Thermochimica Acta, 102 (1986) 249–256
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

CALORIMETRIC STUDY OF VITREOUS AND CRYSTALLINE SODIUM METAPHOSPHATE $NaPO_3$

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(Received 25 November 1985)

ABSTRACT

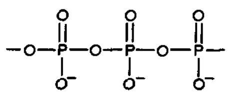
A calorimetric study on the thermodynamic properties of $NaPO_3$ is reported. The heat capacity of crystalline, vitreous and undercooled liquid $NaPO_3$ is measured. It is found that the heat capacity of crystalline orthorhombic α-$NaPO_3$ is described by the Einstein formula with $\theta_E = 516$ K and a pre-exponential constant $A = 144$ J mol^{-1}. The temperature dependence, $\Delta C_p(T)$, of the difference in the heat capacities of the undercooled melt and the crystal is represented by the equation

$$\Delta C_p(T) = 151 - 0.167\, T \text{ J mol}^{-1} \text{ K}^{-1}$$

The enthalpy of melting, $\Delta H_m = 22$ kJ mol^{-1}, the entropy of melting, $\Delta S_m = 24.7$ J mol^{-1} K^{-1}, and the enthalpy of crystallization, $\Delta H_c(T)$, at different temperatures are also determined.

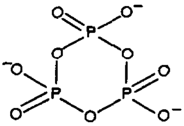
INTRODUCTION

Sodium metaphosphate is a substance which is of interest in many respects. It forms a glass readily (Grahams glass), $(NaPO_3)_x$ [1], whose structure of polymer-like anionic chains is typical of the large group of inorganic glass-forming substances. Hence the structure of vitreous and crystalline $NaPO_3$ has been subject to intensive investigations [1–5]. These investigations have revealed that the main structural units in undercooled $NaPO_3$ melts and in the respective glasses are anionic chains of the type



$$-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-}{|}}{P}}-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-}{|}}{P}}-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-}{|}}{P}}-$$

with a mean degree of polymerisation ranging from 100 to 300 [2,4]. Measurable quantities of anionic rings (up to 10%) are also



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present in molten and vitreous $NaPO_3$ [1,4]. The orthorhombic form, α-$NaPO_3$, is usually obtained upon crystallisation [4]; it is composed of these benzene-like trimetaphosphate structural units, which explains its formula $Na_3[P_3O_9]$. Both this crystalline modification and vitreous $NaPO_3$ are water soluble, a factor which assists structural investigations [1].

Graham's glass is a classical model of the vitreous state, and has been extensively investigated with respect to rheological [6–8] and especially crystallisation aspects. The temperature dependence of the viscosity of $NaPO_3$ has been reported [6,8].

The crystallisation of $NaPO_3$ melts to give the α-$NaPO_3$ form takes place by the structural change described and so is an example of a reconstructive crystallisation process, as shown by detailed investigations [3,4,9,10], where the kinetics of the overall crystallisation rate and its dependence on the dispersion of samples was also studied [11]. The same melt containing active metal cores [12] served as a model for the detailed analysis of the kinetics of nucleation [13,14]. The temperature dependence of the rate of crystal growth of α-$NaPO_3$ from the $NaPO_3$ melt has been determined [15,16].

However very little is known of the thermodynamics of this substance in its different modifications. Existing thermodynamic data for $NaPO_3$ are restricted to an estimation of the enthalpy of melting, ΔH_m, obtained from solubility measurements * ($\Delta H_m = 20.7$ kJ mol^{-1} $NaPO_3$ [17]) and to an estimation of the heat capacity $\Delta C_{p,gl}$ at low temperatures over a relatively limited temperature interval [18]. This substance vitrifies at about 550 K [18] while its melting temperature T_m is 898 K [2]. The lack of detailed information on the thermodynamic properties of $NaPO_3$ restrict the quantitative analysis of the crystallization data.

EXPERIMENTAL

Vitreous $NaPO_3$ was prepared from $NaH_2PO_4 \cdot 2H_2O$ in platinum or porcelain crucibles at 1000°C as described [1,4]. The formation of α-$NaPO_3$ was controlled by X-ray diffraction, paper chromatography and IR spectra [1,4,9,13].

