

1 **Semi-empirical density estimations for binary, ternary and multicomponent alkali**  
2 **nitrate-nitrite molten salt mixtures**

3  
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12  
13 **Abstract:**

14 For sensible thermal energy storage in Concentrating Solar Power (CSP) plants, a  
15 molten salt mixture of 60 wt% sodium nitrate (NaNO<sub>3</sub>) and 40 wt% potassium nitrate  
16 (KNO<sub>3</sub>), known as Solar Salt, is commonly utilized. The paper presents semi-empirical  
17 estimation results of the density of Solar Salt and alternative molten salt mixtures with  
18 low melting temperatures in a range from 70 °C to 140 °C. These mixtures are Hitec,  
19 HitecXL, LiNO<sub>3</sub>-KNO<sub>3</sub>-NaNO<sub>3</sub> and a multi-component mixture. The paper shows that  
20 density values of mixtures can be closely predicted from single salt densities. The paper  
21 examines different estimation rules for mixtures. The quasilinear volumetric additivity  
22 rule (QVAR) is known for ternary reciprocal systems. For the first time, the presented  
23 work extends the QVAR to multicomponent mixtures. Temperature dependent densities  
24 of selected salt mixtures of the system Ca,Li,K,Na//NO<sub>2</sub>,NO<sub>3</sub> were estimated.  
25 Estimations are motivated by a fast and reliable method compared to time-consuming  
26 and error-prone measurements of several mixtures.  
27

28 **Keywords:** Concentrating Solar Power (CSP), Hitec, HitecXL, multi-component salts,  
29 quasilinear volumetric additivity rule  
30

31 **Highlights:**

- 32 - Densities of alternative salt mixtures for line-focusing CSP systems are  
33 validated
- 34 - For the first time the quasilinear volumetric additivity rule is extended and  
35 applied to multicomponent nitrate/nitrite mixtures
- 36 - Consistent liquid density values of eight salts with Ca, K, Li, Na cations and  
37 NO<sub>2</sub> and NO<sub>3</sub> anions are given
- 38 - Obtained density values are correlated to the molar mass and temperature
- 39 - The paper confirms close prediction of liquid densities of mixtures by  
40 estimations from single salt densities  
41  
42

43 **Nomenclature**

44	$a$	Density coefficient	$\text{g/cm}^3$
45	$b$	Temperature dependent density coefficient	$\text{g}/(\text{cm}^3\text{K})$
46	$V$	Molar volume	$\text{cm}^3/\text{mol}$
47	$V_i$	Molar volume of $i$	$\text{cm}^3/\text{mol}$
48	$M$	Molecular weight	$\text{g/mol}$
49	$M_i$	Molecular weight of $i$	$\text{g/mol}$
50	$\rho$	Density	$\text{g/cm}^3$
51	$X_i$	Mol fraction of $i$	1
52	$T$	Temperature	$^{\circ}\text{C}$
53	$E$	Deviation of estimated density value	%
54			

## 55 Introduction

56 At present, the two-tank molten salt storage system is the established commercially  
 57 available concept for solar thermal power plants, also known as Concentrating Solar  
 58 Power (CSP). The thermal energy storage (TES) based on molten salt makes it possible  
 59 to meet the intermediate load profile with dispatchable power generation. Different  
 60 types of TES systems are distinguished: sensible heat, latent heat and chemical heat. In  
 61 sensible heat storage systems the heat capacity of a solid (e.g. ceramic) or liquid (e.g.  
 62 molten salt) material is utilized to store thermal energy. Due to their low vapour  
 63 pressure and ease of operation, as well as comparatively high thermal stability and low  
 64 costs, molten salts are suitable heat storage media [1]. Almost exclusively a non-  
 65 eutectic salt mixture of 60 wt% sodium nitrate and 40 wt% potassium nitrate is utilized.  
 66 This mixture is commonly called Solar Salt. This non-eutectic mixture has a melting  
 67 range rather than a melting point. The typical operation range is from 290 °C to 560 °C  
 68 (limited by the thermal stability). The lower limits of molten salt utilization are defined  
 69 by the melting temperature (or liquidus). The upper limit is defined by factors such as a  
 70 thermal decomposition process, a high vapour pressure or a high corrosion rate of the  
 71 construction material.

72  
 73 In recent years molten salts have been used not only as heat storage medium, but also as  
 74 heat transfer fluid. CSP power tower systems utilize Solar Salt as TES medium and heat  
 75 transfer fluid for the absorption of solar heat in the central receiver. At the time of  
 76 writing, there is also some research and development for line-focusing CSP systems to  
 77 replace the current heat transfer fluid synthetic thermal oil by a molten salt mixture. The  
 78 major line-focusing CSP systems are currently parabolic troughs, but there are also  
 79 some demonstrations on linear Fresnel collectors. For molten salt heat transfer  
 80 applications, freezing of salt should not occur and is a major concern of such systems.  
 81 Unlike power tower systems, which can be drained gravitationally, line-focusing fields  
 82 are large area installations with horizontal pipes with a higher risk of freezing compared  
 83 to towers. Hence, for line focusing technology, alternative molten salt mixtures with a  
 84 lower melting temperature are developed. These are mainly ternary molten salt mixtures  
 85 based on the cations Ca, K, Li and Na and the anions NO<sub>2</sub> and NO<sub>3</sub> which are discussed  
 86 within the presented paper. Furthermore, alternative molten salt mixtures can have the  
 87 advantage of a larger operation window with lower melting temperatures and similar  
 88 thermal stabilities as Solar Salt. Assuming the same amount of salt  $m$  and a constant  
 89 heat capacity  $c_p$ , a larger temperature window  $\Delta T$  directly leads to a higher TES  
 90 capacity  $Q$  ( $Q = m \cdot c_p \cdot \Delta T$ ). Hence, TES investment costs can be reduced by an enlarged  
 91 operation window.

92  
 93 Thermal properties of molten salts, such as the density, are important for modelling and  
 94 thermal design of the whole system. Density values are used to calculate the mass flow  
 95 from the volume flow measurement of molten salt through pipes, but also to calculate  
 96 the volumetric storage capacity. The density of molten salt is typically measured by  
 97 Archimedean type methods, but other methods are also feasible. These are dilatometric,  
 98 flotation, maximum bubble and pycnometric methods [2,3,4].  
 99 Temperature dependent density data of single salts are partly available from Janz [5].  
 100 Some single salt density values are not available mainly due to the instability of these  
 101 salts (e.g., LiNO<sub>2</sub>, Ca(NO<sub>2</sub>)<sub>2</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>). Salt mixtures can have significantly lower  
 102 melting temperatures compared to single salts. In order to estimate the density of these

103 low temperature mixtures, it is important to predict the unknown single salt properties  
104 to extrapolated values and determine densities of mixtures at lower temperatures [3,6].  
105 For other substances than salts, such as organic-water mixtures and molten metals, some  
106 models exist to predict the density of mixtures from the composition, single substance  
107 densities and other parameters (e.g., excess volume) [7,8]. However, published work on  
108 the mixing behaviour of molten salts is limited. Work at Oak Ridge National Laboratory  
109 (ORNL) and Sandia National Laboratories found that the density of a molten salt  
110 mixture could be predicted by weighing the molar volumes of each of the salt  
111 constituents of the mixture by their molar fraction and summing [3,9,10,11]. This  
112 simple linear addition is also known as ideal mixture behaviour, Vegard's law and  
113 Temkin model [7,12,13]. However, some deviations from the simple rule for the  
114 addition of molar volume rule can occur [11]. Bloom, Blander, Ambrosek and others  
115 distinguished between ideal and non-ideal molten salt systems. Bloom and Blander  
116 provide examples of ideal and non-ideal binary systems [4,10]. For a non-ideal mixture  
117 typically the "excess volume" describes the deviation from linear additivity [7,12].  
118 Powers et al. measured small positive excess volume values for the systems  $\text{KNO}_3$ -  
119  $\text{NaNO}_3$  and  $\text{LiNO}_3$ - $\text{NaNO}_3$  with maximum values of  $0.07 \text{ cm}^3/\text{mol}$  at equimolar  
120 compositions [14]. Work at ORNL and Sandia on  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{KNO}_3$ ,  $\text{LiNO}_3$  and  $\text{NaNO}_3$   
121 binary mixtures also showed that the deviation from ideal mixing is small. Hence, the  
122 density of these mixtures is accurately approximated by the linear addition of the molar  
123 volumes [11]. Bradshaw measured the density of the ternary eutectic  $\text{KNO}_3$ - $\text{LiNO}_3$ -  
124  $\text{NaNO}_3$  and several quaternary  $\text{Ca,K,Li,Na}/\text{NO}_3$  mixtures. He found that the molten salt  
125 mixtures showed an ideal mixing behaviour. The molar volume of multi-component  
126 mixtures could be estimated using the linear volumetric additivity rule [3]. Grin'ko and  
127 Protsenko studied the density of the ternary reciprocal system  $\text{K,Ca}/\text{NO}_2,\text{NO}_3$ . They  
128 found that melts of the system  $\text{K,Ca}/\text{NO}_2,\text{NO}_3$  have random ion distributions, and their  
129 molar volumes can be estimated on the basis of ideal mixing behaviour [12].

130

131 It can be seen that nitrate mixtures based on the cations Ca, K, Li and Na have been  
132 previously assessed. However, there is limited work on the temperature dependent  
133 density of mixtures containing mixed  $\text{NO}_2$  and  $\text{NO}_3$  anions. Overall, the development  
134 and assessment of thermal estimation methods to predict densities of salt mixtures play  
135 a crucial role for the advancement of molten salt technology using alternative and  
136 optimised salt mixtures.

137

138 **1. Properties of single salts and definition of salt mixtures**

139 Table 1 gives temperature dependent density data of single salts from Janz in 1988 [5].  
 140 Molar weight data are from the CRC Handbook of Chemistry and Physics [14]. Janz  
 141 does not provide all density values of single salts. For example (water-free)  $\text{Ca}(\text{NO}_3)_2$  is  
 142 thermally unstable above the melting temperature of about 560 °C and data of  $\text{Ca}(\text{NO}_2)_2$   
 143 and  $\text{LiNO}_2$  density data are also not provided by Janz [5].

144  
 145 Table 1. Temperature dependent densities of single salts [5,15].

Salt	Melting Temp. $T_m/^\circ\text{C}$	Mol. Weight $M/(\text{g mol}^{-1})$	Equation $\rho/(\text{g cm}^{-3})$	Accuracy	Temp. range $T/^\circ\text{C}$
$\text{Ca}(\text{NO}_2)_2$	392	132.089	N/A	N/A	N/A
$\text{Ca}(\text{NO}_3)_2$	561	164.087	N/A	N/A	N/A
KCl	771	74.551	$\rho(T) = 1.9766 - 5.831 \times 10^{-4} \cdot (T/^\circ\text{C})$	$\pm 0.5 \%$	780-939
$\text{KNO}_2$	438	85.104	$\rho(T) = 1.985 - 6.67 \times 10^{-4} \cdot (T/^\circ\text{C})$	$\pm 1.5 \%$	440 -500
$\text{KNO}_3$	334	101.103	$\rho(T) = 2.1087 - 7.235 \times 10^{-4} \cdot (T/^\circ\text{C})$	$\pm 0.5 \%$	347 -457
LiCl	610	42.394	$\rho(T) = 1.7660 - 4.328 \times 10^{-4} \cdot (T/^\circ\text{C})$	$\pm 0.5 \%$	621-781
$\text{LiNO}_2$	222	52.947	N/A	N/A	N/A
$\text{LiNO}_3$	253	68.946	$\rho(T) = 1.919 - 5.46 \times 10^{-4} \cdot (T/^\circ\text{C})$	$\pm 1.5 \%$	272-441
$\text{NaNO}_2$	284	68.996	$\rho(T) = 2.022 - 7.46 \times 10^{-4} \cdot (T/^\circ\text{C})$	$\pm 3 \%$	284-450
$\text{NaNO}_3$	306	84.995	$\rho(T) = 2.1247 - 7.15 \times 10^{-4} \cdot (T/^\circ\text{C})$	$\pm 0.5 \%$	310-370

146

147 Table 2 classifies salt mixtures in terms of the number of ions. For example sodium  
 148 nitrate  $\text{NaNO}_3$  consists of the cation Na and anion  $\text{NO}_3^-$ . The table lists some important  
 149 salt mixtures, but many more systems can be found in literature [16]. Selected mixtures  
 150 of the presented work are underlined in column four of Table 2. Reciprocal systems do  
 151 not have a common ion. They are characterized by at least two cations and at least two  
 152 anions (e.g.  $\text{K,Na//NO}_2,\text{NO}_3$ ). Salt mixtures of reciprocal salt systems can be prepared  
 153 by different combination of single salts. Hence, they can be clearly defined by a list of  
 154 cations and a list of anions, which are separated by the symbol “//” (see column three in  
 155 Table 2).

