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Technical Progress Report

Thermophysical Properties of Inorganic Polysulfides

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ABSTRACT

The present project was initiated May 15, 1979, and was undertaken to meet the data needs for thermophysical properties of selected polysulfides, as required directly or indirectly in the advanced battery development programs, and to advance the theoretical studies on the mechanisms of melting of ionic compounds. The research approach is briefly summarized and the accomplishments and status of the three principal tasks that have been undertaken in this initial period are reported: (i) preparative chemistry; (ii) the MSDC-RPI DSC facility; and (iii) thermophysical properties measurements. First results for sodium trisulfide for the melting point, the enthalpy of fusion, and entrophy of fusion are, respectively: 238.7°C, 5538 cal/mol, and 10.83 cal/deg mol.

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Title of Project: Thermophysical Properties of Inorganic Polysulfides

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Scope of Project:

Fundamental thermophysical property measurements of selected inorganic polysulfides.

Salt systems: principally the lithium, sodium, and potassium polysulfide systems; others may be added.

Properties: enthalpies of fusion and (possibly) solid-state transitions; heat capacities (liquids, solids); volume changes on melting; solubilities (phase equilibria); impurity effects (additives: sulfates, sulfites, thiosulfates, hydroxides, oxides...).

Development of techniques for application of differential scanning calorimetry (DSC) for such aggressive materials will be part of this work.

II. Research Approach

For polysulfides nearly all the knowledge has been gained from work coupled directly or indirectly with the advanced battery development programs largely funded by federal sources and/or industrial concerns. The results of our recent data compilations [1,2] clearly show that there is a very basic information gap for this important class of materials relative to: enthalpies of fusion, heat capacities, and volume changes on melting. The present project was initiated May 15, 1979, and was undertaken to meet such data needs through fundamental thermophysical property measurements.

The polysulfides of particular interest are summarized in Table 1. Some of the basic reasons for the selection of these are:

a) the enthalpy of fusion data (and derived entropy of fusions) will be established for a series of sulfur containing anionic species

b) the results for the series S_2^{-2} to S_6^{-2} will enable a study of the mechanism of melting for such interesting species from the viewpoints of statistical thermodynamics

c) the results will also provide a data base for evaluating the empirical and semi-empirical prediction of thermophysical properties of inorganic compounds (for enthalpies and entropies of fusion and heat capacities)

d) from the practical aspects, outstanding data gaps will be closed for molten polysulfide electrolytes in the Na/S and the Li alloy/FeS and Li alloy/FeS_2 advanced battery concepts

Table 1

List of Inorganic Polysulfides

System	mpt.	System	mpt.
Sodium Polysulfides		Potassium Polysulfides	
Na_2S_2	482°C	-	
Na_2S_3	230°C	K_2S_3	205°C
Na_2S_4	294°C	K_2S_4	122°C
Na_2S_5	255°C	K_2S_5	199-205°C
		K_2S_6	190°C
Lithium Polysulfides[a]		Rubidium Polysulfides	
Li_2S_2	-	Rb_2S_2	$\sim$450°C
$Li_2S_{2.92}$	368°(d)	Rb_2S_3	$\sim$180-210°C
Li_2S_4	?	Rb_2S_4	$\sim$165°C
		Rb_2S_5	$\sim$230°C
		Rb_2S_6	
Cesium Polysulfides		Others	
Cs_2S_2	$\sim$460°C	BaS_2	600°C
Cs_2S_3	$\sim$210-215°C	BaS_3	554°C
Cs_2S_4	$\sim$160°C	SrS_2	300°C
Cs_2S_5	$\sim$211°C	SrS_3	>200°C
Cs_2S_6	$\sim$187°C	$BaS_4 \cdot H_2O$	200°C(d)

[a] Lithium polysulfides: the conflicting data (phase diagrams) indicate the need for a new experimental investigation; this is in progress in Southampton, U.K. see ref. 3, B. Cleaver, in lit. cited.

