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Review

Mixing enthalpies of solid solutions $(Cs_{1-x},Rb_x)NO_3$ at $T = (298.15 \text{ and } 473.15)$ K

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ABSTRACT

A previous investigation of the binary phase diagram $(Cs,Rb)NO_3$ has confirmed the existence of two continuous solid solutions $\alpha(Cs_{1-x},Rb_x)NO_3$ and $\beta(Cs_{1-x},Rb_x)NO_3$ stable in the temperature ranges $T = (298 \text{ to } 421)$ K and $T = (439 \text{ to } 503)$ K respectively. The mixing enthalpies of these solid phases, determined by a calorimetric method at $T = (298.15 \text{ and } 473.15)$ K, are presented for the first time. A positive and asymmetric deviation from ideality is observed.

Contents

1. Introduction

$CsNO_3$ exhibits two solid phases under atmospheric pressure. While $RbNO_3$ undergoes between room temperature and its melting temperature the following transitions:

$\alpha \rightarrow \beta \rightarrow \gamma \rightarrow \delta \rightarrow \lambda$. Polymorphic properties of $RbNO_3$ and $CsNO_3$ are given in table 1.

The structures of $\alpha CsNO_3$ and $\beta CsNO_3$ are isomorphous to those of $\alpha RbNO_3$ and $\beta RbNO_3$ respectively [19,21–23]. Our recent redetermination of the phase diagram $(Cs,Rb)NO_3$ [19] has shown the existence of two continuous solid solutions $\alpha(Cs_{1-x},Rb_x)NO_3$ and $\beta(Cs_{1-x},Rb_x)NO_3$, stable at the temperature ranges [298 to 421] K and [439 to 503] K, respectively. The formation of these solid solutions in this system can be easily understood because, on the one hand, $CsNO_3$ and $RbNO_3$ have the same structure and secondly, the cationic radius, $r_{Rb+} = 1.61$ Å and $r_{Cs+} = 1.74$ Å [24], differ slightly.

The determination of consistent thermodynamic properties is of paramount importance to both experimental and theoretical levels. In this context, the study of the consistency between the phase diagram and the thermodynamic properties of many systems is currently used.

In fact, the thermodynamic properties of the solid phases in $(Cs,Rb)NO_3$, for example, are useful in the study of this system. So, we are interested, in this work, to determining for the first time,

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TABLE 1
Polymorphism and the temperature range of the stability at atmospheric pressure.

$RbNO_3$	$CsNO_3$	Crystal form
α (298 to 440) K [1–3,5]		Trigonal [3–9]
	α (296 to 427) K [10–12]	Trigonal [10,11]
β (440 to 509) K [1,3,6,10]		Cubic (CsCl) [3–5,8]
	β (439 to 683) K [1,10–12]	Cubic (CsCl) [1,12]
γ (509 to 560) K [8,10,13,14]		Trigonal [8,9,15]; Tetragonal [3]; Cubic [4,7,14]
δ (560 to 584) K [8,9,16]		Cubic (NaCl) [8]
λ (564 to 584) K [17–20]		?

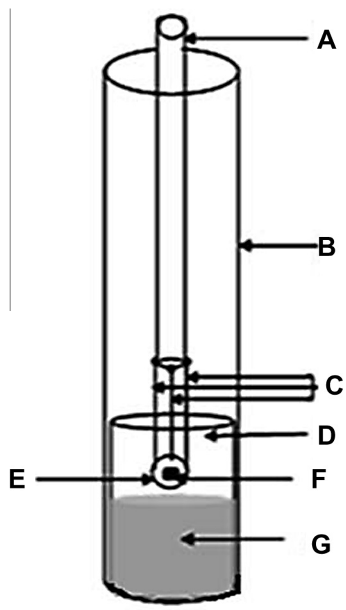

FIGURE 1. Disposition of the sample and the solvent: A, Alumina tube; B, Silica cane; C, Platinum rods; E, Platinum plate; D, Platinum crucible containing the solvent; F, Sample; G, Solvent.

TABLE 2
Characteristics of the measurements by Calset and Isoperibolic calorimeters at $T = 298.15$ K.

Samples	Calorimeters	Mass /mg	Concentrations / mmol · L^{-1}
$RbNO_3$	Isoperibolic	77.7 to 200	1.51 to 3.9
	Calset	9.32 to 111.6	7.9 to 94.6
$CsNO_3$	Isoperibolic	105.2 to 351.1	1.54 to 5.15
$(Cs_{0.2}Rb_{0.8})NO_3$	Calset	35.7 to 74	28.4 to 58.9
$(Cs_{0.32}Rb_{0.68})NO_3$	Calset	31 to 65.1	37.9 to 23.9
$(Cs_{0.35}Rb_{0.65})NO_3$	Isoperibolic	90.6 to 244.3	1.58 to 4.26
$(Cs_{0.43}Rb_{0.57})NO_3$	Isoperibolic	80 to 156	1.36 to 2.66
$(Cs_{0.5}Rb_{0.5})NO_3$	Calset	22 to 84.8	15.3 to 59.1
$(Cs_{0.68}Rb_{0.32})NO_3$	Calset	20.7 to 69.4	14.4 to 48.3
$(Cs_{0.77}Rb_{0.23})NO_3$	Isoperibolic	64.6 to 182	1.1 to 2.83
$(Cs_{0.9}Rb_{0.1})NO_3$	Isoperibolic	87.9 to 249	1.32 to 3.74