156

157 Table 2. Classification of salt systems [17]. Considered mixtures in this work are  
 158 underlined in column four.

Ion No.	System Classification	Example System <sup>#</sup>	Selected Mixture <sup>#</sup>
2	Single salt	$\text{NaNO}_3$ $T_m = 306$ °C $\text{KNO}_3$ $T_m = 334$ °C	Not selected
3	Binary system, common anion	$\text{KNO}_3$ - $\text{NaNO}_3$ (or $\text{K,Na//NO}_3$ )	<u>Solar Salt</u> : $T_{\text{liquidus}} = 260$ °C $\text{KNO}_3$ - $\text{NaNO}_3$ (40-60 wt%),
3	Binary system, common cation	$\text{NaNO}_2$ - $\text{NaNO}_3$ (or $\text{Na//NO}_2,\text{NO}_3$ ) $T_{\text{min}} = 230$ °C	Not selected
4	Ternary additive, common anion	$\text{Ca}(\text{NO}_3)_2$ - $\text{KNO}_3$ - $\text{NaNO}_3$ (or $\text{Ca,K,Na//NO}_3$ )	<u>HitecXL</u> : $T_{\text{eu}} = 135$ °C $\text{Ca}(\text{NO}_3)_2$ - $\text{KNO}_3$ - $\text{NaNO}_3$ (42-43-15 wt%)
4	Ternary additive, common anion	$\text{KNO}_3$ - $\text{LiNO}_3$ - $\text{NaNO}_3$ (or $\text{K,Li,Na//NO}_3$ )	<u>LiNaK-Nitrate</u> : $T_{\text{eu}} = 120$ °C $\text{LiNO}_3$ - $\text{KNO}_3$ - $\text{NaNO}_3$ (30-52-18 wt%)
4	Ternary reciprocal	$\text{K,Na//NO}_2,\text{NO}_3$	<u>Hitec</u> : $T_{\text{eu}} = 142$ °C $\text{KNO}_3$ - $\text{NaNO}_2$ - $\text{NaNO}_3$ (53-40-7 wt%)
5	Quaternary addit., common anion	$\text{Ca,K,Li,Na//NO}_3$ ; $T_{\text{min}} = 90$ -110 °C	Not selected
5	Quaternary reciprocal	$\text{Li,Na,K//NO}_2,\text{NO}_3$ ; $T_{\text{min}} = \sim 80$ °C	Not selected
6	Quinary reciprocal	$\text{Ca,Li,Na,K//NO}_2,\text{NO}_3$	<u>CaLiNaK-NO23</u> : $T_{\text{min}} = \sim 70$ °C; $\text{LiNO}_3$ - $\text{Ca}(\text{NO}_3)_2$ - $\text{NaNO}_2$ - $\text{KNO}_2$ (24.6-13.6-16.8-45.0wt%)

159

<sup>#</sup> Melting temperature  $T_m$ ; Liquidus temperature  $T_{\text{liquidus}}$ ;

160

Eutectic melting temperature  $T_{\text{eu}}$ ; Minimum melting temperature  $T_{\text{min}}$

161

162 **2. Theory and methodology**

163 By far the largest number of salt systems follows a linear density correlation related to  
164 the temperature (Equation 1) [5].

$$\rho(T) = a - b \cdot T \quad (1)$$

166 The molar volume, typically in cm<sup>3</sup>/mol, is given by the molecular weight  $M$  divided by  
167 the density (Equation 2).

$$V(T) = \frac{M}{\rho(T)} \quad (2)$$

170 Inserting Equation 1 in Equation 2 gives Equation 3.

$$V(T) = \frac{M}{a - b \cdot T} \quad (3)$$

173 Molar volume values of Eq. 3 may be approximated by a second order polynomial  
174 (Equation 4) with very small deviations (e.g., for the Hitec mixture 145 – 550 °C with a  
175 deviation of ±0.02 %). A simpler linear fit is less accurate (e.g., for the Hitec mixture  
176 with a deviation of ±0.4 %).

$$V(T) \approx A + B \cdot T + C \cdot T^2 \quad (4)$$

179 Different authors found that the density of many salt mixtures could be closely  
180 predicted by the sum of the molar volumes of each of the salt constituents  $V_i$ , weighted  
181 by the mole fraction  $X_i$  (Equation 5)[3,11]. In this text Eq. 5 is called the “**volumetric**  
182 **additivity rule (VAR)**”. The volumetric additivity implies that the volume of a  
183 mixtures equals the sum of the volumes of the pure components of which the mixture is  
184 compromised [3,18]. Compared to some other work [19], mixtures in the present work  
185 are considered ideal and an additional excess volume term in Eq. 5 is not included. In  
186 order words, for  $V^E = 0$ , the equation reduces to a simple linear combination of the  
187 molar volumes. As mentioned earlier, this assumption is referred to as ideal solution or  
188 Vegard’s law or Temkin model [3,7,11,12].

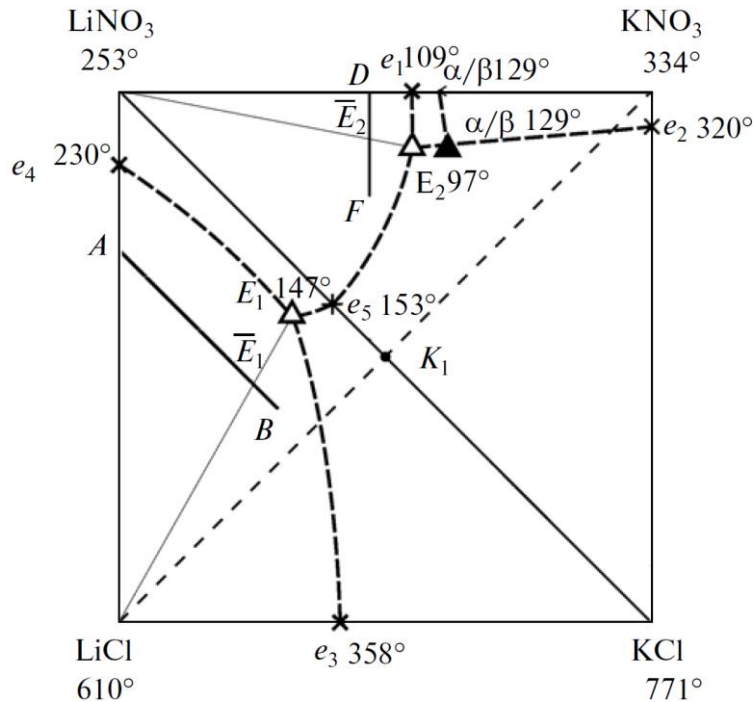
$$V(T) = \sum_{i=1}^N X_i \cdot V_i(T) + V^E(T, X_i) \quad (5)$$

191 The density of the mixture is obtained by Eq. 2 using the volume of the mixture (Eq. 5)  
192 and the molar weight of the mixture  $M$  from Equation 6, where  $M_i$  are the molecular  
193 weights and  $X_i$  are the molar fractions of the single salts or ions.

$$M = \sum_{i=1}^N X_i \cdot M_i \quad (6)$$

196  
197

198 In the following the simplest reciprocal system is selected which is a ternary reciprocal  
 199 system. It will be shown that the introduced VAR method cannot be simply applied to  
 200 reciprocal systems. We discuss as an example the system K,Li//Cl,NO<sub>3</sub>. Figure 1 shows  
 201 the phase diagram of this system [20]. At 367 °C there are several literature density  
 202 values available and this phase diagram has a large liquid area at 367 °C to select  
 203 different compositions. Hence, this temperature was selected as one example to show  
 204 the ambiguity of the VAR method for ternary reciprocal systems.



205  
 206 **Fig 1.** Phase diagram of the system K,Li//Cl,NO<sub>3</sub> [20].  
 207

208 The phase diagram of K,Li//Cl,NO<sub>3</sub> exhibits a minimum melting composition E2 with a  
 209 defined anion ( $X_a$ ) and cation ( $X_c$ ) content shown in Table 3. The authors of ref. [20]  
 210 suggest that composition 1a in Table 3 exhibits the minimum melting point. However,  
 211 just from the molar ion fractions a different contribution of individual salts can result in  
 212 the same ion ratios; this alternative composition is referred to as 1b. Applying Eq. 5  
 213 (with  $V^E = 0$ ) to mixture 1a and 1b results in two different density values although they  
 214 have the same anion and cation fractions (Table 3).  
 215

216 Table 3. Two salt mixtures for the minimum melting composition E2 of the system  
 217 K,Li//Cl,NO<sub>3</sub> in mol%.

Mix.	KCl	KNO <sub>3</sub>	LiCl	LiNO <sub>3</sub>	$X_{cK}$	$X_{cLi}$	$X_{aCl}$	$X_{aNO_3}$
1a	10.5%	44.5%	0	45%	0.55	0.45	0.105	0.895
1b	0	55%	10.5%	34.5%	0.55	0.45	0.105	0.895

218  
 219 As this example shows and Smith and Petersen also stated: “for ternary mixtures of  
 220 reciprocal salt systems [...] there is an ambiguity in the choice of components that leads  
 221 to special difficulties when one attempts a straightforward extension of the additive  
 222 volume principle” [18]. In order to overcome this difficulties, Smith and Petersen



223 proposed an adapted volumetric additivity for ternary reciprocal systems, where  $X_{c1}$  is  
 224 the fraction of the first cation,  $X_{c2}$  is the fraction of the second cation,  $X_{a1}$  is the fraction  
 225 of the first anion,  $X_{a2}$  is the fraction of the second anion and  $V_{11}$ ,  $V_{12}$ ,  $V_{21}$  and  $V_{22}$  are the  
 226 four molar volumes of the single salts (Eq. 7) [18]. In the following, we use the term  
 227 **“quasilinear volumetric additivity rule (QVAR)”** for this adapted version of the  
 228 volumetric additivity rule (VAR). As previously discussed, the sum of all cation and  
 229 anion fractions is one (Eq. 8 and 9).  
 230

$V(T) = X_{c1}X_{a1}V_{11}(T) + X_{c1}X_{a2}V_{12}(T) + X_{c2}X_{a1}V_{21}(T) + X_{c2}X_{a2}V_{22}(T)$	(7)
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231

$X_{c1} + X_{c2} = 1$	(8)
$X_{a1} + X_{a2} = 1$	(9)