Extensions to include such additional systems such as BaS_3, and the rubidium and cesium polysulfide series appears of interest since structural data has been reported (BaS_3; Cs_2S_5; Cs_2S_6; X-ray crystallographic data) and since the possible influence of the cationic species (size, charge density) can be examined from theoretical viewpoints.

The work initially requires a considerable concentration on preparative aspects of inorganic chemistry. Firstly, because such systems are not available from commercial supply houses (with the exception of Na_2S_4), and secondly, because chemical purity is an important consideration.

Relative to the thermophysical properties measurements, calorimetry was selected as the principal experimental method. The instrumental advances in the last two decades have clearly shown that the technique of Differential Scanning Calorimetry (DSC) is capable of precisions and accuracies comparable to the better high temperature calorimetric methods and this approach was selected for the present tasks. The DSC technique has seen widest application in polymer science; applications to inorganic materials are more recent, i.e., the latter is still an emerging area. The experimental tasks in the work of the present period thus have included the acquisition and set-up of a DSC facility dedicated to inorganic materials, and specifically for measurements with such aggressive materials as the polysulfides.

The work to date has been directed as follows:

- preparative chemistry (synthesis and analytical characterization of polysulfides)
- the MSDC-RPI DSC facility (assembly, calibration, computer-coupling, and sample techniques)
- thermophysical property measurements

The results and accomplishments briefly are as follows.

III. Status of Work and Accomplishments

1. Preparation and characterization of polysulfides.

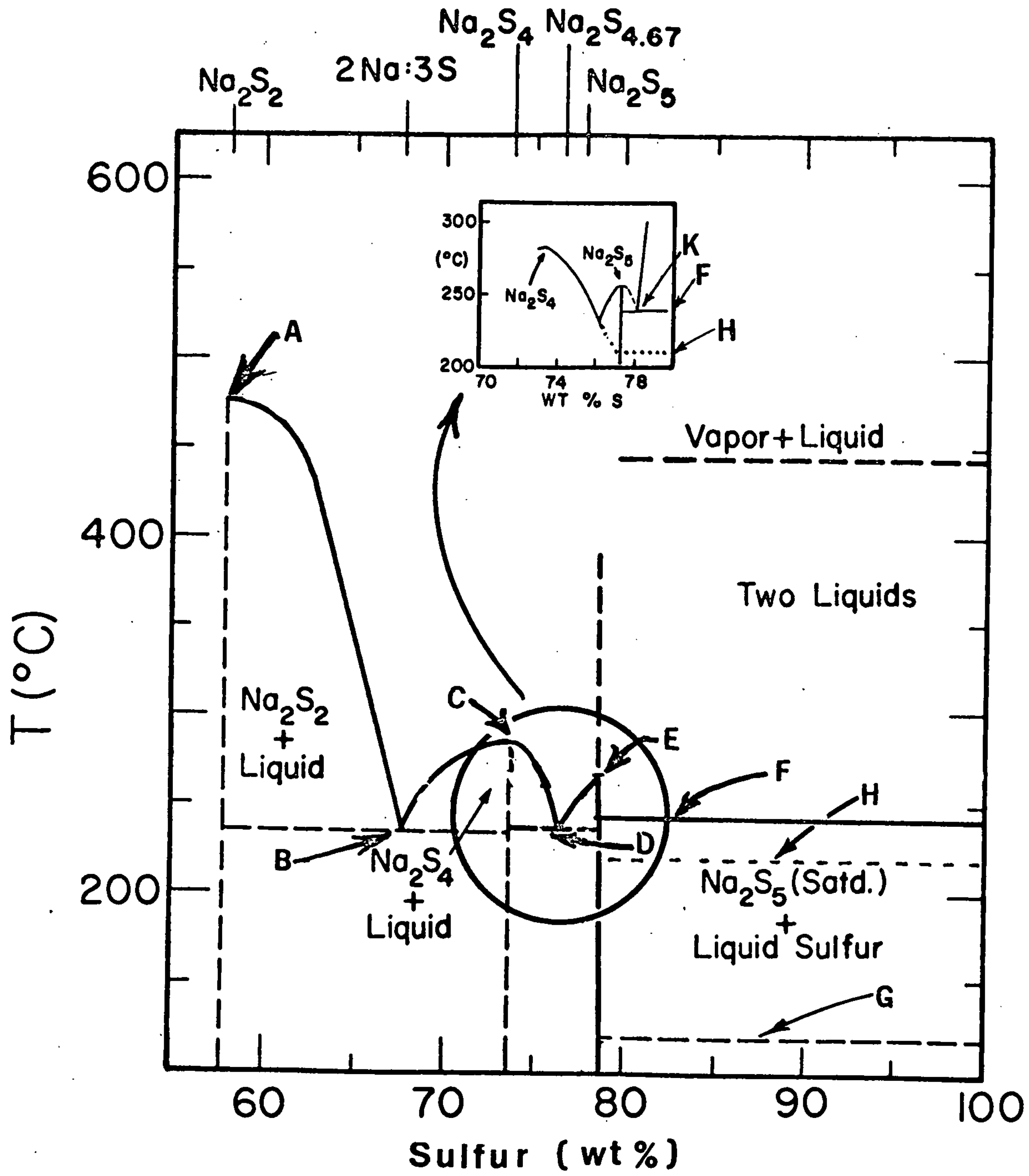
The preparation and characterization of some of the sodium polysulfides has been undertaken as the first task, and is in progress. The phase-diagram for the Sodium-Sulfur system, particularly for the composition range: Na_2S_2 - Sulfur is shown in Figure 1 and summarized in Table 2. The compositions that were selected for the thermophysical studies are: Na_2S_2; Na_2S_3; Na_2S_4 and Na_2S_5.