The heat capacity and enthalpy measurements were obtained using three standard instruments: DSC-2 (Perkin-Elmer), Differential Scanning Analyser (Rigacu) and DSM-2(AS USSR). The calorimeters were calibrated by melting pure metals (In, Sn, Pb, Zn) and using synthetic sapphire (Al_2O_3) as a material with a known heat capacity.

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* Hereafter the thermodynamic data are referred to the formula-weight (101.9) of the substance.

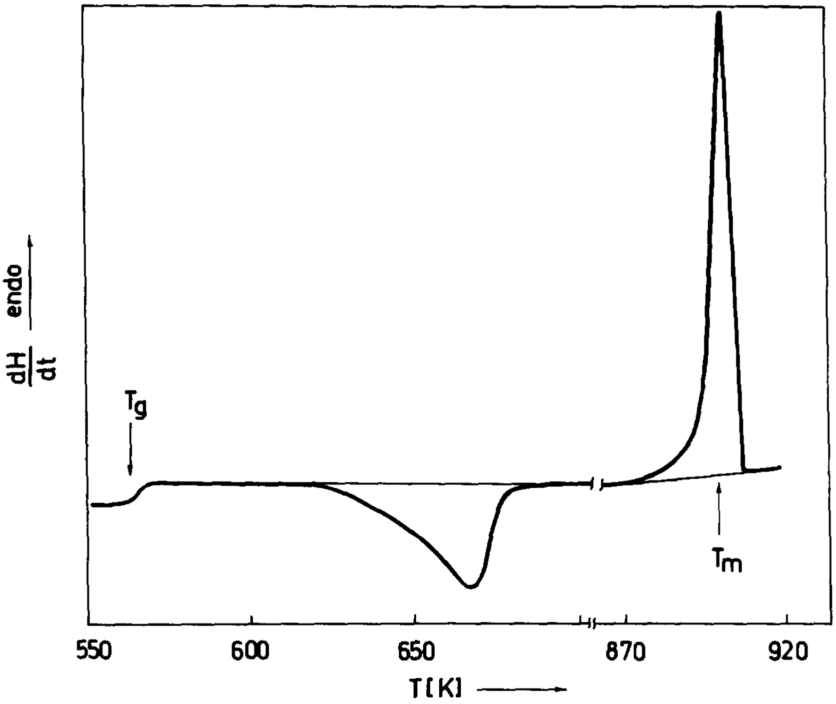

Fig. 1. DSC heating curve of a vitreous $NaPO_3$ sample.

A schematic DSC scan of a sample of vitreous $NaPO_3$ is given on Fig. 1. In the temperature range from 620 to 670 K, the enthalpy change, $\Delta H_c(T)$, accompanying the crystallization of the melt is lower than the enthalpy of melting, ΔH_m. This accords with the positive value of the heat capacity difference, ΔC_p (T), between the liquid and the crystalline phase.

The enthalpy of melting was found to be $\Delta H_m = 22.2 \pm 2$ kJ mol^{-1}, and the entropy, ΔS_m, was found to be $\Delta S_m = 24.7 \pm 2$ J mol^{-1} K^{-1}. These results are in reasonable agreement with preliminary estimations.

Heat capacity values for crystalline, vitreous and liquid $NaPO_3$ are given in Fig. 2, together with the experimental data [18] for the heat capacity of vitreous $NaPO_3$ at relatively low temperatures. It can be seen that the heat capacities of the vitreous and crystalline phases are approximately equal. The solid line (1) is drawn through the C_p data of glass and crystal, according to Einstein's equation

$$C_{p,cr} = A\left(\frac{\theta_E}{T}\right)^2\left(\frac{e^{-\theta_E/T}}{(1-e^{-\theta_E/T})}\right)$$

with $A = 144$ J mol^{-1} and $\theta_E = 516$ K.

