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1 A Critical Review of Eutectic Salt Property Prediction
2 for Latent Heat Energy Storage Systems

3 Ralf Raud^{a,*}, Rhys Jacob^b, Frank Bruno^b, Geoffrey Will^a, Theodore A.
4 Steinberg^a

5 ^a*Queensland University of Technology, 2 George Street, Brisbane, QLD 4000, Australia*

6 ^b*University of South Australia, 101 Currie St, Adelaide, SA 5001, Australia*

7 **Abstract**

According to the SunShot initiative, one sixth of the levelized cost of electricity for Concentrated Solar Thermal Power is thermal energy storage. For this power generation paradigm to be successful, the cost of every sub-system must be dramatically reduced. However, the search space for possible storage mediums is too large for a brute force experimental search to be feasible. Thus, a more refined approach is necessary. In this paper, eutectic salt combinations are considered as storage medium. The state of the selection process for these eutectics is discussed. Various methods to predict the important thermophysical properties are reported and applied to eutectics whose physical properties are known. Based on single salt properties, the density of molten salt eutectics can be predicted, around their melting point, to within 5%. Prediction of the melting point and composition is accurate to within 7%. However, the estimation of latent heat for multi-component eutectics is not always accurate, and requires more work. Finally, the thermal conductivity of multi-component eutectics has not been well studied; further research is required to corroborate the predictions.

8 **1. Introduction**

9 As mitigation of climate change becomes more important, critical exam-
10 inations of all renewable energy production paradigms must be undertaken.

*Corresponding author
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11 Amongst the many possible forms of renewable energy production for large elec-
12 trical grids, Concentrated Solar Thermal Power (CSTP) has the advantage of
13 cheaply storing solar energy during the day to be converted to electrical energy
14 during peak load. However, currently, the cost of CSTP is significantly greater
15 than fossil fuels, making widespread adoption a difficult economic proposition.
16 The U.S Department of Energy Sunshot Initiative and the European equiva-
17 lent, ESTELLA, have both investigated the costs associated with CSTP and
18 have published guidelines for system components such that the system will be
19 economically competitive with fossil fuels. The economics are based on the
20 Levelized Cost of Electricity (LCOE), a comparative method which takes into
21 account capital costs, running costs, and fuel costs over the lifetime of the power
22 plant. These cost targets take into account certain operating parameters; for
23 the storage the parameters include a charge and discharge time of less than six
24 hours and discharge temperatures above 600 °C. In this review, eutectic salts
25 are considered as phase change materials (PCMs) for latent heat thermal energy
26 storage systems (LHTESS).

27 Due to the large number of individual salt species and the even larger number
28 of mixtures, the combination space for eutectic salts is enormous. This leads to
29 every temperature range having a number of potential PCM mixtures, which is
30 an advantage for optimal selection. Kenisarin[1] has published a review with an
31 exhaustive list of experimentally determined latent heats of fusion of eutectics,
32 but this review does not exhaust the list of possible combinations. FactsageTM
33 has published over three hundred binary eutectic phase diagrams; Kenisarin's
34 list does not include a significant fraction of these. Indeed, the possible search
35 space for eutectic salts is in the order of hundreds of thousands. This is the
36 disadvantage of a large search space; to experimentally measure the latent heat
37 of fusion, or even just the melting point, for these salts would be an undertaking

38 for several lifetimes. A better method for the selection of salt eutectics must
39 therefore be developed.

40 The relatively large heat flux required presents another difficulty in the eval-
41 uation of eutectic salts as PCMs. Eutectic salts have relatively low thermal
42 conductivity, which reduces heat transfer. The range of thermal conductivities
43 is quite large, however, and the effect of the thermal conductivity on the system
44 cost must be taken into account. A recent review of potential chloride eutectic
45 PCMs [2] found that this is a necessary step in proper evaluation of PCMs. Some
46 studies [3, 4] have found that a significant portion of the cost of the LHTESS is
47 the containment vessel, while other studies have found that increasing the ther-
48 mal conductivity can lead to dramatic reductions of the system cost [5]. Indeed,
49 the search for higher thermal conductivity PCMs has driven a great deal of re-
50 search into composites which can increase the thermal conductivity[6, 7, 8, 9].
51 Thus, to properly evaluate the PCMs, the thermal conductivity must be known.