A comparison of reported melting points data for this series of polysulfides is summarized in Table 3. The need for further careful measurements is apparent if these temperatures are to be of use as reference points for characterization measurements. Inspection of the phase diagram (Figure 1) also shows that the trisulfide is a eutectic mixture of the two flanking polysulfides, Na_2S_2 and Na_2S_4, respectively, whereas the di, tetra- and pentasulfides occur as well defined compounds. From the somewhat "flat" maxima for the tetra- and pentasulfides, some instability in the molten phases of the tetra and penta may be inferred (i.e., a tendency to dissociate or disproportionate to the polysulfides that flank these compositions).

Preparation (and analytical characterization) of the sodium polysulfides to be used for the thermochemical measurements of this program has been initiated and is in progress. The status of this sub-task is summarized in Table 4.

Figure 1

Phase diagram of the Na - S system for the composition range: Na_2S_2 to 100% Sulfur.



Data from refs. [4] and [6]

[4] E. Rosen and R. Tegman, Chemica Scripta, 2, 221 (1972)

[6] N. K. Gupta and R. P. Tischer. J. Electrochem. Soc., 119, 1033 (1972).

Table 2

Na-S Phase Diagram: Salient Features

Location in Phase Diagram (see: Figure 1)	Characterization and Composition(s)
A	invariant point; Na_2S_2 (peritectic point) composition.
B	three phase line; solids Na_2S_2 and Na_2S_4 and liquid of Na_2S_3 composition, in equilibrium at this eutectic line
C	invariant point; Na_2S_4 compound composition.
D	three phase line; solids Na_2S_4 and Na_2S_5 and liquid of composition $Na_2S_{4.67}$, in equilibrium at this eutectic line
E	invariant point; Na_2S_5 compound composition.
F	three phase line; Na_2S_5 (solid) and two immiscible liquids, one polysulfide-rich (ℓ_1), and the others, sulfur-rich (ℓ_2)
G	three phase line; Na_2S_5 and Sulfur (solids) and ℓ_2
H	three phase line (metastable state); Na_2S_x (solid) and ℓ_1, ℓ_2
K	three phase line; Na_2S_5 and ℓ_1 and ℓ_2; the intersection point extrapolates to a polysulfide composition of $Na_2S_{5.37}$

