# Density and Heat Capacity of Molten $NaNO_2$–$KNO_3$ Mixtures

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**The density and the heat capacity of molten $NaNO_2$–$KNO_3$ mixtures have been measured at ambient pressure with dilatometry and differential scanning calorimetry (DSC), respectively. The molar volume of the mixtures is expressed by $V_m = 38.983 - 1.100X - (1.497 \times 10)X^2 + 7.987X^3 + (0.02400 - 0.02726X + 0.03415X^2 - 0.01875X^3)T$, where $V_m$ is in $cm^3\ mol^{-1}$, $X$ is the mole fraction of $NaNO_2$, and $T$ is the absolute temperature. The thermal expansivities of the mixtures slightly increase with temperature. The heat capacities of pure $NaNO_2$ and $KNO_3$ are estimated at $116.7 \pm 0.6\ J\ mol^{-1}\ K^{-1}$ (571–630 K) and $141.0 \pm 1.3\ J\ mol^{-1}\ K^{-1}$ (630–700 K), respectively. Comparison of the present data of pure $KNO_3$ with those obtained with drop calorimetry shows that the DSC method can yield reliable data also for these mixtures.**

## Introduction

Molten mixtures of $NaNO_2$ and $KNO_3$ are promising as heat reservoir materials (*1*) owing to the low melting points (*2*) and expected high heat capacities.

For obtaining the thermal conductivity, one needs data on the density, the heat capacity, and the thermal diffusivity, the last one now being measured separately with wave-front-shearing interferometry (*3–5*). The densities of the mixtures have been measured with an Archimedes method by Polyakov and Berull (*6*). In the present work, we have remeasured the densities with a dilatometric method. The heat capacities are measured with a differential scanning calorimeter by the method of Angell et al. (*7*).

## Experimental Section

***Chemicals.*** The salts $NaNO_2$ and $KNO_3$ used were of analytical reagent grade. A small amount of moisture which might have been contained was removed with a procedure similar to that previously reported (*8*). The mixtures were prepared by mixing the two salts of known weight, melting, and allowing them to cool. Ultraviolet spectrophotometry (*9*) was used to check that the $NaNO_2$ and $KNO_3$ contained virtually no $NO_3^-$ and $NO_2^-$ ions, respectively. With the same method it was ascertained that the ratio between $NO_2^-$ and $NO_3^-$ ions remained unchanged during the density and heat capacity measurements within the analytical errors.

***Density Measurements.*** A dilatometric method was employed. The apparatus (see Figure 1) was similar to that used by Cho et al. (*10*) or Kawamura (*11*). The electric furnace was made of a transparent fused-silica tube whose external diameter and length were 30 mm and 30 cm, respectively. In order to keep the temperature distribution along the vertical direction as uniform as possible, a stainless-steel tube was inserted inside the fused-silica tube. Two small windows were made so that the meniscus in the dilatometer could be observed with a cathetometer. The crevice between the dilatometric cell and the stainless-steel tube, both at the top and at the bottom, was stuffed with quartz wool. The dilatometric cell was made of transparent fused silica. The volume of the part containing the salts was about 3 $cm^3$ and the inside diameter of the dilatometer was 5 mm. The errors caused by the thermal expansion of fused silica ($5.5 \times 10^{-7}\ K^{-1}$ (*12*)) were negligible in the investigated temperature range; that is, these are estimated at about 0.05% of the density data at most. The cell was calibrated with distilled water at room temperature according to the density data reported by Kell (*13*). The level of the meniscus was read at several temperatures by stopping the rise of temperture for about 5 min. The stability of the temperatures at the measured points was estimated at ±0.3 K.

Table I. Experimental Results of Densities of Molten $KNO_3$ and $NaNO_2$

| $10^{-3}\rho$, kg $m^{-3}$ | temp range, K | $10^{-3}\rho$ at 630 K, kg $m^{-3}$ | ref |
|---|---|---|---|
| | $KNO_3$ Melt | | |
| $2.315 - (0.729 \times 10^{-3})T$ | 620–873 | 1.856 | *19* |
| $2.3479 - (0.7758 \times 10^{-3})T$ | 617–671 | 1.8591 | *16* |
| $2.310 - (0.733 \times 10^{-3})T$ | 619–778 | 1.848 | *20* |
| $2.340 - (0.77 \times 10^{-3})T$ | 613–773 | 1.850 | *6* |
| $2.375 - (0.804 \times 10^{-3})T$ | 632.7–701.4 | 1.868 | this work |
| | $NaNO_2$ Melt | | |
| $2.226 - (0.746 \times 10^{-3})T$ | 568–723 | 1.771[b] | *19* |
| $2.2026 - (0.69 \times 10^{-3})T$ | *a* | 1.7817[b] | *15* |
| $2.129 - (0.60 \times 10^{-3})T$ | 573–773 | 1.766[b] | *6* |
| $2.149 - (0.571 \times 10^{-3})T$ | 600.4–620.5 | 1.801[b] | this work |

[a] Unspecified in the literature (*15*). [b] At 610 K.