the mixing enthalpies of the solid solutions $\alpha(Cs_{1-x},Rb_x)NO_3$ at 298.15 K and $\beta(Cs_{1-x},Rb_x)NO_3$ at $T = 473.15$ K.

2. Measurement method

The mixing enthalpies of the continuous solid solutions $\alpha(Cs_{1-x},Rb_x)NO_3$ and

TABLE 3
Solution enthalpies, $\Delta_{sol}H_j$, at $T = 298.15$ K of $CsNO_3$ in water.

Isoperibolic calorimeter (relative error 3%)	
$C_{i,j}$/mmol · L^{-1}	$\Delta_{sol}H_j$/kJ · mol^{-1}
1.58	39.12
2.5	39.31
3.61	39.08
4.39	39.28
5.14	39.26

$\beta(Cs_{1-x},Rb_x)NO_3$ were determined at $T = (298.15$ and $473.15)$ K respectively by the calorimetric method, using dissolutions of pure nitrates and solid solutions in an appropriate solvent, S, [25].

In practice, the three following reactions were performed inside an isothermal calorimeter:

$$(I) : (1-x)CsNO_3 + S = (CsNO_3)_{1-x}, S \quad \Delta H_1,$$

$$(II) : xRbNO_3 + S = (RbNO_3)_x, S \quad \Delta H_2,$$

$$(III) : (Cs_{1-x}, Rb_x)NO_3 + S = (Cs_{1-x}, Rb_x)NO_3, S \quad \Delta H_3.$$

The mixing enthalpy, $\Delta_{mix}H$, of the solid solution (Cs_{1-x},Rb_x)-NO_3 at the dissolution temperature is given by a combination of the different enthalpies ΔH_1, ΔH_2 and ΔH_3, corresponding to reactions (I), (II) and (III). Then: $\Delta_{mix}H = \Delta H_1 + \Delta H_2 - \Delta H_3$. This applies since that there is no interaction between the solute species occurs in the solvent. In other words, the enthalpy ΔH_4 corresponding to the following reaction must remain zero:

$$(IV) : (CsNO_3)_{1-x}, S + (RbNO_3)_x, S = (Cs_{1-x}, Rb_x)NO_3, S \quad \Delta H_4.$$

In order to verify this condition, the dissolution enthalpies of $CsNO_3$ (respectively $RbNO_3$) in pure solvent and in the solvent containing $RbNO_3$ (respectively $CsNO_3$) have been compared. In the two cases the results are identical; therefore, the assumption $\Delta H_4 = 0$ is correct at high dilution.

To overcome the experimental difficulty of dissolving exact quantities of $(Cs_{1-x},Rb_x)NO_3$, $(0 \leqslant x \leqslant 1)$, we adopted the most commonly used procedure which consists of measuring the enthalpies of solution of the solids at high dilution and extrapolate the results at infinite dilution. The mixing enthalpies in these solid solutions are then deduced from the equation:

$$\Delta_{mix}H^{\circ}((Cs_{1-x}, Rb_x)NO_3, T) = (1-x)\Delta_{sol}H^{\infty}(CsNO_3, T) + x\Delta_{sol}H^{\infty}(RbNO_3, T) - \Delta_{sol}H^{\infty}((Cs_{1-x}, Rb_x)NO_3, T). \quad (1)$$

3. Experimental

$CsNO_3$, $RbNO_3$, KNO_3 and $NaNO_3$ were purchased from Sigma–Aldrich (with purities of $CsNO_3$: 99 wt%, $RbNO_3$: 99.7 wt%, KNO_3 and $NaNO_3$: >99 wt%). $LiNO_3$ was purchased from alfa Aesar with purity of 99.0 wt%. All these nitrates were used without further purification but dried for more than 24 h in a desiccator.

The solid solutions in the system $(Cs,Rb)NO_3$ were prepared by ultimately mixing weighed amounts of pure nitrates $CsNO_3$ and $RbNO_3$ in a Pyrex crucible. In order to get homogeneous mixtures without decomposition, mixtures, 2 g, were previously melted several times at a temperature a few degrees over the melting point.

Measurements of enthalpies of solution of $\alpha(Cs_{1-x},Rb_x)NO_3$ and $\beta(Cs_{1-x},Rb_x)NO_3$ were carried out at $T = (298.15$ and $473.15)$ K, respectively.