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Review

Mixing properties in the continuous solid solution of the system ($CsNO_3$ + $TlNO_3$) at T = 473 K

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ABSTRACT

Previous work on the binary phase diagram ($CsNO_3$ + $TlNO_3$) showed, in particular, the existence of a continuous solid solution, $Cs_xTl_{1-x}NO_3$. It extends over the whole composition range between T = 430 K and T = 480 K. Mixing enthalpies of the solid solutions $Cs_xTl_{1-x}NO_3$ are measured at T = (473 ± 1) K, for the first time, by using a drop calorimetric method. They exhibit a positive and asymmetrical deviation from ideality.

Contents

1. Introduction

In solid state thallium nitrate has, at atmospheric pressure, three polymorphic forms: α, β and γ denoted also, I, II and III respectively [1–6]. γ$TlNO_3$ is the low temperature allotropic form having an orthorhombic structure. By heating, γ$TlNO_3$ acquires progressively a hexagonal structure β, then cubic structure, α [1–6]. Wallerant [7] and Clark and Reinhardt [8] mentioned that β$TlNO_3$ adopts a rhombohedral structure, while Cleaver et al. [9] mentioned that it is pseudo-hexagonal.

The majority of the γ/β transition temperature values is in the range T = 349 K to T = 353 K [3,6,8,10–16]. The β/α transition is

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TABLE 1
Polymorphism and the range temperature of the stability at pressure $p = 0.1013$ MPa.

$CsNO_3$	$TlNO_3$	Cristal structure
β(II) :$T = 298$ to $T = (429 \pm 5)$ K [13,17,26–41]	γ(III): $T = 298$ to $T = (351 \pm 2)$ K [3,6,8,10–16]	Orthorhombic [1–6]
		Hexagonal [2,24–26]
	β(II): $T = (351 \pm 2)$ K to $T = (417.5 \pm 2.5)$ K [3,6,8,10,11,13–17]	Hexagonal [1–6], Rhombohedral [7,8], Pseudo-hexagonal[9]
α(I): $T = (429 \pm 5)$ to $T = (681 \pm 4)$ K [13,17,27,30–32,34–36,39–41,46–53]		Cubic [2,26,42–45].
	α(I) : $T = (417.5 \pm 2.5)$ K to $T = (480.5 \pm 2.5)$ K [3,6,8,13,16–23]	Cubic [1–6]

reported between $T = 415$ K and $T = 420$ K according to most authors [3,6,8,10,11,13–17]. Gossner [12] has found $T = 424$ K for this transition. This value deviates slightly from those mentioned above.

The results found by various authors for the melting temperature are consistent with each other and are located in the range $T = 478$ K to $T = 483$ K [3,6,8,13,16–23].

Cesium nitrate can exist at atmospheric pressure in two polymorphic forms (α and β). $\beta CsNO_3$ is stable at room temperature and crystallizes in the hexagonal system, with P_{3_1} space group [2,24–26]. It undergoes a phase transition between $T = 424$ K and $T = 434$ K [13,17,26–41] to rich a cubic phase $\alpha CsNO_3$ (CsCl type) [2,26,42–45].

The almost of the values of the melting temperature of cesium nitrate are between $T = 677$ K and $T = 685$ K [13,17,27,30–32,34–36,39–41,46–53]. The value obtained by Kleppa and McCarty [54] ($T = 690$ K) deviates from the other results.

The temperature range of the stability of the different polymorphic forms of $CsNO_3$ and $TlNO_3$ and their structures are given in table 1. $\alpha CsNO_3$ and $\alpha TlNO_3$ phases are isomorphous [1].

Our recent determination of the ($CsNO_3 + TlNO_3$) phase diagram [13] has shown a cubic continuous solid solution $\alpha Cs_xTl_{1-x}NO_3$. Its stability depends on both composition and temperature; between $T = 430$ K and $T = 480$ K, it extends over the whole area of the composition. The formation of this cubic solid solution [7,13,17,55], can be easily justified by the common cubic structure of both nitrates $\alpha CsNO_3$ and $\alpha TlNO_3$ and also by the small difference between the sizes of the cationic radii ($r_{Cs^+} = 1.67$ Å and $r_{Tl^+} = 1.50$ Å) [56].