***Heat Capacity Measurements.*** A Perkin-Elmer Model DSC-2 differential scanning calorimeter was used. A synthetic sapphire crystal was used as a reference material (*14*). The samples investigated were prepared by putting a small amount of the chemicals on a weighed sample pan, covering with a lid, and keeping them melting for about 30 min so as to obtain good contact with the pan. Calibration runs were carried out by using the same pans as the ones used for the reference material and the samples. Two kinds of pans, gold and aluminum, were used, and no differences in the measured quantities were found. No weight loss of the pans containing the salts was detected during one run of measurement. This indicated that neither evaporation nor decomposition of the samples occurred and that the samples probably did not react with the pans. The heat capacities were measured by raising the temperature at a rate of 20 K $min^{-1}$.

## Results and Discussion

***Molar Volume.*** The data on the densities of pure $NaNO_2$ and $KNO_3$ are given in Table I where they are compared with some other available data; our data for $NaNO_2$ and $KNO_3$ are close to those obtained by Frame et al. (*15*) and by Smith and Artsdalen (*16*), whose deviations fall 1.08% at 610 K and 0.48% at 630 K, respectively. This would show that our method yields approximately satisfactory data also for the mixtures. It is, however, noted that our dilatometric method tends to give a little greater value than those of the previous authors, and Polyakov and Berull (*6*) obtained smaller values.

Since it has been reported that $NaNO_2$ decomposes into $NaNO_3$ and $N_2$ above 603 K (*17*), the densities have been

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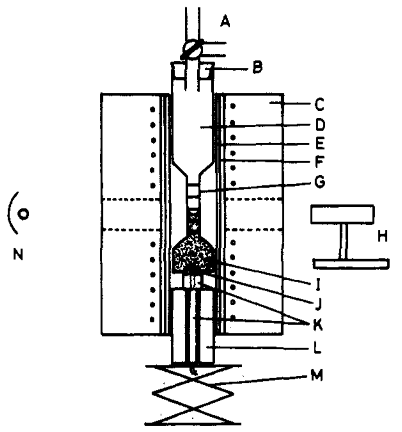

**Figure 1.** Dilatometer and support assembly: (A) three-way cock, (B) silicone stopper, (C) electric furnace, (D) loading tube, (E) stainless-steel tube, (F) fused-silica tube, (G) dilatometer, (H) cathetometer, (I) sample melt, (J) CA thermocouple, (K) alumina sheath, (L) alumina brick, (M) laboratory jack, (N) light source.

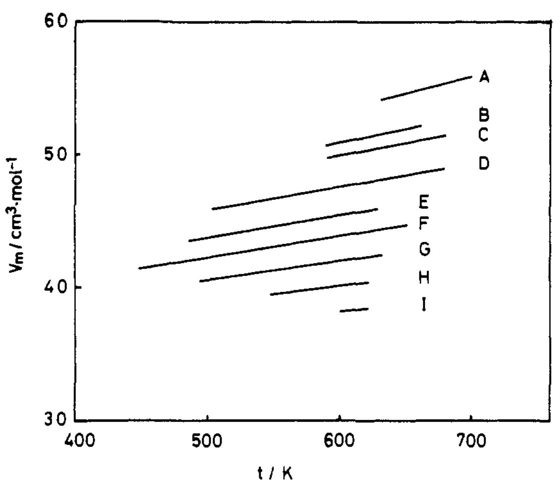

**Figure 2.** Molar volumes of molten $NaNO_2$-$KNO_3$ mixtures: (A) 0.00, (B) 13.08, (C) 22.35, (D) 37.73, (E) 50.14, (F) 62.46, (G) 74.84, (H) 87.39, and (I) 100.00 mol % $NaNO_2$.

