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Melting and Premelting Properties of the KNO_3–$NaNO_2$–$NaNO_3$ Eutectic System

George J. Janz* and Giai N. Truong

Cogswell Laboratory, Rensselaer Polytechnic Institute, Troy, New York 12181

The melting and premelting properties of the KNO_3–$NaNO_2$–$NaNO_3$ eutectic system (mp 140 °C) have been investigated by the technique of differential scanning calorimetry, from ambient temperatures to ~520 °C (790 K). The enthalpies of fusion and solid-state transitions, and the heat capacities for this system in the polycrystalline and molten states, have been measured and are reported. Measurements of these properties were extended to $NaNO_2$, and these results are also reported.

The eutectic mixture 53 wt % KNO_3–40 wt % $NaNO_2$–7 wt % $NaNO_3$ has been used since 1937 as a heat-transfer medium (*1*, *2*) because of its low cost and good compatibility with common structural materials. This mixture is known as HTS_1 (heat-transfer salt) and also as HITEC (Du Pont trade name). For additional background information, see the recent survey by Rottenburg (*2*). The present study was aimed at obtaining more reliable enthalpy of fusion and heat capacity data in connection with evaluations of this eutectic relative to thermal storage in electric utility load leveling concepts and in solar energy utilization projects. Measurements were extended to investigations of the solid-state-transition data and to an investigation of $NaNO_2$, and these results are also reported.

The differential scanning calorimetric facility and its application to other salt systems, such as sodium polysulfides and the $NaNO_3$–KNO_3 system (HTS_2; drawsalt), have been described elsewhere (*3–5*), and it is sufficient here to note some of the experimental points relative to the present measurements. The accuracy limits of the calorimetric measurements were established to be as follows: temperature, ~±0.5 °C; enthalpies, ~±1.0%; and heat capacities, ~±2.0%. Aluminum and gold DSC sample pans were used respectively for measurements in the lower and higher temperature ranges. Measurements were made with instrument heating and cooling rates of 10 K min^{-1}, and with the rate of energy input set at 0.5 mcal min^{-1}. The in-capsule DSC technique developed in this laboratory (*3–5*) was used throughout for all sample preparations.

Spectroscopic grades of KNO_3, $NaNO_2$, and $NaNO_3$ (purities, 99.999%) were used after oven drying at 150 °C under dynamic vacuum to remove ambient atmospheric moisture. The data sets for the enthalpies were based on a series of five (repetitive) sets of measurements; for the heat capacities two sets of measurements, similarly, were made for each sample. The results for HTS_1 and $NaNO_2$ are summarized in Tables I and II, respectively. For $NaNO_3$ and KNO_3, see ref *5*.

***HTS_1*.** Solid-state-transition data for HTS_1 have not been measured earlier so that intercomparisons are not possible. The only earlier investigation of the enthalpy of fusion is that of Goodwin and Kalmus (drop calorimetry) (*6*). They reported a value of 1.9 kcal mol^{-1}, i.e., a value ~33% lower than that found in the present work, i.e., 2.52 kcal/mol^{-1}. In the technique of drop calorimetry, the enthalpy of fusion is derived from melt → solid transition measurements, i.e., crystallization change, whereas, with the DSC technique, the enthalpy data are derived from both the process of melting and the process of crystallization. The DSC technique, thus, is a preferred approach for such melting–crystallization studies since the opportunity for cross-check measurements is an inherent part of this method. The lower value in the earlier study would be understood if only a partial crystallization had occurred in the "drop" technique. The melting point for HTS, observed in the present work, i.e., 140 °C (413 K), is in exact accord with the literature value, 140 °C (see ref *1* and *2*).

Table I. Melting and Premelting Enthalpies for HTS_1 and $NaNO_2$

	HTS_1	$NaNO_2$
Solid-State Transition		
T_{tr}, K	363	437
ΔH_{tr},^{a} kcal mol^{-1}	0.750	0.420
Solid-Liquid Transition (Melting-Crystallization)		
T_{mp}, K	413	554
ΔH_{fus},^{a} kcal mol^{-1}	2.52	3.34

^{a} For conversion to SI units, 1 cal = 4.184 J; for the mixture, HTS_1, the "molecular weight" is calculated from the principles of mole fraction additivity and the molecular weights of the single salts.

Table II. Heat Capacity Data for HTS_1 and $NaNO_2$

HTS_1		$NaNO_2$	
T, K	C_p,^{a} cal mol^{-1} deg^{-1}	T, K	C_p,^{a} cal mol^{-1} deg^{-1}
330	24.28	330	22.49
340	25.12	350	22.89
350	30.41	400	28.71
363	solid-state transition	420	32.96
413	mp	437	solid-state transition
440	31.42	450	31.40
450	31.41	480	31.09
500	31.96	500	31.82
550	31.84	554	mp
600	31.14	570	28.61
650	30.92	600	28.63
700	30.71	630	28.17
750	30.75	650	27.71
790	30.64	670	27.50

^{a} For conversion to SI units, see footnote of Table I.

The heat capacity results in the present work (Table II) agree quite well with the results reported by Goodwin and Kalmus (*6*): solid, C_p = 26.96 cal mol^{-1} deg^{-1} (300–400 K); liquid, C_p = 31.42 cal mol^{-1} deg^{-1} (420–850 K). The results reported by Voskresenskaya et al. (*7*) could not be reproduced: solid, C_p increases from 38.58 (304 K) to 42.67 (409 K) cal mol^{-1} deg^{-1}; liquid, C_p decreases from 51.8 (430 K) to 36.6 (775 K) cal mol^{-1} deg^{-1}. These results appear incorrect, but there are insufficient details given in the communication (*7*) to understand the possible causes for these departures.