Table 3

Melting Point Data for the Na_2S_2-Sulfur Composition
Range of the Na-S System

Location in Phase Diagram (refer: Fig. 1)	Temperature, t (°C)			
	Tegman [4]	Tischer [6]	Janz-76 [5]	Additional
Na_2S_2 (A)	478° ± 5°	475°	484°	455° [7]
three phase line (B)	240° ± 2°	235°	230°	-
Na_2S_4 (C)	294° ± 2°	285°	292°	280° [7]
three phase line (D)	248° ± 2°	237°	-	-
Na_2S_5 (E)	270° ± 5°	258°	254°	255° [7] 258° [8]
three phase line (F)	253° ± 2°	242°	-	-
three phase line (G)	118° ± 2°	118°	-	-
three phase line (H)	227°	-	-	-
three phase line (K)	253° ± 2°	-	-	-

[4] Tegman, R., Ph.D. Thesis, Umea, Sweden (1974); see also; R. Tegman, et. al., Acta Chemica Scand., 25, 3329 (1971); Chemica Scripta, 2, 63, 221 (1972).

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[7] LeToffe, J. M., et. al., Bull. Soc. Chim. Fr., 3(4) 395 (1976).

[8] Feher, F., and Berthold, H. J., Z. anorg. allg. Chem., 273, 144 (1953).

Table 4

Summary of Polysulfides Preparative Sub-Tasks and Status

[Status of Work: A, completed; B, in progress; C, next priority; D, under consideration]

System	Status	System	Status
Sodium Polysulfides		Potassium Polysulfides	
Na_2S_2	B	-	
Na_2S_3	A,B	K_2S_3	C
Na_2S_4	B	K_2S_4	C
Na_2S_5	B	K_2S_5	C
		K_2S_6	C
Lithium Polysulfides		Rubidium Polysulfides	
Li_2S_2	D	Rb_2S_2	
$Li_2S_{2.9}$	D	Rb_2S_3	
Li_2S_4	D	Rb_2S_4	
		Rb_2S_5	D
		Rb_2S_6	D
Cesium Polysulfides		Others	
Cs_2S_2		BaS_2	
Cs_2S_3		BaS_3	B,C
Cs_2S_4		SrS_2	
Cs_2S_5	D	SrS_3	
Cs_2S_6	D	$BaS_4 \cdot H_2O$	

2. The MSDC-RPI DSC Facility

In the present period a DSC Facility has been designed and assembled from commercially available units. The facility centers around a Perkin-Elmer DSC Model-2 calorimeter as the basic component with accessories for base-line corrections, graphical recording, computer-assisted data acquisition and data analysis system, and the quantitative accurate measurement of small masses as required for this calorimetric technique.

The facility also includes a series of sample pan crimping presses and glove bags, suitable for mass determinations and sample encapsulations under inert atmospheres. The salient components of this facility are listed in Table 5, together with acquisition information.

In addition to the assembly of the above facility, several sub-tasks were undertaken to "run-in" the DSC-2 calorimeter, viz:

- preparation for a "User's Guide" for operation of the Perkin-Elmer DSC-2 and SAZ Accessory

  This was undertaken to supplement the Perkin-Elmer manual; emphasis is placed on the precautionary measures to be observed and the manipulation of the various instrumental controls to obtain optional temperature scans [9]

- calibration of the DSC-2 instrument for temperature and energy measurements in the range from 50°C to 730°C

The purpose of this task was to supplement the manual operational mode of the DSC-2 instrument with an automated mode for: integration and base-line correction (enthalpies of fusion, transition, and chemical reaction), and the measurement of smaller heat effects (heat capacities). This consisted of two tasks. An interface to connect the DSC-2 directly with the Cromemco Z-2 minicomputer was needed. This has been designed and was constructed for this purpose. Computer programs (Software-Packages) were required for the energy measurements and data-base storage capabilities. The software for the integration (heats) fusion, transition, reaction) has been completed, evaluated, and is operational.