52 Despite several recent reviews collating data on large numbers of salts [1,
53 2, 10, 11], little data has been collected on the thermal conductivity of molten
54 salts. This is a conclusion which a number of works cite as causing difficulty
55 in the accurate assessment of molten salts [12, 13]. Recent works also detail
56 several issues with experimental determination of the latent heat of salts; Jiang
57 et al. [14] found salt creep to be an issue which prevented their results to
58 correlate with other authors. Williams [15] found salt creep and atmospheric
59 contamination to be a pressing issue which could damage delicate instruments.
60 Gomez [13] also found atmospheric contamination to be an issue; most salts are
61 hygroscopic and absorb water even in relatively dry laboratories. This makes
62 accurate property assessment difficult, and may be behind the discrepancy in a
63 number of recorded measurements [1]. Finally, while a large database of eutectic
64 salt properties exists [16], several studies have not supported its data [13, 17].

65 With the ever present experimental issues, and to narrow down candidates
66 for testing, the search space of possible eutectics must be narrowed down. To
67 accomplish this, the relevant PCM properties must be estimated. First, the
68 relative composition must be determined as the thermophysical properties are
69 calculated based on the mass or molar concentrations of individual component
70 salts. Second, the latent heat of fusion must be accurately estimated. The
71 primary purpose of a LHTESS is to store energy, thus, the amount of energy
72 which is able to be stored is the primary driver of the cost of the PCM. Finally,
73 the density and thermal conductivity of the eutectic informs the design of a
74 containment vessel; a highly dense and highly conductive PCM is preferable, as
75 a smaller containment vessel is required to contain the PCM, further reducing
76 the cost. However, this does not consider the potential corrosive interaction
77 between the PCM and the containment vessel.

78 In this paper, several previously presented theories on calculating the concen-
79 tration, melting point, latent heat, density, and thermal conductivity of molten
80 eutectic salts are critically evaluated. The results of these theories are compared
81 to reliable experimental data on binary and ternary eutectics. Gaps in the the-
82 oretical assessment of the aforementioned properties are discussed; the filling
83 of these gaps will allow for targeted optimization of the selection of PCMs for
84 LHTESS.

85 **2. Component Concentrations and Melting Point**

86 The prediction of the melting point and individual component concentration
87 of a eutectic, based on the component salts, is necessary for the prediction of
88 other properties as it determines the relative weight of the single salt properties
89 in influencing the properties of the eutectic which is formed. A method to predict
90 eutectic composition has been suggested by Brunet et al.[18] This method is

91 based on Raoult's Law:

$$\mu_i = \mu_i^* + RT \ln\left(\frac{x_i}{a_i}\right). \quad (1)$$

92 where μ_i is the chemical potential, μ_i^* is the chemical potential of the ideal
93 component, x_i is the molar concentration, and a_i is the activity coefficient,
94 respectively, of component "i." Brunet assumes that the activity is proportional
95 to the concentration. The objective is an equilibrium solution, thus, Brunet
96 assumes $\mu_i = 0$. With some derivation, Brunet proposes that:

$$R \ln(x_i) = -\frac{H_i}{T} + \frac{H_i}{T_i}. \quad (2)$$

97 where T_i is the melting temperature of the individual component in Kelvin, T
98 is the melting temperature of the eutectic, R is the gas constant, and H_i is
99 the latent heat of the pure substance. Thus, for an n-component mixture, the
100 following system of equations is developed:

$$\begin{aligned} R \ln(x_i) + \frac{H_i}{T} - \frac{H_i}{T_i} &= 0, \\ \sum_{i=1}^n x_i &= 1. \end{aligned} \quad (3)$$