232

233 Smith and Petersen compared own experimental density results with different estimated  
 234 densities for the ternary reciprocal system K,Li//Cl,NO<sub>3</sub>. Table 4 shows the recalculated  
 235 results, where  $\rho_{EXP}$  refers to experimental values,  $\rho_{VAR}$  to estimated values using the  
 236 volumetric additivity rule (VAR) defined in Eq. 5 and  $\rho_{QVAR}$  to estimated values using  
 237 the quasilinear volumetric additivity rule (QVAR) defined in Eq. 7. There are no  
 238 differences between VAR and QVAR values for binary systems (or edges) of the  
 239 ternary reciprocal system. Hence, binary systems are not shown and Table 4 lists values  
 240 within the square of the ternary reciprocal system. Table 4 shows two alternative  
 241 choices (a and b) with two or three salts giving the same molar ion fractions. From  
 242 Table 4, it can be seen that  $\rho_{QVAR}$  values are not affected by these two choices of  
 243 components. However,  $\rho_{VAR}$  values are inconsistent and differ depending on the choices  
 244 of components. The effect also exists for mixtures with all four salts, but is not listed in  
 245 Table 4 since it does not show the effect as strong as mixtures with two or three salts.  
 246

247 Table 4. Experimental and estimated densities of the system K,Li//NO<sub>3</sub>,Cl at T= 367 °C.

Mix.	KCl	KNO <sub>3</sub>	LiCl	LiNO <sub>3</sub>	X <sub>cK</sub>	X <sub>cLi</sub>	X <sub>aNO<sub>3</sub></sub>	X <sub>aCl</sub>	$\rho_{\text{EXP}}(T)/$ (g cm <sup>-3</sup> )	$\rho_{\text{VAR}}(T)/$ (g cm <sup>-3</sup> )	$\rho_{\text{QVAR}}(T)/$ (g cm <sup>-3</sup> )
1a	0	25%	50%	25%	0.25	0.75	0.5	0.5	1.715	1.725	1.718
1b	25%	0	25%	50%	0.25	0.75	0.5	0.5	1.715	1.711	1.718
2a	25%	0	0	75%	0.25	0.75	0.75	0.25	1.738	1.730	1.739
2b	0	25%	25%	50%	0.25	0.75	0.75	0.25	1.738	1.743	1.739
3a	16%	25%	59%	0	0.41	0.59	0.25	0.75	1.709	1.726	1.718
3b	41%	0	34%	25%	0.41	0.59	0.25	0.75	1.709	1.712	1.718
4a	0	41%	50%	9%	0.41	0.59	0.5	0.5	1.739	1.752	1.742
4b	41%	0	9%	50%	0.41	0.59	0.5	0.5	1.739	1.731	1.742
5a	25%	16%	0	59%	0.41	0.59	0.75	0.25	1.760	1.755	1.762
5b	0	41%	25%	34%	0.41	0.59	0.75	0.25	1.760	1.767	1.762
6a	0	75%	25%	0	0.75	0.25	0.75	0.25	1.799	1.811	1.802
6b	25%	50%	0	25%	0.75	0.25	0.75	0.25	1.799	1.799	1.802

248

249 Eq. 10 and 11 define deviations between measured density values  $\rho_{\text{EXP}}$  and the two  
250 estimated values  $\rho_{\text{VAR}}$  and  $\rho_{\text{QVAR}}$ .

251

$E_{\text{VAR}}(T) = \frac{\rho_{\text{VAR}}(T) - \rho_{\text{EXP}}(T)}{\rho_{\text{EXP}}(T)} 100\%$	(10)
$E_{\text{QVAR}}(T) = \frac{\rho_{\text{QVAR}}(T) - \rho_{\text{EXP}}(T)}{\rho_{\text{EXP}}(T)} 100\%$	(11)

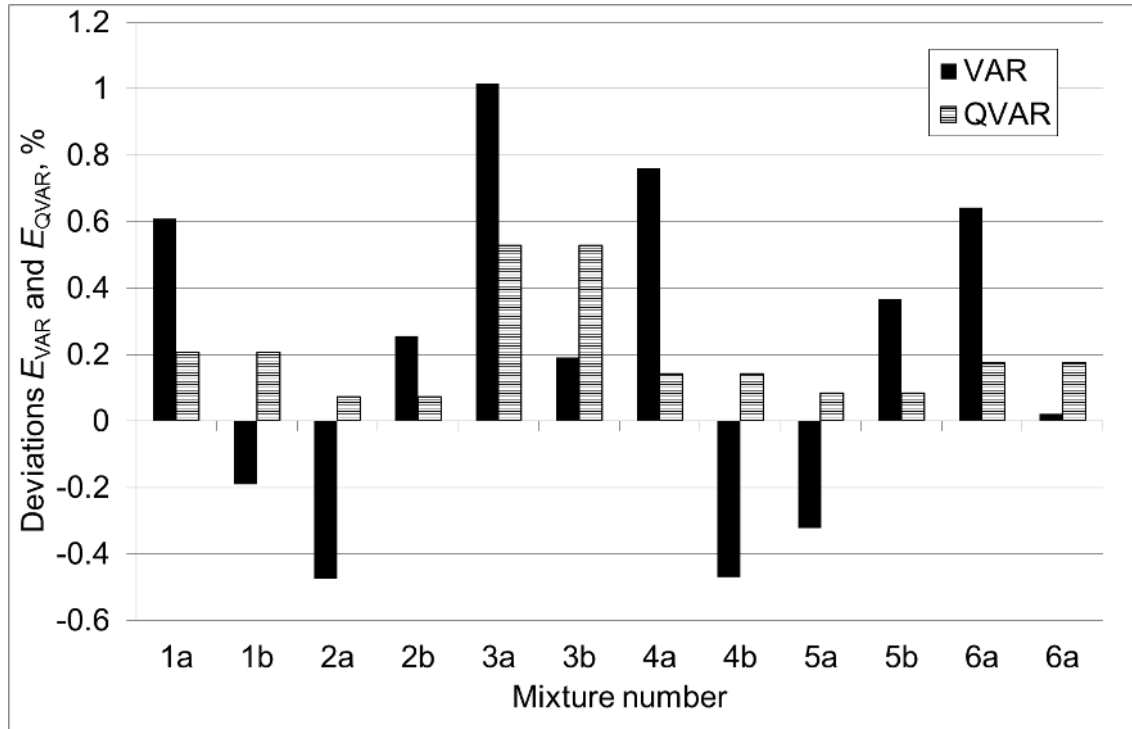
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253 Figure 2 plots deviations of all mixtures in Table 4 as compared to the experimental  
254 values. It can be seen that a and b compositions result in the same  $E_{\text{QVAR}}(T)$  value as  
255 previously discussed. Figure 2 shows that positive deviation values of the VAR method  
256 are up to about +0.5 % whereas deviations of the QVAR method show only negative  
257 deviation values. Maximum negative deviation values are about -1 % for the VAR  
258 method and -0.6 % for the QVAR method. Hence, the deviation window is only about  
259 one third, if the VAR method (-1 % to +0.5 %) and QVAR method (-0.5 % to +0 %) are  
260 compared.

261 The accuracy limit of single salts of the system K,Li//Cl,NO<sub>3</sub> is  $\pm 0.5$  % except LiNO<sub>3</sub>  
262 with a higher uncertainty value of  $\pm 1.5$  %. These uncertainties have the same order of  
263 magnitude as the obtained deviations in Figure 2. Also, only some experimental points  
264 of the system K,Li//Cl,NO<sub>3</sub> are available. Hence, an absolute judgement about the  
265 improvement of the QVAR compared to the VAR method for the entire K,Li//Cl,NO<sub>3</sub>  
266 system is not possible. Nevertheless, the analysis showed that the QVAR method  
267 compared to the VAR method leads to lower deviations and consistent averaged density  
268 values for the examined ternary reciprocal system.

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**Fig 2.** Analysis of the deviation of the VAR and QVAR method for the system K,Li//NO<sub>3</sub>,Cl .

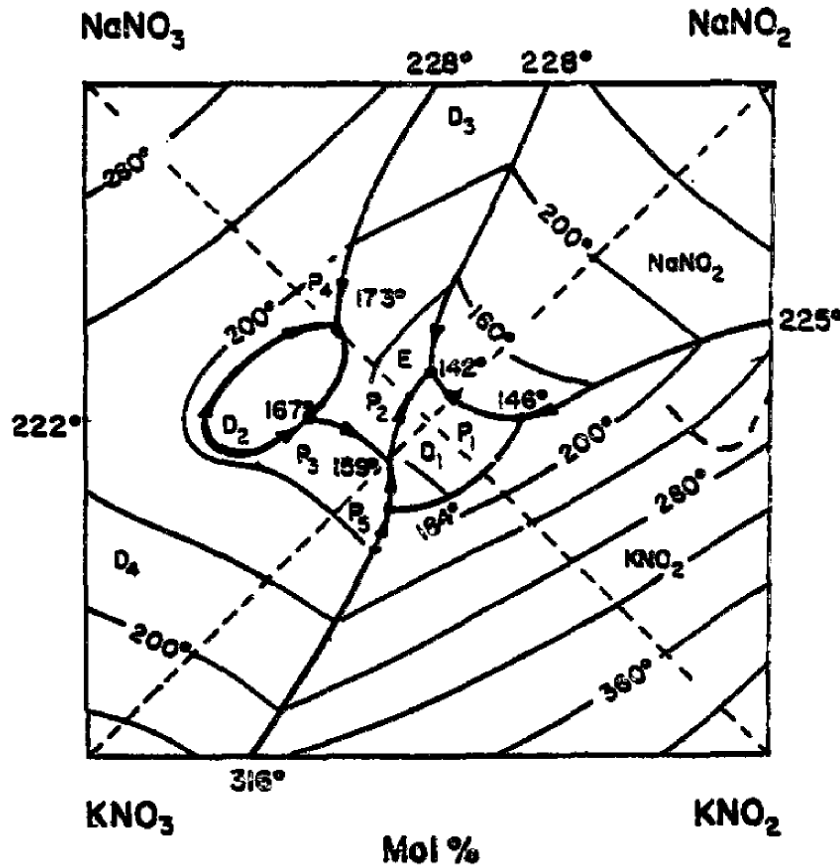
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276 **3. Results and discussion for K,Na//NO<sub>2</sub>,NO<sub>3</sub> and subsystems**277 **3.1 The ternary reciprocal system K,Na//NO<sub>2</sub>,NO<sub>3</sub>**278 Figure 3 gives the phase diagram of the system K,Na//NO<sub>2</sub>,NO<sub>3</sub> from reference [21].

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280

281 **Fig 3.** Phase diagram of the system K,Na//NO<sub>2</sub>,NO<sub>3</sub> from Janz [21].