Glasses are non-equilibrium systems with "frozen-in" structures. Hence $C_{p,gl}$ accounts for the vibrational energy of the molecules only. On the other

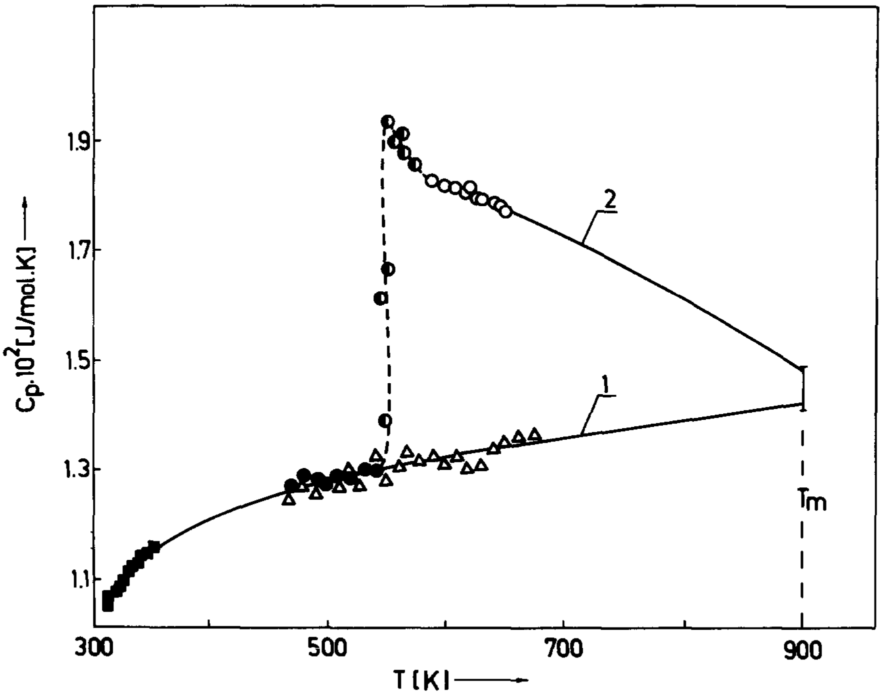

Fig. 2. Heat capacity of $NaPO_3$: △, crystal; ○, undercooled melt; ◐, glass-transition region; ●, vitreous $NaPO_3$; ■, vitreous $NaPO_3$, according to data from ref. 18. Curve 1 is calculated according to the Einstein equation; curve 2 is constructed from curve 1 with ΔC_p-values according to eqn. (1).

hand, the heat capacity $C_{p,liq}$ of the undercooled liquid includes a configurational term accounting for the structural changes of the melt with temperature (i.e. $C_{p,liq} \neq C_{p,cr}$ while $C_{p,gl} = C_{p,cr}$).

Upon heating to the temperature range where vitrification occurs the properties of the substance change abruptly when the non-equilibrium glass becomes a metastable undercooled melt. The mode of this change depends on both cooling and heating rates as well as on the whole previous thermal history of the samples. For this reason thermodynamic significance was attributed only to the heat capacity measurements below the lower limit (540 K) and above the upper limit (590 K) of the vitrification range. The dashed curve in Fig. 2 corresponds to the $C_p(T)$ dependence obtained from quenched samples heated at a rate of 12.5 K min^{-1}. It is well known that this kinetic "nose" in the $C_p(T)$ curve depends on the scanning rate q^+. At the lowest heating rates the "nose" is practically absent. Figure 3 illustrates the manner in which the vitrification temperature, T_g, was found to depend on q^+. No measurements on $C_{p,liq}$ were possible above 640 K because the crystallization rate becomes measurable above this temperature. The estimated value of $\Delta C_p(T_m)$ is given by a vertical bar in Fig. 2. It was found (Fig. 2) that the

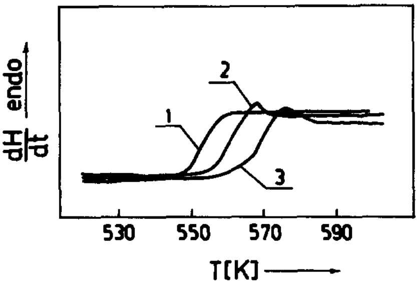

Fig. 3. DSC curves of vitreous $NaPO_3$ samples, obtained with different heating rates q^+: curve 1, $q^+ = 0.3$ K min^{-1}; curve 2, $q^+ = 3.1$ K min^{-1}; curve 3, $q^+ = 12.5$ K min^{-1}.