- ancillary facilities

  For the small mass measurements (milligram, amounts, accurate to microgram increments) a Kahn Microbalance has been obtained as a dedicated facility. All measurements with extremely hydroscopic materials (e.g., polysulfides) are accomplished in a dry isolation chamber under dry argon or nitrogen at atmospheric pressure. Use of the Kahn balance to monitor the atmosphere (with polysulfide in an open pan on the balance) has been found to be an extremely sensitive technique for environment integrity.

Various sample sealing procedures have been examined and tested using an ancillary furnace to cycle the specimens thermally (to 400°C), followed by leak tests. A technique for hermetically sealing polysulfides to withstand such thermal cycles has been achieved. The entire sealing assembly is used with the Kahn balance in the same dry isolation chamber, i.e., to by-pass exposure to atmospheric moisture in this procedural step.

Table 5

The MSDC-RPI DSC-2 Facility

Component or Item			
#	Part	Description	Acquired
		<u>A: The calorimeter</u>	
1	DSC-2	Perkin-Elmer DSC-2 and programmable controller (50°-730°C)	1979 (this contract)
		<u>B: Manual mode</u>	
2	XY	Honeywell x-y recorder	1978 (RPI)
3	SAZ	P-E scanning auto-zero (base line correction)	1979 (this contract)
4	P	planimeter	1977 (RPI)
		<u>C: Computer mode: Hardware</u>	
5	CrZ-2	Cromemco micro-processor	1979 (RPI)
6	TTVD	Textronix Terminal $\bar{c}$ visual display	1978 (RPI)
7	THCD	Textronix Hard Copy display	1978 (RPI)
8	CrDDD	Cromemco Dual Disc Drive	1979 (RPI)
9	INTF	MSDC-RPI Interface, coupling (1) and (5-8)	1979 (RPI)
		<u>D: Sample Facilities</u>	
10	KMB	Kahn microbalance	1979 (this contract)
11	PE-SP	P-E sample crimping presses (3 kinds)	1979 (this contract)
12	ISC	Isolation chambers, dry gases, etc.	1979 (RPI)
		<u>E: Computer mode: Software Packages</u>	
13	DISCOLL	data-collection programs	1979 (RPI)
14	H-UTINT	enthalpy measurement programs	1979 (RPI)
15	C-UTINT	heat-capacity measurement programs	in progress; 1979 (RPI)

3. Thermophysical Property Measurements

The thermophysical property measurements to date have been largely those necessary to complete the following:

- temperature calibrations for the temperature range: 50°-730°C
- energy calibration measurements (for ΔH°_{fus}; ΔH°_{trans} measurements)

In addition some measurements [for the enthalpy of fusion (and entropy)] for potassium nitrate, KNO_3, and sodium trisulfide, Na_2S_3, have been initiated.

For the calibrations, the reference materials and calibration points were: Indium metal (m.pt. 156.62°C, ΔH°_f, 6.79 cal/g); Tin metal (m.pt. 231.64°C, ΔH°_f, 14.45 cal/g); Lead metal (m.pt. 326.46°C; ΔH°_f, 5.50 cal/g); Zinc metal (m.pt. 418.52°C, ΔH°_f, 25.9 cal/g); Potassium Sulfate, K_2SO_4 (m.pt. 583.12°C, ΔH°_f, 7.95 cal/g) and Potassium Chromate, K_2CrO_4 (m.pt. 670.70°C; ΔH°_f, 8.50 cal/g).