Table II. Density Equations of Molten $NaNO_2$-$KNO_3$ Mixtures[a]

| $X(NaNO_2)$, mol % | $10^{-3}a$, kg $m^{-3}$ | $10^{-3}b$, kg $m^{-3}$ $K^{-1}$ | $\sigma$, kg $m^{-3}$ | temp range, K | exptl point |
|---|---|---|---|---|---|
| 0.00 | 2.375 | 8.04 | 1.03 | 632.7-701.4 | 14 |
| 13.08 | 2.357 | 7.54 | 0.44 | 588.8-662.1 | 34 |
| 22.35 | 2.332 | 7.43 | 0.73 | 552.9-680.7 | 54 |
| 37.73 | 2.289 | 6.94 | 0.63 | 504.3-678.8 | 66 |
| 50.14 | 2.308 | 7.30 | 0.81 | 486.3-629.5 | 59 |
| 62.46 | 2.256 | 6.84 | 0.69 | 447.7-650.7 | 79 |
| 74.84 | 2.206 | 6.16 | 1.12 | 494.2-631.8 | 51 |
| 87.39 | 2.186 | 6.07 | 0.92 | 547.5-621.9 | 31 |
| 100.00 | 2.149 | 5.71 | 0.14 | 600.4-620.5 | 10 |

[a] $\rho = a - (b \times 10^{-4})T$; $\sigma$ = standard deviation.

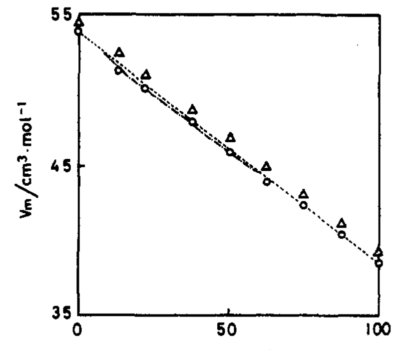

**Figure 3.** Isotherm of molar volumes of molten $NaNO_2$-$KNO_3$ mixtures at 620 K (maximum departure from the additivity: 0.515% at 13.08 mol % $NaNO_2$): (O) this work, (Δ) Polyakov and Beruli, (- - -) additivity, (— · —) eq 2.

Table III. Experimental Results for Heat Capacity of Pure $KNO_3$ Melt

| $C_p$, J $mol^{-1}$ $K^{-1}$ | temp range, K | method | ref |
|---|---|---|---|
| 130 ± 0[a] | 653 | drop calorimetry | 21 |
| 135.6 ± 2.1 | 610-663 | drop calorimetry | 22 |
| 141.0 ± >2.8[a] | 611-684 | drop calorimetry | 23 |
| 141.0 ± 1.3 | 630-700 | DSC | this work |

[a] Heat capacity estimated from the data in the literature.

Table IV. Heat Capacities of Molten $NaNO_2$-$KNO_3$ Mixtures

| $X(NaNO_2)$, mol % | $C_p$, J $mol^{-1}$ $K^{-1}$ | temp range, K |
|---|---|---|
| 0.00 | 141.0 ± 1.3 | 630-700 |
| 24.84 | 133.5 ± 1.3 | 549-700 |
| 52.41 | 123.8 ± 1.7 | 548-700 |
| 74.92 | 122.6 ± 1.7 | 548-700 |
| 100.00 | 116.7 ± 0.8 | 571-630 |

measured in a relatively limited temperature range in the present work. Both thermal decomposition and evaporation are negligible since no weight loss of the samples was detected during experiment.

The measured densities can be well expressed with linear functions of temperature as listed in Table II. The original data for the $NaNO_2$-$KNO_3$ mixtures are provided as supplementary material. (See paragraph at end of text regarding supplementary material.) The molar volumes calculated from the densities are illustrated in Figure 2. The composition dependence of the molar volumes at 620 K is shown in Figure 3, which reveals that the measured values deviate slightly negatively from the additivity. The data obtained by Polyakov and Beruli (*6*) are also shown in Figure 3 for comparison. Our data are about 2% greater than theirs over the measured composition range.

We have tried to apply to the molar volume $V_m$ an empirical equation of the form proposed by Mochinaga et al. (*18*):

$$V_m = \sum_0^3 a_n X^n + \left(\sum_0^3 b_n X^n\right)T \tag{1}$$

where $a_n$ and $b_n$ are constants, $X$ is the mole fraction of $NaNO_2$, and $T$ is the absolute temperature. At first, the values of $a_0$ and $b_0$ are determined at $X = 0$, and those of $a_0 + a_1 + a_2 + a_3$ and $b_0 + b_1 + b_2 + b_3$ are calculated at $X = 1$. Then, the other constants are obtained with a least-squares regression. Thus, the molar volume of these mixtures is represented by

$$V_m = 38.983 - 1.100X - (1.497 \times 10)X^2 + 7.987X^3 + (0.02400 - 0.02726X + 0.03415X^2 - 0.01875X^3)T \tag{2}$$

The standard deviation of this empirical equation from the experimental values is ca. 0.13 $cm^3$ $mol^{-1}$. The thermal expansivities defined as $\alpha = b/(a - bT)$ increase with temperature at all compositions and decrease with mole fraction of $NaNO_2$ at constant temperatures.