heat capacity difference $\Delta C_p \equiv C_{p,liq} - C_{p,cr}$ decreases linearly with temperature

$$\Delta C_p(T) = a - bT, \text{ for } 580 \leqslant T \leqslant 640 \text{ K} \tag{1}$$

where $a = 151$ J mol^{-1} K^{-1} and $b = 0.176$ J mol^{-1} K^{-2}.

Considering the thermodynamic relation

$$\Delta H(T) = \Delta H_m - \int_T^{T_m} \Delta C_p(T) \mathrm{d}T \tag{2}$$

and assuming that experimentally-determined $\Delta C_p(T)$ values (eqn. (1)) can be extrapolated to the melting point, the temperature dependence of the enthalpy difference between liquid and crystalline $NaPO_3$, $\Delta H(T)$, is

$$\Delta H(T) = \Delta H_m - (1 - T/T_m)\left[aT_m - bT_m^2(1 + T/T_m)/2\right] \tag{3}$$

The measured values for enthalpy of melting and enthalpy of crystallization, $\Delta H(T)$, for $NaPO_3$ are given in Fig. 4. The solid line represents values calculated according to eqn. (3) with the above values of a and b, so that $\Delta H(T_g) \approx 14$ kJ mol^{-1} and $\Delta S(T_g) \approx 11$ J mol^{-1} K^{-1}.

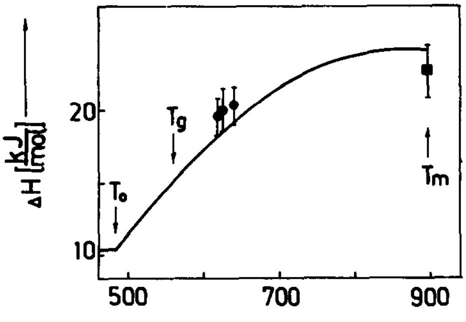

Fig. 4. Temperature dependence of ΔH for $NaPO_3$: ●, direct DSC measurements of the enthalpy of crystallisation $\Delta H_c(T)$ and ■, of the enthalpy of melting ΔH_m; the solid line is calculated from the $\Delta C_p(T)$ dependence, eqn. (3).

DISCUSSION

One of the most important characteristics of undercooled melts is the thermodynamic driving force, $\Delta\mu$, for crystallization. This function is determined by the difference in the molar free energies of the undercooled melt and the crystal. Considering eqn. (1) the $\Delta\mu$ (T) dependence can be expressed [19] as

$$\Delta\mu(T)/\Delta H_\mathrm{m} = (1 - T/T_\mathrm{m})[(1 - a_0) + b_0(1 - T/T_\mathrm{m})/2] - a_0 \frac{T}{T_\mathrm{m}} \ln(T/T_\mathrm{m}) \qquad (4)$$

where $a_0 = a/\Delta S_\mathrm{m}$ and $b_0 = bT_\mathrm{m}/\Delta S_\mathrm{m}$

The J.J. Thomson approximation [19] follows from eqn. (4) for $\Delta C_\mathrm{p} = 0$,

$$\Delta\mu(T) = \Delta S_\mathrm{m}(1 - T/T_\mathrm{m}) \qquad (5)$$

It is convenient to express the logarithmic term in eqn. (4) as

$$\ln X \cong -2(1 - X)/(1 + X) \quad X \leqslant 1 \qquad (6)$$

When eqn. (6) and eqn. (4) are combined the following approximations for $\Delta\mu(T)$ are obtained: (i) for $b_0 = 0$ and $a_0 = 1.5$ the Hoffman formula [20] (see also ref. 21)

$$\Delta\mu = \Delta S_\mathrm{m} T(1 - T/T_\mathrm{m})/T_\mathrm{m} \qquad (7)$$

is obtained; (ii) for $b_0 = 0$ and $a_0 = 1$ the Thomson–Spaepen equation [23]

$$\Delta\mu = 2\Delta S_\mathrm{m} T(1 - T/T_\mathrm{m})/T_\mathrm{m}(1 + T/T_\mathrm{m}) \qquad (8)$$

follows.