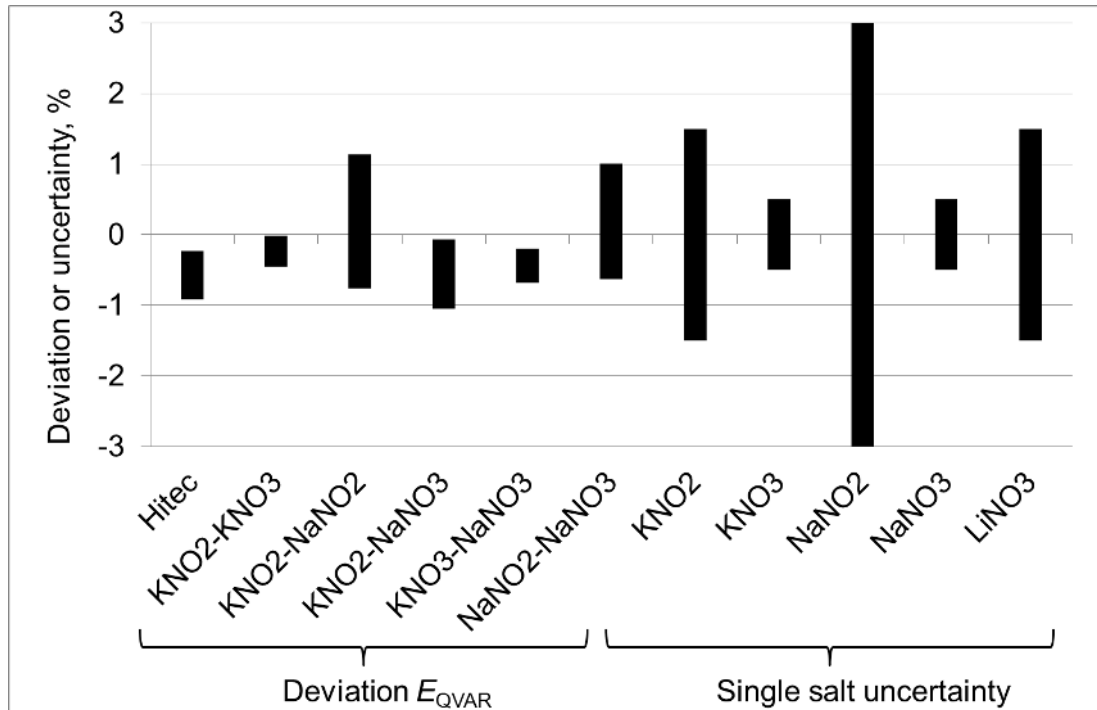
282

283 In reference [21], only limited further experimental density measurement data of the  
 284 system K,Na//NO<sub>2</sub>,NO<sub>3</sub> could be identified. Therefore, density values were estimated  
 285 using experimental data from different sources. Density values of binary systems with  
 286 common anions (KNO<sub>2</sub>-NaNO<sub>2</sub>, KNO<sub>3</sub>-NaNO<sub>3</sub>), cations (KNO<sub>2</sub>-KNO<sub>3</sub>, NaNO<sub>2</sub>-  
 287 NaNO<sub>3</sub>) and pseudobinary KNO<sub>2</sub>-NaNO<sub>3</sub> were taken from Janz [5,22]. Also values  
 288 from the minimum melting mixture Hitec with the composition 53 wt% KNO<sub>3</sub>,  
 289 40 wt% NaNO<sub>2</sub> and 7 wt% NaNO<sub>3</sub> were used [23,24]. Density values at the minimum  
 290 and maximum temperature for each composition and all mixtures were selected. In total  
 291 100 experimental density values were used. We compared these experimental density  
 292 values with computed values in terms of the deviation  $E_{QVAR}(T)$  (Eq. 11).

293 Figure 4 shows minimum and maximum deviations  $E_{QVAR}(T)$  for these binary systems  
 294 and the Hitec mixture (for simplicity single computed values of all mixtures are not  
 295 shown). For comparison, Figure 4 gives the uncertainty of single salt density as  
 296 compared to experimentally gained values.

297 For all estimations the deviation between computed and experimental values was below  
 298  $\pm 1.15\%$ . For all other systems, it can be seen that deviations between estimated and  
 299 experimental values are within the uncertainty of the density values of the single salts.

300 Although there is an incomplete set of experimental density data inside the system  
 301  $K,Na/NO_2,NO_3$  it can be assumed that the QVAR method can be applied for the entire  
 302  $K,Na/NO_2,NO_3$  system with a high accuracy, since deviations of the four edge systems,  
 303 a crossing line and the Hitec system are within the uncertainty of the density values of  
 304 the single salts.  
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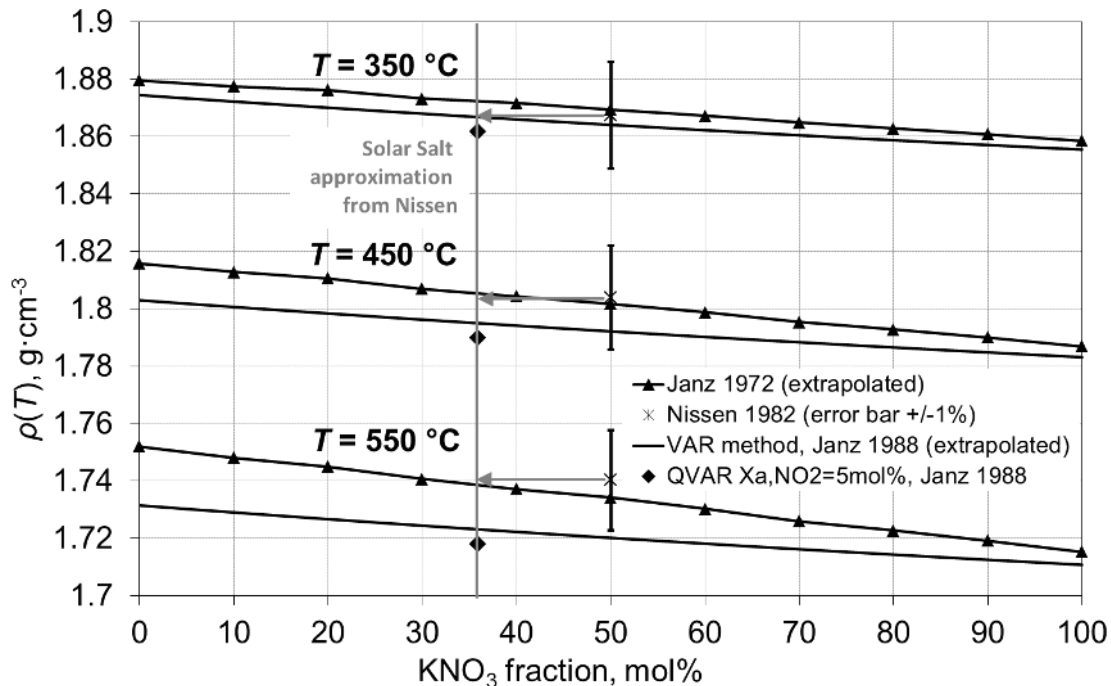


306  
 307 **Fig 4.** Analysis of the deviations of the QVAR method for the system  $K,Na/NO_2,NO_3$   
 308 compared to single salt density uncertainties [5].

### 309 3.2 “Solar Salt” mixture

310 For sensible thermal energy storage and as heat transfer fluid in CSP plants, a molten  
 311 salt mixture of 60 wt% sodium nitrate ( $NaNO_3$ ) and 40 wt% potassium nitrate ( $KNO_3$ ),  
 312 or 64.1 mol%  $NaNO_3$  and 35.9 mol%  $KNO_3$  is almost exclusively utilised [25].  
 313 Compared to the eutectic composition with 46 wt%  $NaNO_3$  and 54 wt%  $KNO_3$  (or 50-  
 314 50 mol%), Solar Salt contains a larger fraction of  $NaNO_3$ , which has a higher heat  
 315 capacity and typically also lower costs compared to  $KNO_3$ . Hence, it is advantageous to  
 316 increase the fraction of  $NaNO_3$  compared to the eutectic mixture. Figure 5 plots density  
 317 values versus the composition of the system  $KNO_3-NaNO_3$  for the three temperatures  
 318 450, 500 and 550 °C. **Janz** reviewed density measurements of the entire system  $KNO_3-$   
 319  $NaNO_3$  from 12 groups and recommended density values in 1972, which are also  
 320 presented in Figure 5 [22]. Table 5 gives the interpolated density equations of Solar Salt  
 321 from the mixtures 70 mol%  $NaNO_3$  - 30 mol%  $KNO_3$  and 60 mol%  $NaNO_3$  - 40 mol%  
 322  $KNO_3$  reported by Janz from 1972 [22]. It should be noted that the upper temperature  
 323 limit of this data is 450 °C and Figure 5 shows extrapolated values to 550 °C for  
 324 comparison. **Nissen** measured the density of the 50-50 mol%  $NaNO_3-KNO_3$  mixture  
 325 from 300 °C to 600 °C [26]. Although, these measurements were performed for the  
 326 equimolar mixture and not for Solar Salt, correlations based on these measurements are  
 327 widely accepted for Solar Salt (e.g. Bradshaw [27], Pacheco [28], System Advisor  
 328 Model (SAM)). Figure 5 shows this approximation with grey arrows. It is pointed out  
 329 that utilization of equimolar mixture as Solar Salt data leads to an overestimation of  
 330 density of about 0.4 % at 550 °C.

331 For estimated Solar Salt densities from single salts, the uncertainty of single salt values  
 332 can be another significant error source. For example Janz revised widely accepted  
 333 density correlations from 1972 for  $\text{KNO}_3$  and  $\text{NaNO}_3$  in 1988 with changes up to 1.2 %.  
 334 In 1988, **Janz** reported revised  $\text{KNO}_3$  and  $\text{NaNO}_3$  density correlation with lower density  
 335 values (Table 1, Figure 5)[5]. Figure 5 shows estimated density values for the system  
 336  $\text{KNO}_3$ - $\text{NaNO}_3$  using single salt data from Janz [5] and the VAR method. Single salt  
 337 values are valid until 460 °C ( $\text{KNO}_3$ ) and 370 °C ( $\text{NaNO}_3$ ) [5] and Figure 5 shows  
 338 extrapolated values until 550 °C. It can be seen that values at 550 °C deviate slightly  
 339 more than 1 % between data from Nissen and the VAR method. It can be concluded that  
 340 differences occur mainly due to corrected density values from Janz from 1972 [22] to  
 341 1988 [5]. Newer values are lower, e.g. for extrapolated values at 550 °C for  $\text{NaNO}_3$   
 342 about 1.2 % and for  $\text{KNO}_3$  about 0.2 %.  
 343 Another aspect is the non-ideal mixing behaviour of Solar Salt. **Powers** measured a  
 344 small positive excess volume of the system  $\text{KNO}_3$ - $\text{NaNO}_3$  [14]. For Solar Salt a value of  
 345  $0.06 \text{ cm}^3/\text{mol}$  can be estimated ( $V^E = 0.26 \text{ cm}^3/\text{mol} \cdot 0.64(1-0.64)$ ). This value  
 346 corresponds to a density increase of about 0.1 %. It can be concluded that the density  
 347 increase of 0.1% is rather small and can be neglected compared to other effects  
 348 discussed previously.  
 349



350 **Fig 5.** Liquid density values of the system  $\text{KNO}_3$ - $\text{NaNO}_3$  for three temperatures from  
 351 different sources [22,26] and own estimations based on data from Janz 1988 [5].  
 352  
 353

354 Another source of uncertainty is the formation of nitrite ions in Solar Salt at high  
 355 operation temperatures. The equilibrium of nitrate and nitrite depends on the  
 356 temperature and oxygen partial pressure (Eq. 12)[29]. In fact nitrite formation occurs  
 357 also in other alkali nitrate mixtures. Nitrite formation is pronounced for low partial  
 358 pressure of oxygen (e.g. lower oxygen partial pressure than in atmospheric air) and at  
 359 higher temperatures (e.g. above 400 °C). Hence, due to this nitrate decomposition with  
 360 release of oxygen as gas some errors of density values can occur for all alkali nitrate  
 361 mixtures.  
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Table 5 and Figure 5 show results about the impact of nitrite formation on the density of Solar Salt. For high-temperature operation an approximate value of  $X_{aNO_2} = 5$  mol% can be assumed [17]. The formation of nitrite ions reduces the density of Solar Salt. In order to assess the impact of nitrite formation on the Solar Salt density, density values of mixtures with the VAR-method (without nitrite) and QVAR-method (with 5 mol% nitrite) were computed (using salt properties from Janz [5]). It was found that the impact of nitrite formation on density variation is rather small. For the formation of 5 mol% nitrite in Solar Salt, the density values are reduced by about 0.005 g/cm<sup>3</sup> or 0.3 %. Hence, this conversion leads to an overestimation of Solar Salt density values of about 0.3 %, if nitrite formation is neglected.

