       |             |              |
| layer melts |       |             |              |
| 118°C       |       |             |              |
| and the    |       |             |              |
| hexasulfide |       |             |              |
| layer melts |       |             |              |
| 188°C       |       |             |              |

(a) for conversion of SI units to other units: 4.184 J = 1 cal.

Table 3. Heat Capacity-Temperature Equations

| Composition | t range (°C) | C_p = a + bt + ct² (J deg⁻¹ mol⁻¹) |
|-------------|--------------|----------------------------------|
|             |              | a       | b x 10³ | c x 10⁶ |
| K₂S₂        | 57°-450°     | 110.47  | 64.58   | -       |
| K₂S₃        | 57°-252°     | 158.46  | -438.27 | 1890.29 |
|             | 327°-492°    | 709.56  | -2859.30| 3906.18 |
| K₂S₄        | 57°-130°     | 146.90  | 425.43  | -       |
| K₂S₅        | 57°-177°     | 176.41  | 274.32  | -       |
| K₂S₆        | 57°-150°     | 185.04  | 427.81  | -       |

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| t (°C) | $c_p$ | $C_p$ | t (°C) | $c_p$ | $C_p$ |
|-------|-------|-------|-------|-------|-------|
|       |       |       |       |       |       |
| K$_2$S$_2$ |       |       | K$_2$S$_5$ |       |       |
| 60    | 0.80  | 114.3 | 60    | 0.81  | 192.9 |
| 100   | 0.82  | 116.9 | 100   | 0.85  | 203.8 |
| 200   | 0.87  | 123.4 | 200   | 0.91  | 217.6 |
| 300   | 0.91  | 129.8 | 300   | 0.93  | 223.0 |
| 400   | 0.96  | 136.3 | 400   | 1.21  | 290.2 |
| 450   | 0.98  | 139.5 | m.pt. |       |       |
| 487   | m.pt. |       | 225   | 1.21  | 290.2 |
| 507   | 1.13  | 160.2 | 325   | 1.21  | 290.2 |
| 550   | 1.13  | 160.2 | 375   | 1.21  | 290.2 |
| 590   | 1.13  | 160.2 |       |       |       |
| K$_2$S$_3$ |       |       | K$_2$S$_7.05$ |       |       |
| 60    | 0.80  | 139.0 | 60    | 0.78  | 210.7 |
| 100   | 0.77  | 133.6 | 100   | 0.84  | 227.8 |
| 200   | 0.84  | 146.4 | 200   | 0.93  | 253.5 |
| 250   | 0.96  | 167.0 | m.pt. |       |       |
| 302   | m.pt. |       | 215   | 1.14  | 308.3 |
| 330   | 1.10  | 191.4 | 320   | 1.14  | 308.3 |
| 350   | 1.07  | 186.4 | 350   | 1.14  | 308.3 |
| 400   | 1.09  | 190.6 |       |       |       |
| 450   | 1.23  | 213.9 |       |       |       |
| 490   | 1.41  | 246.4 |       |       |       |
| K$_2$S$_4$ |       |       | K$_2$S$_{10.84}$ |       |       |
| 60    | 0.83  | 172.4 | 60    | 0.55  | 169.4 |
| 100   | 0.91  | 189.5 | 100   | 0.55  | 169.4 |
| 120   | 0.95  | 197.9 | 120   | 0.56  | 172.1 |
| 130   | 0.97  | 202.2 | 130   |       |       |
|       |       |       | m.pt. |       |       |
| 154   | m.pt. |       | 118   | S melting |       |
| 175   | 1.12  | 233.2 | 189   | K$_2$S$_{6}$ melting |       |
| 300   | 1.12  | 233.2 | 260   | 0.55  | 169.4 |
| 475   | 1.12  | 233.2 | 280   | 0.54  | 166.5 |
|       |       |       | m.pt. |       |       |
| 330   | 1.12  | 233.2 | m.pt. |       |       |
|       |       |       | 118   | S melting |       |
| 475   | 1.12  | 233.2 | 189   | K$_2$S$_{6}$ melting |       |
| 300   | 1.12  | 233.2 | 260   | 0.55  | 169.4 |
| 475   | 1.12  | 233.2 | 280   | 0.54  | 166.5 |
|       |       |       | m.pt. |       |       |
| 330   | 1.12  | 233.2 |       |       |       |
|       |       |       | m.pt. |       |       |
| 330   | 1.12  | 233.2 | m.pt. |       |       |

Table 4. Heat Capacity Data

$[c_p, J \ deg^{-1} g^{-1}; C_p, J \ deg^{-1} mol^{-1}]$
| $t$ (°C) | $c_p$ ($K_2S_4$) | $c_p$ ($K_2S_5$) | $t$ (°C) | $c_p$ ($K_2S_4$) | $c_p$ ($K_2S_5$) |
|---------|----------------|----------------|---------|----------------|----------------|
| -15°    | 0.73 151.7     |                | -15°    | 0.71 170.5     |                |
| -10°    | 0.73 151.4     |                | -10°    | 0.72 171.5     |                |
| -5°     | 0.74 152.8     |                | -5°     | 0.73 173.2     |                |
| 0°      | 0.75 155.4     |                | 0°      | 0.74 175.6     |                |
| 5°      | 0.76 157.3     |                | 5°      | 0.73 174.9     |                |
| 10°     | 0.76 156.3     |                | 10°     | 0.74 176.6     |                |
| 20°     | 0.77 158.4     |                | 20°     | 0.75 178.2     |                |
| 40°     | 0.79 162.5     |                | 40°     | 0.78 185.5     |                |
| 45°     | 0.93 186.6     |                | 45°     | 0.85 203.1     |                |
| 50°     | 1.23 255.2     |                | 50°     | 1.07 254.4     |                |
| 55°     | 1.14 234.8     |                | 55°     | 1.27 303.0     |                |
| 60°     | 1.14 234.8     |                | 60°     | 1.16 276.5     |                |
| 70°     | 1.14 234.8     |                | 70°     | 1.16 276.5     |                |
| 75°     | 1.14 234.8     |                | 75°     | 1.16 276.5     |                |

$t_g = 46.9°C$  
$t_g = 49.4°C$
Figure 1.
Phase diagrams for the systems K$_2$S-sulfur and Na$_2$S-sulfur

Figure 2.
DSC scans illustrating thermicity of preparative reactions and of melting for a series of potassium polysulfides.

(a) thermicity of reactions observed by the in-situ DSC preparative technique: A: sulfur melting zone; B: chemical reaction zone; (b) fusion endotherms for sulfur and five polysulfides
Melting-crystallization behavior on thermal cycling a series of potassium polysulfides.

For the tetra-sulfide, the open circles show the DSC heating scan for a sample that had been "aged" in the molten state (~ 800 hrs, at 315°C); no crystallization was observed on cooling from the molten state to ambient temperatures.

Figure 3.
The thermal behavior observed for polysulfide compositions greater than 71 wt% sulfur.

The DSC scans for "melting" are shown for two polysulfide compositions, $K_2S_{7.06}$ (74.3% sulfur) and $K_2S_{10.84}$ (81.6% sulfur), respectively. The behavioral pattern is that of the melting of a mixture of sulfur and $K_2S_6$ to form two immiscible liquid phases.