A detailed investigation has shown that $1.5 < a_0 < 2$ and $b_0 = 0$ applies for organic polymers, while the Thomson–Spaepen formula has usually been applied [19,23,24] for metallic melts. It is of interest to note that for a number of undercooled metallic melts ΔC_p decreases linearly with temperature according to eqn. (1). The experimental data for a_0 and b_0 [25,26] are listed in Table 1. Results for $NaPO_3$ are also included in Table 1. A similar $\Delta C_\mathrm{p}(T)$ dependence was observed [27] for a highly undercooled metallic

TABLE 1

Summary of heat capacity data

Substance	a_0	$-b_0$
Bi	1.20	1.15
Sn	1.33	1.41
In	2.19	2.28
Se	2.05	1.37
$NaPO_3$	6.11	6.07

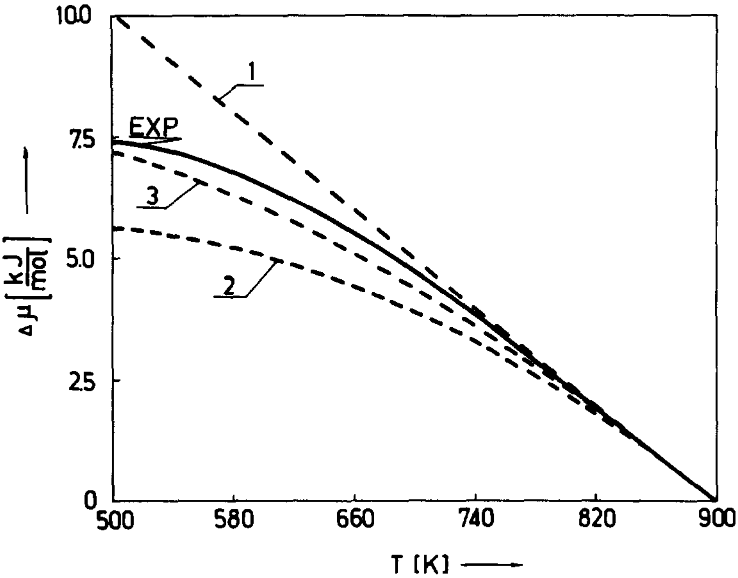

Fig. 5. Temperature dependence of $\Delta\mu$ for $NaPO_3$: line 1, according to eqn. (5); line 2, according to eqn. (7); line 3, according to eqn. (8); solid line, experimentally observed course.

glass-forming alloy. It can be seen that, unlike polymer melts, for metals $a_0 = -b_o$ i.e. for metals ΔC_p is negligible in the vicinity of T_m ($\Delta C_p(T_m) \approx 0$).

Figure 5 shows that for $NaPO_3$ the $\Delta\mu(T)$ experimental curve can be approximated with sufficient accuracy by eqn. (8). Our numerical calculations show that for $0.55 < T/T_m < 1$ the $\Delta\mu(T)$ dependence can be described with sufficient accuracy over the range $3.5 < a_0 = -b_0 < 6.5$. However, for metallic substances $1.1 < a_0 = -b_0 < 2.2$, so that in the same temperature range, $0.55 < T/T_m < 1$, the $\Delta\mu(\mathrm{T})$ dependence can be described approximately as

$$\Delta\mu(T) = 2\Delta S_m T(1 - T/T_m)(1.5 - 0.5T/T_m)/(1 + T/T_m)T_m \qquad (9)$$

Our investigation indicates that according to the temperature dependence of their thermodynamic properties inorganic chain glasses behave like undercooled metallic melts or metallic glass-forming alloys.

ACKNOWLEDGEMENTS

The authors are indebted to Professor A. Feltz and Dr. W. Ludvig for the control determination of ΔH_m values for $NaPO_3$, performed in the Institute of Inorganic Chemistry of the Fr. Schiller University (Jena, DDR).

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