Table 5. Density of Solar Salt from different authors (\* interpolated values).

Author, year	Equation $\rho(T)$ / (g cm <sup>-3</sup> )	Temp. range	Reference
Janz 1972	$\rho(T) = 2.106 - 6.684 \times 10^{-4} \cdot (T/^\circ\text{C})$	350-450 °C	21
Nissen 1982*	$\rho(T) = 2.090 - 6.36 \times 10^{-4} \cdot (T/^\circ\text{C})$	300-600 °C	25
VAR, Janz 1988	$\rho(T) = 2.118 - 7.185 \times 10^{-4} \cdot (T/^\circ\text{C})$	See Table 1	5
QVAR, $X_{aNO_2}=5$ mol%, Janz 1988	$\rho(T) = 2.113 - 7.184 \times 10^{-4} \cdot (T/^\circ\text{C})$	See Table 1	5

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\* Equimolar mixture measurements utilized as Solar Salt data

Overall, it can be stated that different effects lead to lower density values of Solar Salt compared to published values by Nissen. Newer revised lower single salt values from Janz in 1988, the assumption of 5 mol% NO<sub>2</sub><sup>-</sup> formation and the application of the QVAR method lead to a 1.2 % lower density value at 550 °C of Solar Salt compared to the commonly applied value from Nissen (Figure 5)[25].

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### 3.3 "Hitec" mixture

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Since about 1940 a ternary molten salt mixture is commercially used as heat transfer fluid [23,30]. Figure 3 gives the literature phase diagram with the minimum melting composition E with a melting temperature of 142 °C. This minimum melting mixture is typically called Hitec. Table 6 gives this minimum melting composition 1a in mol%. Table 6 also shows the fraction of the anions and cations and an alternative mixture 1b which has the same molar ion fractions as mixture 1a.

There are several literature sources which give the density of Hitec as a function of temperature [23,31,32] and these values agree closely (deviations smaller  $\pm 1$  %). Janz gives a linear fit for density values in g/cm<sup>3</sup> using original values from Kirst [23] for the temperature range from 197 °C to 597 °C with an uncertainty of  $\pm 2$  % [21]. The original linear equation from Janz was converted from Kelvin to °C (Eq. 13).

$\rho_{\text{EXP,Hitec}}(T) = 2.0889 - 7.497 \times 10^{-4} \cdot (T/^\circ\text{C})$	(13)
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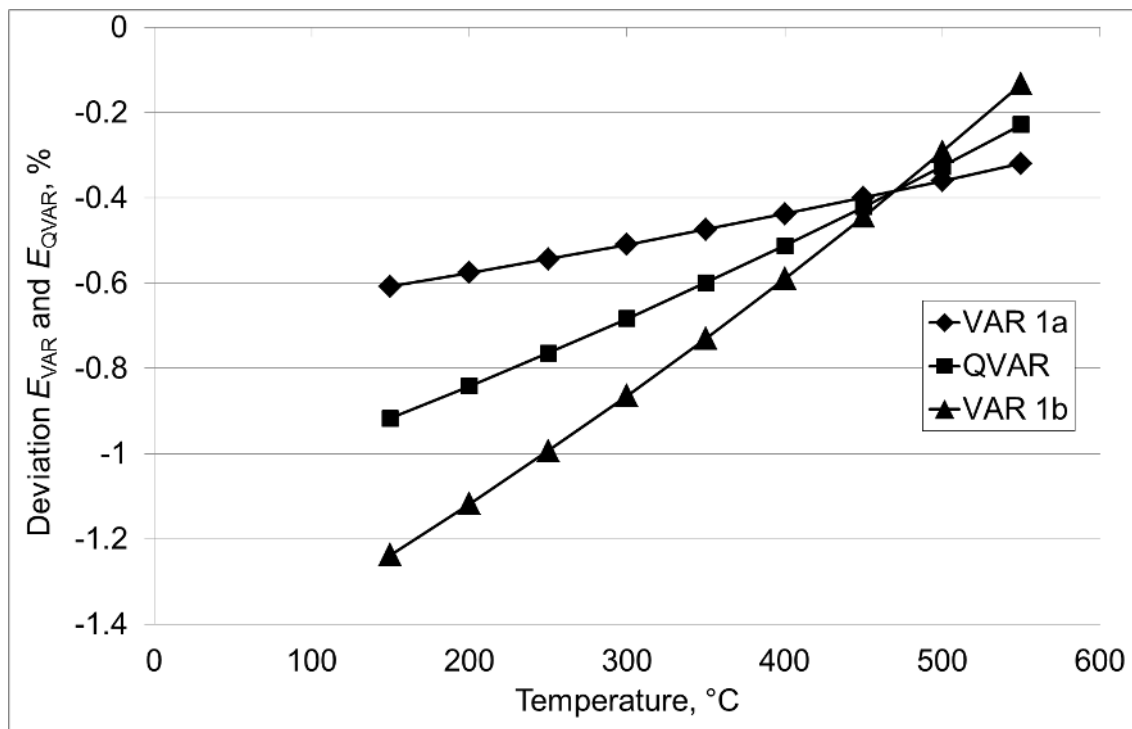
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400 Table 6 shows the density values at 150 °C for experimental values (Eq. 13), the VAR  
 401 method (Eq. 5) and the QVAR method (Eq. 7). As discussed before, the VAR method  
 402 gives ambiguous values. Hence it is inconsistent and is purely shown for completeness.  
 403 Figure 6 shows an error analysis of the minimum melting Hitec mixture depending on  
 404 the temperature. It can be seen that the deviations between measured and estimated  
 405 densities is larger at lower temperatures. Estimated densities are lower in all cases  
 406 compared to the measured densities for this particular mixture. This may be due to an  
 407 excess volume of this ternary mixture or inaccurate experimental values of single salts  
 408 or the ternary mixture. The uncertainty of the single salts  $\text{KNO}_3$  and  $\text{NaNO}_3$  is low  
 409 ( $\pm 0.5\%$ ). The nitrite salts show a larger uncertainty ( $\text{KNO}_2 \pm 1.5\%$  and  $\text{NaNO}_2 \pm 3\%$ ).  
 410 Janz gives an uncertainty of  $\pm 2\%$  Hitec measurement values. The deviation between  
 411 QVAR method and measured results is smaller than 1%. Hence, deviations of estimated  
 412 densities by the QVAR method are within the uncertainty of measured values.

413  
 414 Table 6. Two salt mixtures for the minimum melting Hitec composition of the system  
 415  $\text{K}_2\text{Na}/\text{NO}_2, \text{NO}_3$  in mol%. The temperature  $T$  for the density values is 150 °C.

Mix.	$\text{KNO}_2$	$\text{KNO}_3$	$\text{NaNO}_2$	$\text{NaNO}_3$	$X_{\text{cK}}$	$X_{\text{cNa}}$	$X_{\text{aNO}_2}$	$X_{\text{aNO}_3}$	$\rho_{\text{EXP}}(T)/$ ( $\text{g cm}^{-3}$ )	$\rho_{\text{VAR}}(T)/$ ( $\text{g cm}^{-3}$ )	$\rho_{\text{QVAR}}(T)/$ ( $\text{g cm}^{-3}$ )
1a	0	44.2%	48.9%	6.9%	0.442	0.558	0.489	0.511	1.976	1.964	1.958
1b	44.2%	0	4.7%	51.1%	0.442	0.558	0.489	0.511	1.976	1.952	1.958

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418  
 419 **Fig 6.** Analysis of the deviations of VAR and QVAR method compared to measured  
 420 values for the minimum melting Hitec mixture of the system  $\text{K}_2\text{Na}/\text{NO}_2, \text{NO}_3$ .  
 421



#### 4. Results and discussion for the ternary additive “LiNaK-Nitrate” mixture

Applications of the nitrite-free binary mixture K,Li//NO<sub>3</sub> include vulcanization of rubber in salt baths and the heat transfer fluid area [33]. Compared to K,Li//NO<sub>3</sub>, the ternary system Li,K,Na//NO<sub>3</sub> (named LiNaK-Nitrate here) shows improved properties in terms of reduced LiNO<sub>3</sub> contents (as an expensive compound) and a lower melting temperature. In addition to vulcanization and heat transfer applications, thermal energy storage systems in concentrating solar power plants is another potential application field for this ternary mixture [34-37]. Figure 7 shows the phase diagram of the system LiNaK-Nitrate from Bergman [38]. In addition, Carveth and Mantha also studied the phase diagram of this system (not shown) [39,40]. Bergman gives the ternary eutectic point with a melting temperature of 120 °C with a composition of 30.0 wt% LiNO<sub>3</sub>, 52 wt% KNO<sub>3</sub> and 18 wt% NaNO<sub>3</sub>. For further density estimation, this composition is selected.