Temperature correction factors for the measurement range from 50°C to 730°C (upper limit, DSC-2) were thus determined.

Enery calibration for enthalpy measurements, using the preceding reference data base, have been in progress, and the "Instrument Constant" has thus been gained. With these data, the measurements can be extended to quantitative determination of the transition temperatures (solid-state transitions; melting points) and the corresponding enthalpies.

Energy calibration measurements to establish the instrument constants for heat capacities remain to be undertaken.

The status of the thermophysical properties measurements tasks is summarized in Table 6. Relative to the calibration cross-check measurements for ΔH°_f, KNO_3 is currently under investigation. In addition, aliquots of Na_2S_3 (see earlier, this report) are being used for first such exploratory measurements. The results may be summarized as follows:

$\underline{KNO_3}$: ΔH°_{fus}, 2397 cal/mol
T_f 335.0°C (cf. lit. 2400 cal/mol [12-17])

$\underline{Na_2S_3}$: ΔH°_{fus}, 5538 cal/mol;
T_f 238.7°C ΔS°_{fus}, 10.8_3 cal/deg mol

The values for the trisulfide are "first-time" values; literature data (for comparison) are non-existent.

Pronounced super-cooling of the polysulfide melts (presumably due to formation of the glassy state) is observed; super-cooling to some 150° below the melting point (freezing point), 238°C, is observed. These observations confirm the super-cooling effects noted by Tegman [4] in the studies of the phase-equilibrium diagram using the techniques of hot-stage microscopy and thermal analysis.

Table 6

Thermophysical Properties Measurements: Status

[Status of Work: A, completed; B, in progress; C, to be undertaken; D, under consideration]

Task	Status
1. Temperature calibration - DSC-2	A
2. Energy calibration -DSC-2	
heats: ΔH_f; ΔH_{trans}	A,B
heat capacity: Cp	B,C
3. Calibration cross-check measurements	
heats: ΔH_f, ΔH_{trans}	B
heat capacities	C
4. Sodium polysulfides	
Na_2S_3	A,B
Na_2S_4, Na_2S_5 and mixtures	C
trace impurity effects	C
5. Potassium Polysulfides, Barium Polysulfides	C
6. Lithium, Rubidium and Cesium Polysulfides	D

The interpretation of these results for Na_2S_3 in terms of "ionic-melting" is in progress; however the results (above) are provisional and additional measurements using a series of Na_2S_3 samples (prepared by different synthetic routes) are in progress.

IV. Meetings, Lectures and Discussions

Meetings:

1. Sodium Sulfur Battery Review: General Electric Research Company, Research and Development Laboratory, Schenectady, N.Y. (1979).
2. International Molten Salts Symposium: Meeting of the International Society of Electrochemistry, Trondheim, Norway (August, 1979).
3. High Temperature Battery Symposium: National Meeting of the Electrochemical Society, Los Angeles, CA (October, 1979).
4. DOE Battery and Electrochemical Contractor's Conference, Arlington, VA (December, 1979).

Lectures:

Based on present project (Thermophysical properties measurements: molten polysulfides): none

Discussions:

R. Tischer (Ford, Detroit, F. Ludwig, Ford-Aeronautronic): Na-S battery system and this project.

M. Breiter, Bruce Dunn (General Electric Co.): data needs for the Na-S battery development program.

H. V. Venketasetty (Honeywell Corporate Research Center): lithium metal techniques, lithium battery research.

J. Braunstein (ORNL), F. Marikar (Gould), and R. Murphy (Wilson Greatbatch): in areas of molten salts and alkali metal techniques.

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[2] Ibid, II. Molten Salts: Data on Single and Multi-Component Salt Systems", G. J. Janz, C. B. Allen, N. P. Bansal, R. M. Murphy, and R. P. T. Tomkins, (MSDC-RPI); Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (US), 61, Part II, (April 1979); U. S. Gov't Printing Office, Washington, D. C. 20402.

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