So we are interested, in the present work, to determine for the first time, the mixing enthalpies of the solid solutions $\alpha Cs_xTl_{1-x}NO_3$ at $T = (473 \pm 1)$ K. Such data are of great importance in the study of the consistency between the phase diagram and the other thermodynamic properties of any system. In fact, the mixing enthalpies of the solid solutions, for example, are useful in the study and the optimization of ($CsNO_3 + TlNO_3$) binary system.

2. Investigation method

Mixing enthalpies of the binary solid solutions $Cs_xTl_{1-x}NO_3$ can be obtained experimentally by calorimetric technique. In this investigation, pure nitrates and solid solutions are dissolved in the ternary eutectic mixture E(Li, Na, K)NO_3 (used as solvent [57]).The choice of this solvent, S, is notified by its temperature stability field as well as its rapid dissolution of the studied nitrates.

The procedure adopted, in this work, for determining the mixing enthalpies of the solid solutions is to measure, in a same solvent, S, the solution enthalpies at high dilution [58–61] of the solids $CsNO_3$, $TlNO_3$ and $Cs_xTl_{1-x}NO_3$. The processes are then schematized as:

(a) $xCsNO_{3(sd)} + S = (CsNO_3)_x$, S $\quad \Delta H_a = x\Delta_{sol}H(CsNO_3,sd)$.
(b) $(1-x)TlNO_{3(sd)} + S = (TlNO_3)_{1-x}$, S $\quad \Delta H_b = (1-x)\ \Delta_{sol}H(TlNO_3,sd)$.
(c) $Cs_xTl_{1-x}NO_{3(sd)} + S = Cs_xTl_{1-x}NO_3$, S $\quad \Delta H_c = \Delta_{sol}H(Cs_xTl_{1-x}NO_3,sd)$.

These reactions were performed inside an isothermal calorimeter at the same temperature $T = (473 \pm 1)$ K.

The mixing enthalpy $\Delta_{mix}H$ of the solid solution $Cs_xTl_{1-x}NO_3$ at the dissolution temperature referred to the pure nitrates at the same temperature is given by combination of the different enthalpies, ΔH_a, ΔH_b, ΔH_c corresponding to reactions (a), (b) and (c) so that

$\Delta_{mix}H = \Delta H_a + \Delta H_b - \Delta H_c$, when the following reaction,

$Cs_xTl_{1-x}NO_3$, S = $(CsNO_3)_x$, S + $(TlNO_3)_{1-x}$, S, is athermic. In other words, there is no interaction between the solute species occurs in the solvent.

Therefore, this condition imposes that the dissolutions of pure nitrates (a) and (b), conducted separately, lead to the same result as their simultaneous dissolution. This hypothesis is valid when:

- No interactions of $CsNO_3$ and $TlNO_3$ occur in the solvent.
- The $CsNO_3$ and $TlNO_3$ concentrations, for the different baths corresponding to the three reactions (a), (b) and (c) are identical. For reactions at infinite dilution these conditions are obviously verified.

To verify the first hypothesis, the solution enthalpy of $CsNO_3$ (or $TlNO_3$) was measured in the pure solvent then in the same solvent containing $TlNO_3$ (or $CsNO_3$). In both cases, the measured enthalpies are substantially equal. There is therefore no measurable interaction between nitrates in the solvent.

To overcome the experimental difficulty of dissolving exact quantities of solutes in the solvent, the results are extrapolated at infinite dilution. Then, mixing enthalpies of the solid solutions

TABLE 2
Provenance and purity of the products used in this study.

Chemical name	Source	State	Purification method	Initial mass fraction purity[a]	Further treatments before use
Lithium nitrate	Alfa Aesar GmbH & Co K G	Powder	None	0.99	Drying in a desiccator at $T = 380$ K for more than 24 h.
Potassium nitrate	Alfa Aesar GmbH & Co K G	Powder	None	>0.99	
Sodium nitrate	Alfa Aesar GmbH & Co K G	Powder	None	>0.99	
Cesium nitrate	Sigma–Aldrich	Powder	None	>0.99	
Thallium nitrate	Sigma–Aldrich	Powder	None	>0.99	

[a] Purity grade as given by the supplier.