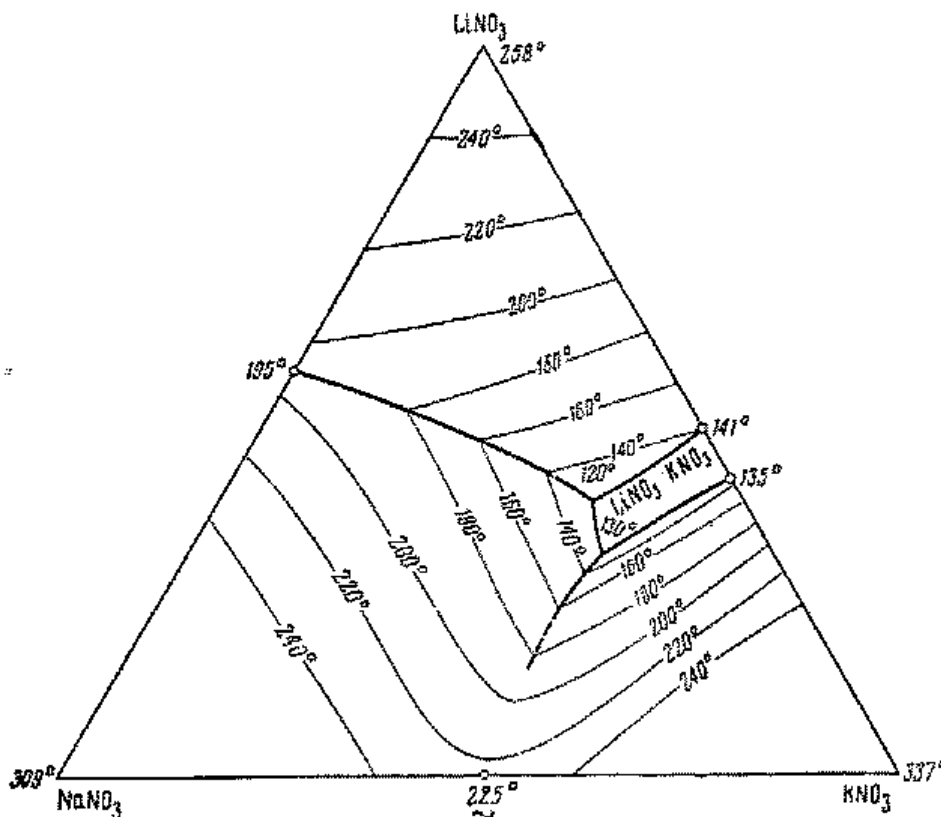


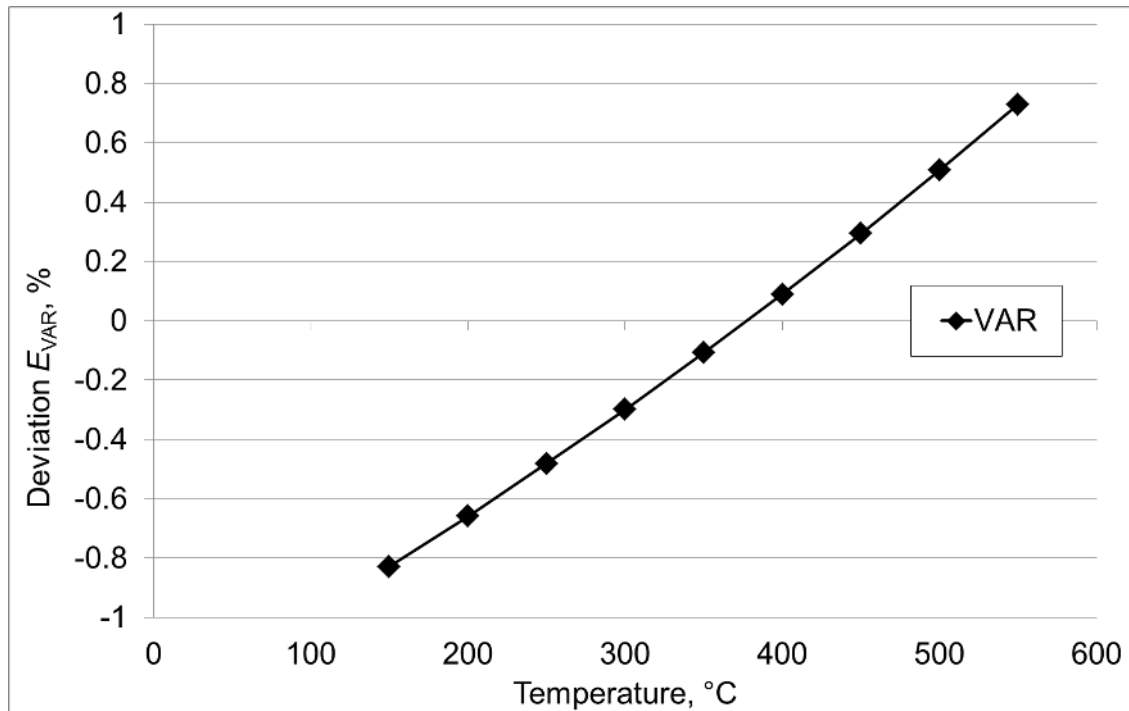
Fig 7. Phase diagram of the LiNaK-Nitrate system from Bergman [39].

Bradshaw gives experimental density data in g/cm<sup>3</sup> of the ternary eutectic LiNaK-Nitrate in a range from 150 °C to 500 °C. The deviation of single measurement points from the linear equation (Equation 14) was less than 0.2 % [3].

$$\rho_{\text{EXP,LiNaK-Nitrate}}(T) = 2.0777 - 7.352 \times 10^{-4} \cdot (T/^\circ\text{C}) \quad (14)$$

Figure 8 shows minimum and maximum deviations  $E_{\text{VAR}(T)}$  for ternary eutectic LiNaK-Nitrate of experimental data from Bradshaw (Equation 14) and estimated values by the VAR method (since this system has only one anion the QVAR method is not employed). Experimental data were extrapolated from 500 °C to 550 °C. Above about 380 °C estimated data are larger than experimental density data, whereas below 380 °C

449 estimated data are smaller than experimental data. It can be seen that the maximum  
450 deviation is 0.9 %. For comparison, Figure 4 gives the uncertainty of single salt density  
451 values ( $\text{KNO}_3 \pm 0.5 \%$ ,  $\text{LiNO}_3 \pm 1.5 \%$ ,  $\text{NaNO}_3 \pm 0.5 \%$ ) [5]. Hence, deviations between  
452 estimated and measured values are within the uncertainty of  $\text{LiNO}_3$  density value.  
453



454 **Fig 8.** Analysis of deviations of the VAR method compared to measured values for the  
455 LiNaK-Nitrate mixture .  
456  
457  
458

## 459 5. Results and discussion for the “HitecXL” mixture

460 Figure 9 shows the phase diagram of the ternary additive system Ca,K,Na//NO<sub>3</sub> from  
 461 Bergman [41]. There is some discussion about the eutectic composition as discussed by  
 462 Gomez and Bauer [42,43]. For further discussion we assume the following minimum  
 463 melting composition: Ca(NO<sub>3</sub>)<sub>2</sub>-KNO<sub>3</sub>-NaNO<sub>3</sub> (42-43-15 wt%) and use HitecXL as an  
 464 abbreviation.

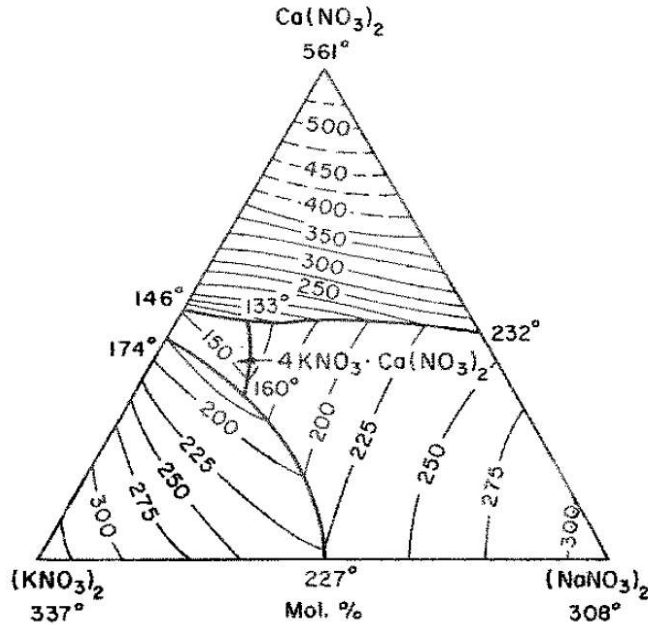


FIG. 1074.—System (KNO<sub>3</sub>)<sub>2</sub>-(NaNO<sub>3</sub>)<sub>2</sub>-Ca(NO<sub>3</sub>)<sub>2</sub>.

A. G. Bergman, I. S. Rassonskaya, and N. E. Shmidt,  
*Izvest. Sektora Fiz.-Khim. Anal., Inst. Obshchei Neorg.  
 Khim., Akad. Nauk S.S.S.R., 26, 156 (1955).*

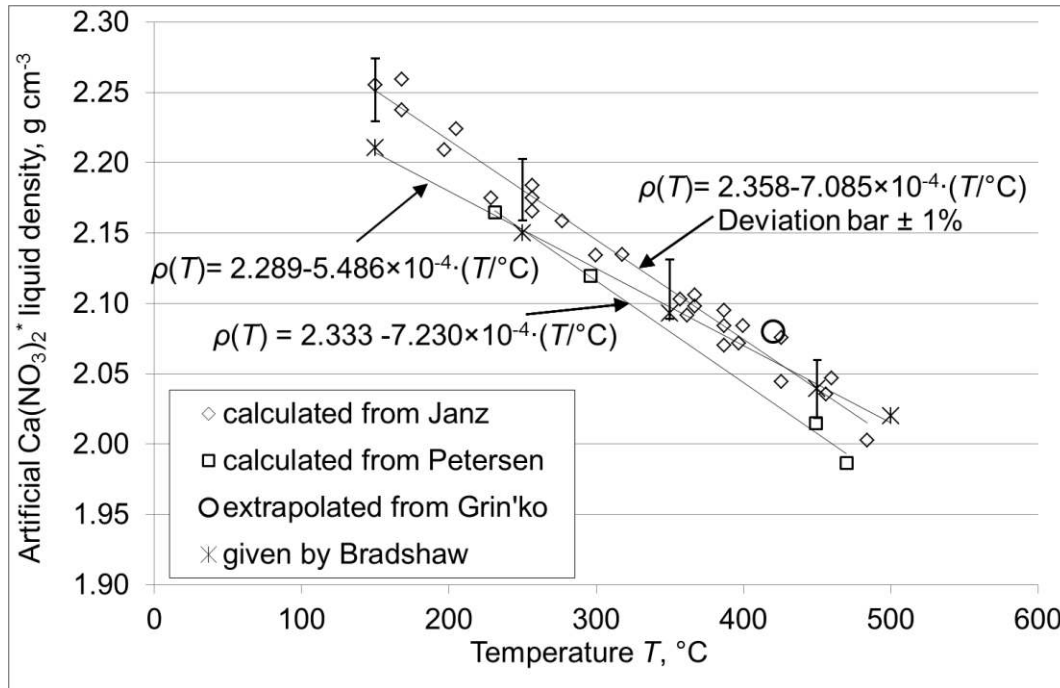
465  
 466 **Fig 9.** Phase diagram of the system Ca,K,Na//NO<sub>3</sub> from Bergman [41].  
 467

468 Measurement values of the density of the single salt Ca(NO<sub>3</sub>)<sub>2</sub> are not available due to  
 469 its instability above the melting temperature of about 560 °C. Hence, we use a backward  
 470 approach to estimate an artificial density value for Ca(NO<sub>3</sub>)<sub>2</sub> from the experimental  
 471 density values of mixtures at lower temperatures. For this purpose Equation 5 is  
 472 rearranged and gives Equation 15. Equation 2 converts molar volumes of Ca(NO<sub>3</sub>)<sub>2</sub> to  
 473 artificially estimate liquid densities values  $\rho_{\text{Ca(NO}_3)_2^*}$ . This estimated values are below  
 474 the freezing temperature of Ca(NO<sub>3</sub>)<sub>2</sub> with the aim to estimate densities of low-melting  
 475 temperature salt mixtures containing Ca(NO<sub>3</sub>)<sub>2</sub>.  
 476

$$V_{\text{Ca(NO}_3)_2}(T) = \frac{V_{\text{exp,Ca,K,Na//NO}_3}(T) - X_{\text{KNO}_3} \cdot V_{\text{KNO}_3}(T) - X_{\text{NaNO}_3} \cdot V_{\text{NaNO}_3}(T)}{X_{\text{Ca(NO}_3)_2}} \quad (15)$$

477  
 478 Figure 10 plots estimated artificial Ca(NO<sub>3</sub>)<sub>2</sub> liquid density values  $\rho_{\text{Ca(NO}_3)_2^*}$  using  
 479 Equation 2 and 15. A large number of molar volume values  $V_{\text{exp,Ca,K,Na//NO}_3}$  in  
 480 Equation 15 from the systems Ca(NO<sub>3</sub>)<sub>2</sub>-KNO<sub>3</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>-NaNO<sub>3</sub> and Ca(NO<sub>3</sub>)<sub>2</sub>-  
 481 KNO<sub>3</sub>-NaNO<sub>3</sub> from Janz were used [5]. In order to reduce the errors of estimated  
 482  $V_{\text{Ca(NO}_3)_2}$  values, data with molar calcium nitrate fraction  $X_{\text{Ca(NO}_3)_2} < 0.2$  were excluded.  
 483 Petersen also gives measured temperature dependent densities of the two mixtures  
 484 20 mol% Ca(NO<sub>3</sub>)<sub>2</sub>-80 mol% KNO<sub>3</sub> and 30 mol% Ca(NO<sub>3</sub>)<sub>2</sub>-70 mol% KNO<sub>3</sub> [44]. The  
 485 plotted data points in Figure 10 refer to the minimum and maximum temperature for the