101 which can be solved numerically. Brunet compares results from Eq. (3) to
102 experimental data. Only results for eutectic salt mixtures are considered here
103 and are presented in Table 1. The results of Brunet's method to predict the
104 composition and temperature do not match the experimental data¹, which im-
105 plies that the theory has a fundamental flaw. This method cannot be used to

Table 1: Collected results from Brunet et al. [18] via Eq. (3)

Eutectic Salt	Theoretical Concentration	Experimental Concentration	RMS Error
	mol%	mol%	%
$\text{K}_2\text{SO}_4 + \text{Li}_2\text{SO}_4$	24/76	28/72	4
$\text{K}_2\text{SO}_4 + \text{Li}_2\text{SO}_4 + \text{Na}_2\text{SO}_4$	10/58/32	9/78/13	15.9
LiF + NaF	76/24	50/50	26
LiF+ NaF + KF	61/14/25	47/11/42	12.8
KCl + LiCl	30/70	41/59	11
KBr + LiBr	24/76	40/60	16
	Theoretical Temperature	Experimental Temperature	Error
	°C	°C	%
$\text{K}_2\text{SO}_4 + \text{Li}_2\text{SO}_4$	666	535	16.2
$\text{K}_2\text{SO}_4 + \text{Li}_2\text{SO}_4 + \text{Na}_2\text{SO}_4$	526	512	1.8
LiF + NaF	606	484	16.1
LiF+ NaF + KF	499	454	6.2
KCl + LiCl	467	361	16.7
KBr + LiBr	439	348	14.7

106 estimate the composition of new eutectic mixtures.

107 Sun et al.[19] have used the Wilson Equation to determine the melting point
108 and composition of eutectics with more than two components. Their method
109 relies on experimentally verified binary compositions. Wilson[20] expressed the
110 adjustable components, Λ_{ij} , in terms of the molar volume of the molecules and

¹When predicted temperatures, densities, or thermal conductivities are compared, the following equation is used to determine the "error:"

$$\text{Error} = 100 \cdot \left| \frac{V_{\text{theory}} - V_{\text{experiment}}}{V_{\text{experiment}}} \right|$$

where V is a value such as temperature or thermal conductivity. In the case of component concentrations, as in the following sections, the RMS error is given by:

$$\text{RMS} = \sqrt{\frac{\sum_i^n (x_{i,\text{theory}} - x_{i,\text{experiment}})^2}{n}}$$

111 their interaction energies. Sun et al. solved for these adjustable components
 112 based on experimentally verified binary data, then calculated the activity coef-
 113 ficients for a quaternary eutectic system. These activity coefficients were used
 114 in Eq. (3) to determine the melting point and composition of the eutectic. The
 115 Wilson Equation, for m salts is:

$$\ln(a_k) = -\ln\left(\sum_{j=1}^m x_j \Lambda_{kj}\right) + 1 - \sum_{i=1}^m \left(\frac{x_i \Lambda_{ik}}{\sum_{j=1}^m x_j \Lambda_{ij}}\right). \quad (4)$$

116 In this case, the x_i in Eq. (3) is replaced with $a_i * x_i$. This method was applied
 117 to the ternary system of $\text{Li}_2\text{CO}_3 + \text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3$, and the results are
 118 shown in Table 2.

119 Of note is that the binary $\text{Li}_2\text{CO}_3 + \text{K}_2\text{CO}_3$ system, used in the calcula-
 120 tion of the ternary carbonate system, has two eutectic points. However, the
 121 composition and temperature of one of those eutectic points, when used to cal-
 122 culate the activity coefficients, did not have a solution. Thus, the 41.6 mol%
 123 Li_2CO_3 eutectic was used in the calculations presented in Table 2. Again, these
 124 results show little correlation to experimentally verified eutectic compositions
 125 and melting points. This means Sun et al.'s method must be rejected for the
 126 prediction of new eutectic mixtures.