***$NaNO_2$*.** The melting point (281 °C) is virtually in exact agreement with that reported by Kozlowski and Bartholemew (*8*), i.e., 282 °C. The enthalpy of fusion reported by Voskresenskaya et al. (*7*), i.e., 3.0 kcal mol^{-1}, is about 10% lower than the value from the present measurements (Table I; 3.34 kcal mol^{-1}). No earlier enthalpy values for the solid-state transition in $NaNO_2$ were found.

The solid-state heat capacity data (Table I) may be expressed by the equations

$$C_p = 174.692 - 0.915T + 0.00137T^2 \quad (330\text{–}420\ \text{K})$$

$$C_p = 453.823 - 1.809T + 0.00193T^2 \quad (450\text{–}500\ \text{K})$$

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The heat capacity data for molten $NaNO_2$ show a slight negative temperature dependence over the temperature range investigated (570-670 K). Attempts to extend the measurements to higher temperatures were unsuccessful, due to the onset of higher noise-to-signal levels, and due to sample-pan seal ruptures. For a discussion of the possible factors contributing to these difficulties, see ref *5*.

Inspection of the heat capacity data reported for $NaNO_2$ by Voskresenskaya et al. (*7*) shows that for the solid state the agreement is good with the presently reported values; however, for the liquid state there is marked disagreement. Thus, from 570 to 630 K, Voskresenskaya et al. (*7*) reported that the C_p values decrease from 42.1 to 39.2 cal mol^{-1} deg^{-1}; the results from the present measurements are, in comparison, as follows: 570 K, 28.6 cal mol^{-1} deg^{-1}; 630 K, 28.2 cal mol^{-1} deg^{-1}, respectively. During the preparation of our present communication, density and heat capacity data for the molten $NaNO_2$–KNO_3 system were reported by Iwadate et al. (*9*); as part of their investigation, measurements for molten $NaNO_2$ were also undertaken. For $NaNO_2$, C_p was found to be 27.89 cal mol^{-1} deg^{-1} and to be constant at this value ($\sim\pm1\%$) over the temperature range 571-630 K. The accuracy of our method is estimated to be $\sim\pm2.0\%$ in heat capacity measurements; i.e., the results are in accord with ref *9* within the limits of accuracy of the measurement technique.

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Registry No. KNO_3, 7757-79-1; $NaNO_2$, 7632-00-0; $NaNO_3$, 7631-99-4.

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Excess Enthalpies of Cycloheptane + *n*-Alkane and Cyclooctane + *n*-Alkane

Emmerich Wilhelm*
Institut für Physikalische Chemie, Universität Wien, A-1090 Wien, Austria

Americo Inglese
Istituto di Chimica Fisica, Università di Bari, Bari, Italy

Jean-Pierre E. Grolier
Laboratoire de Thermodynamique et Cinétique Chimique, Université de Clermont II, F-63170 Aubière, France

Molar excess enthalpies H^E have been measured as a function of composition at 298.15 K and atmospheric pressure for each of the binary liquid mixtures cycloheptane (c-C_7H_{14}) + *n*-heptane, + *n*-nonane, + *n*-tetradecane, and cyclooctane (c-C_8H_{16}) + *n*-heptane, + *n*-nonane, and + *n*-tetradecane with a flow calorimeter of the Picker design, equipped with separators. In both series H^E increases with increasing chain length *n* of the *n*-alkane, with the increments per CH_2 group being smaller for the cyclooctane series than for the cycloheptane series. At equimolar composition, $H^E(x = 0.5)/(J\ mol^{-1})$ of c-C_7H_{14} + *n*-C_nH_{2n+2} is 234.2 for $n = 7$, 267.0 for $n = 9$, and 357.6 for $n = 14$, respectively, and that of c-C_8H_{16} + *n*-C_nH_{2n+2} is 226.6 for $n = 7$, 249.3 for $n = 9$, and 322.8 for $n = 14$.

Introduction

In a series of articles (*1–6*), we recently reported molar excess enthalpies H^E of binary liquid mixtures composed of either a five- or a six-membered cyclic ether and various second components, ranging from *n*-alkanes to *n*-alkanoic acids. In addition, molar excess volumes were determined, as a function of temperature, for several mixtures of cyclic ether + *n*-alkane (*7*). In order to obtain more information as to the influence of (a) ring size and (b) chain length of the *n*-alkane, we measured calorimetrically H^E for the six binary mixtures cycloheptane (c-C_7H_{14}) + *n*-heptane, + *n*-nonane, + *n*-tetradecane, and cyclooctane (c-C_8H_{16}) + *n*-heptane, + *n*-nonane, and + *n*-tetradecane at 298.15 K and atmospheric pressure, thus complementing literature data on cyclopentane + *n*-alkane (*8*) and cyclohexane + *n*-alkane (*9*). These measurements will be used later for a comprehensive discussion, in terms of group-contribution theory (*10*), of the thermodynamic behavior of mixtures containing cyclic ethers.

Table I. Experimental Densities ρ of Pure Liquids at 298.15 K and Comparison with Selected Literature Data

	$\rho/(kg\ m^{-3})$	
compd	exptl	lit.
cycloheptane	806.9	806.56 (*13*)
cyclooctane	832.1	832.02 (*13*)
n-heptane	679.3	679.51 (*14*)
n-nonane	713.9	713.81 (*14*)
n-tetradecane	759.3	759.3 (*14*)