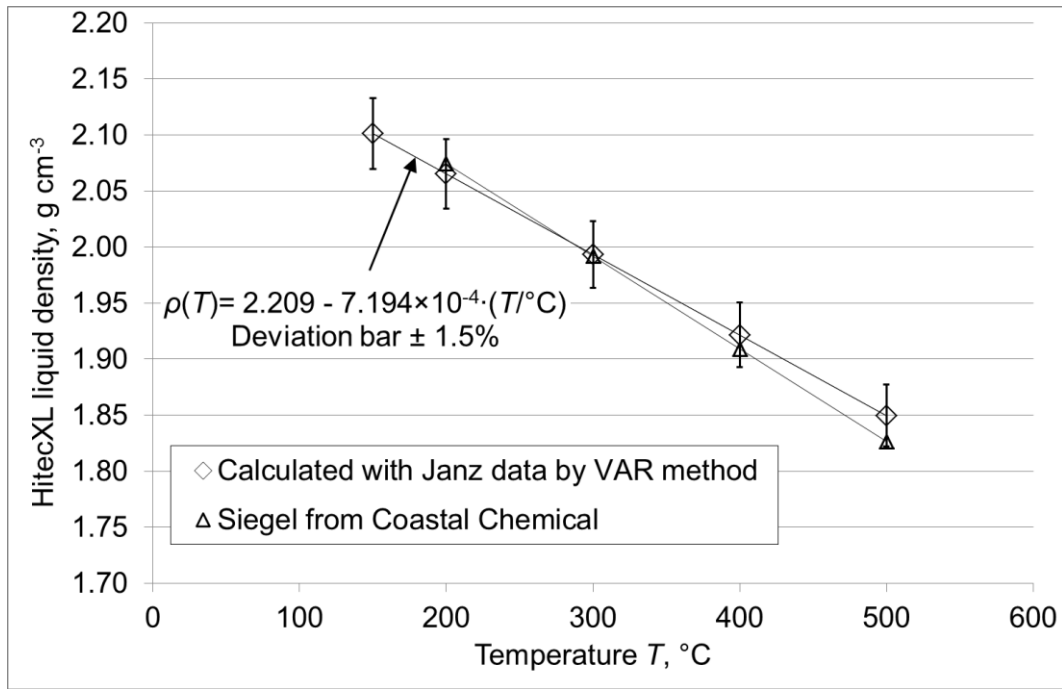
486 given temperature range. A fit with a linear regression was applied. Single data points  
 487 from Janz are all within an deviation band of  $\pm 1\%$  compared the linear fit. It can be  
 488 seen that the slope coefficient of the function from Janz and Petersen is virtually the  
 489 same. There is an offset of the density values from Janz and Petersen. Data from Janz  
 490 are about  $1.5\%$  higher compared to data from Petersen in the temperature range  $250\text{ }^\circ\text{C}$   
 491 to  $450\text{ }^\circ\text{C}$  [5,44]. Due to the larger data basis, for further estimations the linear fit from  
 492 data from Janz is selected (Equation 16).  
 493



494 **Fig 10.** Estimated artificial  $\text{Ca}(\text{NO}_3)_2^*$  liquid density values from densities of  
 495  $\text{K,Ca,Na/NO}_3$  mixtures by Bradshaw, Janz, Grin'ko and Petersen [3,5,12,44].  
 496  
 497

$\rho_{\text{Ca}(\text{NO}_3)_2}(T)^* = 2.358 - 7.085 \times 10^{-4} \cdot (T/^\circ\text{C})$	(16)
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498  
 499 Figure 11 shows temperature dependent density data of the mixture HitecXL. Data are  
 500 from Siegel which refers to a personal communication to the company Coastal  
 501 Chemical) [45] and own estimations. Own estimations are based on the VAR method  
 502 with density equations of single salts from Table 1 (for  $\text{NaNO}_3$  and  $\text{KNO}_3$ ) and  
 503 Equation 16 (for  $\text{Ca}(\text{NO}_3)_2$ ). As can be seen that these estimations are in agreement to  
 504 data provided by Siegel within  $\pm 1.5\%$ .  
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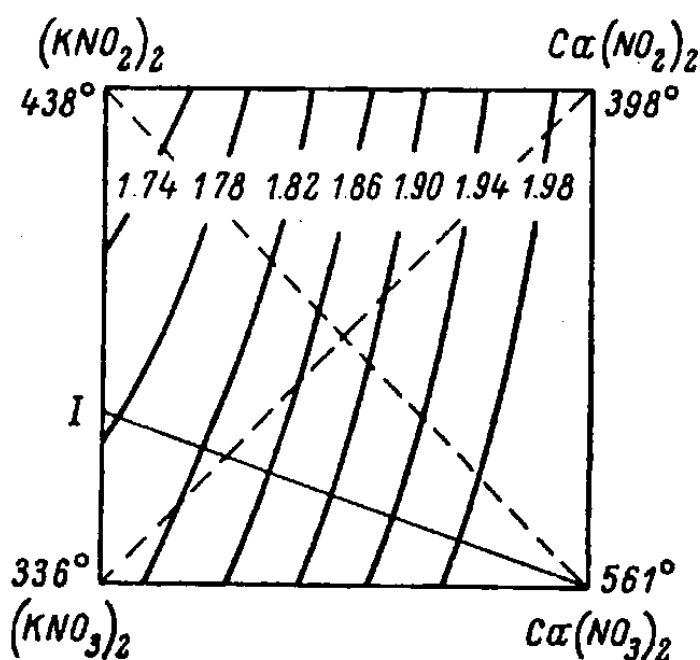
**Fig 11.** HitecXL liquid density values from Siegel [45] and estimated values within this work from Janz using the VAR method [5,44].

## 510 6. Results and discussion for the “CaLiNaK-NO23” mixture

511 For density estimation of the quinary reciprocal system Ca,K,Li,Na/NO<sub>2</sub>,NO<sub>3</sub> density  
 512 data of Ca(NO<sub>2</sub>)<sub>2</sub> and Li(NO<sub>2</sub>)<sub>2</sub> are required. As for Ca(NO<sub>3</sub>)<sub>2</sub> in the previous section,  
 513 density values of Ca(NO<sub>2</sub>)<sub>2</sub> and Li(NO<sub>2</sub>)<sub>2</sub> are commonly not available. In a previous  
 514 work, the minimum melting composition LiNO<sub>3</sub>-Ca(NO<sub>3</sub>)<sub>2</sub>-NaNO<sub>2</sub>-KNO<sub>2</sub> (24.6 - 13.6 -  
 515 16.8 - 45.0 wt%) was identified [46]. CaLiNaK-NO23 is the abbreviation of this  
 516 mixture. In order to estimate the temperature dependent density of this mixture, in the  
 517 following the density functions of Ca(NO<sub>2</sub>)<sub>2</sub> and Li(NO<sub>2</sub>)<sub>2</sub> are identified.

518 Grin'ko and Protsenko give the projection of the density isotherms of the system  
 519 Ca,K/NO<sub>2</sub>,NO<sub>3</sub> at 420 °C (Figure 12)[12]. They also give a direct temperature  
 520 dependent correlation of the density of Ca(NO<sub>2</sub>)<sub>2</sub> for the temperature range 398 °C to  
 521 434 °C (Equation 17).

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**Fig 12.** Projection of the density isotherms of the system Ca,K/NO<sub>2</sub>,NO<sub>3</sub> at 420 °C from Grin'ko and Protsenko [12].

$$\rho_{\text{Ca(NO}_2)_2}(T)^* = 2.289 - 5.4 \times 10^{-4} \cdot (T / ^\circ \text{C}) \quad (17)$$

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Protsenko et al. also measured the temperature dependent densities of the binary system LiNO<sub>2</sub>-LiNO<sub>3</sub>. They found that the density and molar-volume isotherms of this system are strictly linear and these properties are additive [47]. Extrapolated measured values of LiNO<sub>3</sub> from Protsenko agree within a deviation of ±0.8 % compared to values for LiNO<sub>3</sub> from Janz (see Table 1). Hence, it can be assumed that also LiNO<sub>2</sub> values have a high accuracy. Equation 16 is a linear fit for the LiNO<sub>2</sub> density values for the measurement range 220-280 °C.

$$\rho_{\text{LiNO}_2}(T)^* = 1.742 - 4.70 \times 10^{-4} \cdot (T / ^\circ \text{C}) \quad (18)$$

537

538 Equation 7 gives the molar volume for ternary reciprocal systems using the QVAR  
 539 method. In order to estimate the molar volume of the quinary reciprocal systems  
 540 Equation 7 is extended. Equation 19 gives the molar volume for quinary reciprocal  
 541 systems (e.g., Li,K,Ca,Na //NO<sub>2</sub>,NO<sub>3</sub>), where the sum of all cations and anions remains  
 542 unity (Equation 20 and 21).  
 543

$$V(T) = X_{c1}X_{a1}V_{11}(T) + X_{c1}X_{a2}V_{12}(T) + X_{c2}X_{a1}V_{21}(T) + X_{c2}X_{a2}V_{22}(T) + X_{c3}X_{a1}V_{31}(T) + X_{c3}X_{a2}V_{32}(T) + X_{c4}X_{a1}V_{41}(T) + X_{c4}X_{a2}V_{42}(T) \quad (19)$$

544

$$X_{c1} + X_{c2} + X_{c3} + X_{c4} = 1 \quad (20)$$

$$X_{a1} + X_{a2} = 1 \quad (21)$$

545

546 Table 8 gives the equation of the temperature dependent density of the LiNO<sub>3</sub>-  
 547 Ca(NO<sub>3</sub>)<sub>2</sub>-NaNO<sub>2</sub>-KNO<sub>2</sub> (24.6 - 13.6 - 16.8 - 45.0 wt%) minimum melting temperature  
 548 mixture using the QVAR-method. The density value at 300 °C of this quinary reciprocal  
 549 system is about 6 % lower compared to Solar Salt.