***Heat Capacity.*** In order to compare the accuracy of the present work with that of the previous works (*21-23*), we have given the data on the heat capacity of pure $KNO_3$ in Table III. This would indicate that the DSC method yields reliable data. The heat capacities of the $NaNO_2$-$KNO_3$ mixtures averaged over the investigated temperature ranges are tabulated in Table IV. The temperature dependence is not detected above the experimental errors. The additivity is found to hold approximately for the heat capacities of these mixtures.

### Acknowledgment

We express our sincere gratitude to Professor J. Mochinaga for his suggestion in measuring the density.

### Glossary

| | |
|---|---|
| $a$, $b$ | constants of the density equation |
| $a_n$, $b_n$ | $n$th constants of eq 2 |
| $C_p$ | heat capacity at ambient pressure, J mol$^{-1}$ K$^{-1}$ |
| $T$ | temperature, K |
| $V_m$ | molar volume, cm$^3$ mol$^{-1}$ |
| $X$ | mole fraction of $NaNO_2$ |

*Greek Letters*

| | |
|---|---|
| $\alpha$ | thermal expansivity, K$^{-1}$ |
| $\rho$ | density, kg m$^{-3}$ |
| $\sigma$ | standard deviation of the density equation, kg m$^{-3}$ |

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Received for review April 20, 1981. Revised manuscript received October 5, 1981. Accepted February 9, 1982.

**Supplementary Material Available:** All of the original data on the density of molten $NaNO_2$–$KNO_3$ mixtures are listed ( 9 pages). In this data file, the densities of the mixtures are expressed as linear functions of temperature by a least-squares method. Four significant figures are given for density and temperature in each case (for example, 1.795 g cm$^{-3}$ and 620.5 K). Ordering information is given on any current masthead page.

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# Low-Temperature Heat Capacity and Entropy of Oxalic Acid and of Biuret

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**The low-temperature heat capacities of oxalic acid, $(COOH)_2$, and biuret, $NH_2CONHCONH_2$, were measured over the range 10–320 K by adiabatic calorimetry. The heat capacities ($C_p$), entropy ($S°$), and Gibbs function ($(G° - H_0°)/T$) at 298.15 K were calculated to be 25.31, 27.62, and −13.32 cal mol$^{-1}$ deg$^{-1}$, respectively, for oxalic acid and 31.39, 34.91, and −17.53 cal mol$^{-1}$ deg$^{-1}$, respectively, for biuret.**

In a continuing program of the measurement of thermochemical properties of materials of interest in fertilizer technology, the heat capacities of oxalic acid, $(COOH)_2$, and biuret, $NH_2CONHCONH_2$, were measured by adiabatic calorimetry over the temperature range 10–320 K. Related thermodynamic properties were derived.

### Materials and Handling

Oxalic acid dihydrate was prepared by recrystallizing reagent oxalic acid from distilled water and filtering on fritted glass. The damp crystals were transferred to a large crystallizing dish and allowed to dry in the laboratory atmosphere for several days with occasional stirring. Two samples of the air-dried material titrated with standard $KMnO_4$ solution showed the material to contain 100.0% and 100.3%, respectively, of the dihydrate.

The calorimeter was filled with the oxalic acid dihydrate and dried by vacuum desiccation over $MgClO_4$ until the weight loss of the compound was 28.72% (stoichiometric for water of crystallization is 28.58%). The more than theoretical weight loss for the formation of anhydrous oxalic acid was attributed to some sublimation. Samples desiccated in a similar manner to 28.68% weight loss and titrated with standard $KMnO_4$ solution contained 100.2% and 100.2%, respectively, anhydrous oxalic acid. The dry weight was corrected for buoyancy in air on the basis of a density of 1.89 g cm$^{-3}$ (*1*) to give 50.5119 g or 0.561 02 mol in the calorimeter. The gram formula weight was taken as 90.035 84. The air in the calorimeter was replaced with helium by evacuating to a pressure of 100 mm and then relieving to atmospheric pressure with helium. This cycle was repeated twice, and then the pressure was adjusted to give the same mass of helium as was used in measurements on the empty calorimeter.

After the measurements were completed, the calorimeter was opened in the laboratory atmosphere. The material in the calorimeter was caked, and only a small portion could be removed in a dry condition in about 0.5 h. Two samples of this material titrated with standard $KMnO_4$ solution showed the material to contain 99.9% and 99.7%, respectively, anhydrous oxalic acid. The slightly less than theoretical anhydrous oxalic