## 550 7. Summary of available and estimated density correlations of single salts

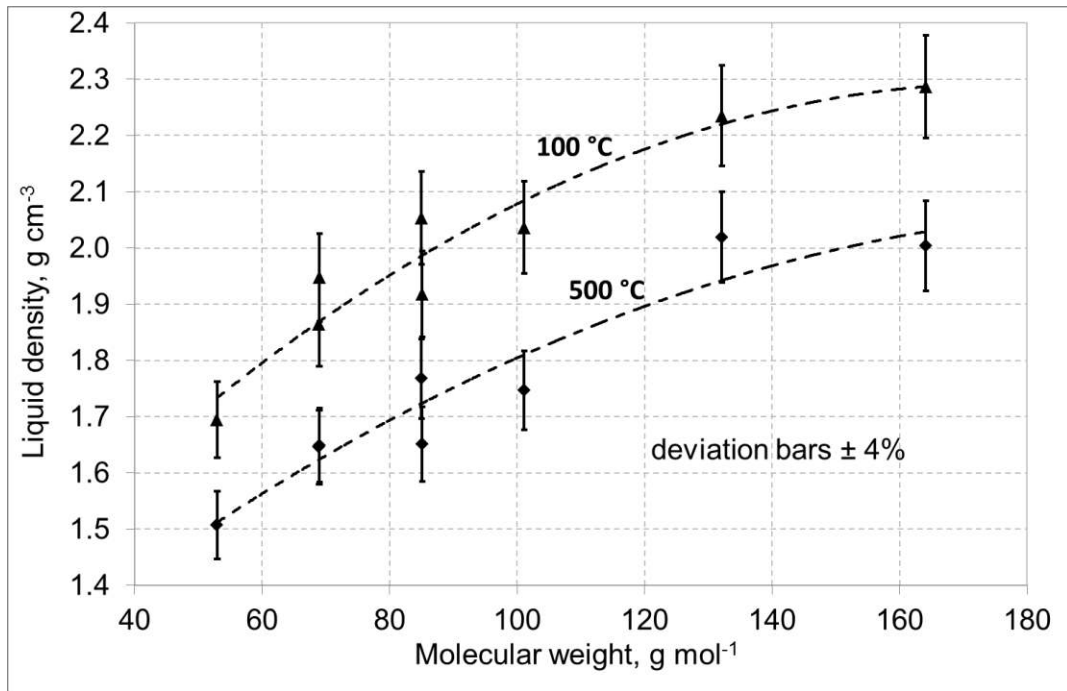
551 This work lists known temperature dependent density equation of single salts from  
 552 literature (Table 1). Density equations for Ca(NO<sub>2</sub>)<sub>2</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>, LiNO<sub>2</sub> were not  
 553 available, since these compounds tend to be unstable above their melting temperature.  
 554 Nevertheless in order to estimate the density of molten salt mixtures with lower melting  
 555 temperatures, it is useful to define an artificial density function for these density  
 556 estimations (Table 7). The accuracy of the Ca(NO<sub>2</sub>)<sub>2</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>, LiNO<sub>2</sub> density  
 557 equations was estimated by an empirical correlation. Figure 13 shows the liquid density  
 558 versus the molecular weight of the single salts defined in Table 1 and Table 7. It can be  
 559 seen that for both 100 °C and 500 °C density values follow an empirically fitted second  
 560 order polynomial. The maximum deviation of ± 4 % between each single salt value and  
 561 the polynomial is assumed to be the accuracy for the Ca(NO<sub>2</sub>)<sub>2</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>, LiNO<sub>2</sub> salts.  
 562 With respect to the temperature range, it should be noted that the melting temperature  
 563 and the thermal stability limit of the selected mixture can restrict the temperature range  
 564 100 to 500 °C.  
 565

566 Table 7. Temperature dependent artificial densities of single salts obtained in this work.

Salt	Melting Temp. $T_m/^\circ\text{C}$	Mol. Weight $M/(\text{g mol}^{-1})$	Density equation $\rho(T)/(\text{g cm}^{-3})$	Accuracy	Temp. range, °C
Ca(NO <sub>2</sub> ) <sub>2</sub>	392	132.089	$\rho(T)^* = 2.289 - 5.40 \times 10^{-4} \cdot (T/^\circ\text{C})$	± 4 %	100 – 500
Ca(NO <sub>3</sub> ) <sub>2</sub>	561	164.087	$\rho(T)^* = 2.358 - 7.085 \times 10^{-4} \cdot (T/^\circ\text{C})$	± 4 %	100 – 500
LiNO <sub>2</sub>	222	52.947	$\rho(T)^* = 1.742 - 4.70 \times 10^{-4} \cdot (T/^\circ\text{C})$	± 4 %	100 – 500

567 \* = artificial density below the melting temperature to estimate densities of mixtures

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 574

**Fig 13.** Liquid (artificial) density vs. molecular weight of the single salts  $\text{Ca}(\text{NO}_2)_2$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{LiNO}_2$ ,  $\text{LiNO}_3$ ,  $\text{KNO}_2$ ,  $\text{KNO}_3$ ,  $\text{NaNO}_2$  and  $\text{NaNO}_3$  at 100 °C and 500 °C to estimate the uncertainty of  $\text{Ca}(\text{NO}_2)_2$ ,  $\text{Ca}(\text{NO}_3)_2$  and  $\text{LiNO}_2$  values.



## 575 8. Summary and conclusion

576 Exact knowledge of molten density values of salt mixtures is essential for modelling,  
 577 thermal design, as well as process measuring and control technology for Concentrating  
 578 Solar Power (CSP) plants. At the time of writing, Solar Salt (60 wt%  $\text{NaNO}_3$  and  
 579 40 wt%  $\text{KNO}_3$ ) represents the heat storage medium in virtually all commercial CSP  
 580 plants. For line-focusing CSP systems, there is currently some research and  
 581 development interest to replace synthetic thermal oil by a molten salt mixture as heat  
 582 transfer fluid. This demands salt mixtures with sufficiently low melting temperatures to  
 583 avoid freezing and sufficiently high thermal stabilities. The paper presented density  
 584 values of promising salt mixtures for this purpose. It is feasible to measure the density  
 585 of such mixture (e.g. Archimedean method). However, such measurements are time-  
 586 consuming and error-prone. Also, there is not only the salt mixture density, but there are  
 587 multiple selection criteria. Hence, a fast density assessment of a plurality of salt mixture  
 588 is of interest. For these reasons, we presented in this paper methods to estimate densities  
 589 of molten salt mixtures based on single salt properties.

590 Table 8 presents density correlations of commonly considered mixtures for line-  
 591 focusing CSP systems. For **Solar Salt**, most commonly a correlation from Nissen is  
 592 utilized. We critically assessed uncertainties of Solar Salt density values in this paper.  
 593 Aspects included the selection of the correct composition, the uncertainty of single salt  
 594 values, the non-ideal mixing behaviour and the nitrite formation. Considering a correct  
 595 composition and newer single salt values, it can be stated that Solar Salt has 10 %  
 596 lower density values at 550 °C compared to commonly applied values from Nissen (see  
 597 Table 8). This density value is about 1.2 % lower, if additionally nitrite formation is  
 598 included.

599 The **Hitec** mixture is a well-known mixture but a theoretical prediction of the density  
 600 based on single salt densities was not available. The system is a ternary reciprocal  
 601 system with two cations and two anions. It was shown in this paper that simple  
 602 estimation by the VAR method gives ambiguous results and should not be utilized. We  
 603 present for the first time a density estimation of Hitec by the QVAR method from the  
 604 single salts. The deviation between QVAR results and measurements were smaller than  
 605 1 %.

606 For the **LiNaK-Nitrate** mixture single salt densities were readily available. It is a  
 607 ternary additive system which can be estimated by the VAR. The deviation between  
 608 VAR results and measurements were smaller than  $\pm 0.9$  % and this is below the  
 609 uncertainty of the  $\text{LiNO}_3$  density values of  $\pm 1.5$  %.

610 **HitecXL** is also a ternary additive system which contains  $\text{Ca}(\text{NO}_3)_2$ .  $\text{Ca}(\text{NO}_3)_2$  is  
 611 thermally unstable above the melting temperature. Hence, liquid density data are not  
 612 readily available. Hence, we used a backward approach to estimate and compare  
 613 artificial density correlations for  $\text{Ca}(\text{NO}_3)_2$  from different literature sources.

614 Experimental HitecXL data from Siegel and estimated values by the VAR method  
 615 agreed within a deviation band of  $\pm 1.5$  %.

616 As a result it can be stated that for Solar Salt, Hitec, LiNaK-Nitrate and HitecXL  
 617 differences between available measurement values and estimated density values by the  
 618 VAR and QVAR deviated less than  $\pm 1.5$  %. Considering typical uncertainties of single  
 619 salt densities and typical measurement uncertainties of mixtures (typically  $\pm 0.5$ -3 %),  
 620 the VAR and QVAR can closely predict densities of mixtures. Several subsystems of  
 621 the system Ca,K,Li,Na/ $\text{NO}_2$ , $\text{NO}_3$  were analysed. We could not identify hints of  
 622 significant non-ideal mixing behaviour within these subsystems. Hence, it can be  
 623 assumed that the entire system Ca,K,Li,Na/ $\text{NO}_2$ , $\text{NO}_3$  shows as a good approximation

624 ideal mixing properties (or additional excess volumes can be neglected). With this work  
 625 consistent density correlations of all eight single salts of the system  
 626 Ca,K,Li,Na//NO<sub>2</sub>,NO<sub>3</sub> are available including artificial liquid density correlations for  
 627 Ca(NO<sub>3</sub>)<sub>2</sub>, LiNO<sub>2</sub> and Ca(NO<sub>2</sub>)<sub>2</sub>, which tend to be unstable above the their melting  
 628 temperature.  
 629 The known QVAR method for the ternary reciprocal system was extended to the  
 630 quinary reciprocal **CaLiNaK-NO23** mixture. The extended QVAR method allowed  
 631 estimation of the density of this minimum melting composition (see Table 8).  
 632  
 633 Table 8. Summary of density equations for discussed molten salt mixtures. Common  
 634 equation from literature and equations using the VAR and QVAR-method with  
 635 consistent single salt densities are given.

Acronym, Salt mixture (composition)	Density Equation $\rho(T)/(\text{g cm}^3)$	Temp. range
Solar Salt, KNO <sub>3</sub> -NaNO <sub>3</sub> (40-60 wt%)	$\rho(T) = 2.090 - 6.36 \times 10^{-4} \cdot (T/^\circ\text{C})$ [26] $\rho(T) = 2.118 - 7.185 \times 10^{-4} \cdot (T/^\circ\text{C})$ (VAR)	300 – 600 °C 290 – 560 °C
Hitec KNO <sub>3</sub> -NaNO <sub>2</sub> -NaNO <sub>3</sub> (53-40-7 wt%)	$\rho(T) = 2.084 - 7.32 \times 10^{-4} \cdot (T/^\circ\text{C})$ [31] $\rho(T) = 2.065 - 7.140 \times 10^{-4} \cdot (T/^\circ\text{C})$ (QVAR)	200 – 500 °C 150 – 500 °C
LiNaK-Nitrate LiNO <sub>3</sub> -KNO <sub>3</sub> -NaNO <sub>3</sub> (30-52-18 wt%)	$\rho(T) = 2.0777 - 7.352 \times 10^{-4} \cdot (T/^\circ\text{C})$ [3] $\rho(T) = 2.051 - 6.639 \times 10^{-4} \cdot (T/^\circ\text{C})$ (VAR)	200 – 500 °C 150 – 500 °C
HitecXL Ca(NO <sub>3</sub> ) <sub>2</sub> -KNO <sub>3</sub> -NaNO <sub>3</sub> (42-43-15 wt%)	$\rho(T) = 2.240 - 8.27 \times 10^{-4} \cdot (T/^\circ\text{C})$ [45] $\rho(T) = 2.209 - 7.194 \times 10^{-4} \cdot (T/^\circ\text{C})$ (VAR)	200 – 500 °C 200 – 500 °C
CaLiNaK-NO23 LiNO <sub>3</sub> -Ca(NO <sub>3</sub> ) <sub>2</sub> -NaNO <sub>2</sub> -KNO <sub>2</sub> (24.6 - 13.6 - 16.8 - 45.0 wt%)	$\rho(T) = 2.035 - 6.506 \times 10^{-4} \cdot (T/^\circ\text{C})$ (QVAR)	100 – 400 °C

636  
 637 Overall, the presented work contributed to a better understanding of density estimation  
 638 of salt mixtures from single salt data. The accuracy could be improved further, if a  
 639 better data basis of single salt density equations with lower uncertainties would be  
 640 available in the future. If ideal mixing properties of mixtures can be confirmed,  
 641 estimations by the VAR and QVAR is a more efficient way of density determination  
 642 compared to individual measurements of mixtures. As shown in this paper, density  
 643 estimations are also applicable for reciprocal and multicomponent mixtures. This will  
 644 allow for efficient optimisation of salt mixtures for line-focusing CSP systems in the  
 645 future. In addition, the applied methodology can be used not only for the discussed  
 646 system Ca,K,Li,Na//NO<sub>2</sub>,NO<sub>3</sub> and its subsystems, but also for other salt systems with  
 647 ideal mixing properties.  
 648

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