127 Martynova and Susarev [21] have proposed using a geometric method based
 128 on the triangular Gibbs diagrams to compute the ternary eutectic. This is done
 129 by computing the intersection of the two most stable folds, where the folds join
 130 the binary eutectic point on a side of the Gibbs diagram to the opposite corner.
 131 Fig. 1 is a visual representation of these features. The stability of the fold is
 132 determined by computing the deviation of the corresponding secant, where the
 133 secant is the line joining the other binary eutectic points. First, the derivatives
 134 $(A_i^{i,j})$ are calculated:

$$A_i^{i,j} = \frac{2.3}{x_j^{i,j}} \ln\left(\frac{T_i x_i^{i,j}}{T_{fus}^{i,j}}\right). \quad (5)$$

Table 2: Results of method outlined by Sun et al.[19]

Eutectic Salt	Theoretical Concentration	Experimental Concentration	RMS Error
	mol%	mol%	%
$\text{Li}_2\text{CO}_3 + \text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3$	57.3/28.9/13.9	43.5/31.5/25	10.3
$\text{Li}_2\text{SO}_4 + \text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4$	70.1/28.3/1.6	78/13/9	10.8
$\text{LiF} + \text{NaF} + \text{KF}$	24.2/13.1/62.7	46.5/11.5/42	17.6
	Theoretical Temperature	Experimental Temperature	Error
	K	K	%
$\text{Li}_2\text{CO}_3 + \text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3$	769	670	14.8
$\text{Li}_2\text{SO}_4 + \text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4$	880	785	12.1
$\text{LiF} + \text{NaF} + \text{KF}$	736	727	1.2

135 where $x_i^{i,j}$ is the concentration of component i in the binary eutectic of i and j ,
 136 and $T_{fus}^{i,j}$ is the melting temperature of said eutectic.

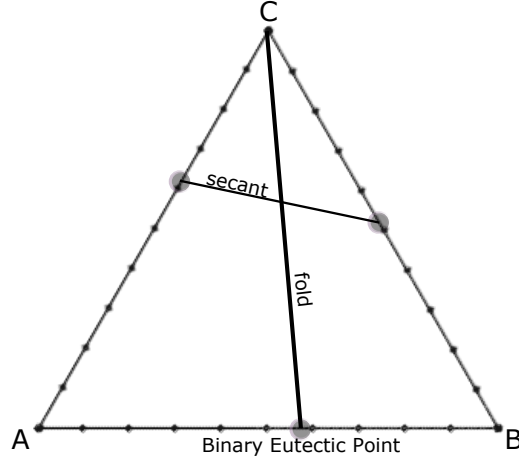


Figure 1: A gibbs triangle with the fold and secant of component 'C' labelled.

137 The stability ($P(i)$) of fold i is calculated via:

$$P(i) = |(A_j^{i,j} - A_k^{i,k})(A_j^{j,k} + A_k^{j,k})|. \quad (6)$$

138 Trunin et al. [22] assert that for systems wherein the minimum $P(i) < 0.15$ the
 139 following equations are used to determine the component concentrations of the
 140 ternary eutectic:

$$\begin{aligned}
 x_x &= \frac{x_x^{x,z} x_z^{y,z}}{x_x^{x,z} x_z^{y,z} + x_z^{x,z} x_y^{y,z} + x_z^{x,z} x_z^{y,z}} \\
 x_y &= \frac{x_z^{x,z} x_y^{y,z}}{x_x^{x,z} x_z^{y,z} + x_z^{x,z} x_y^{y,z} + x_z^{x,z} x_z^{y,z}} \\
 x_z &= \frac{x_z^{x,z} x_z^{y,z}}{x_x^{x,z} x_z^{y,z} + x_z^{x,z} x_y^{y,z} + x_z^{x,z} x_z^{y,z}}
 \end{aligned} \tag{7}$$

141 where (xyz) is the rotation of (ijk) such that $P(x) < P(y) < P(z)$.

142 For systems wherein the minimum $P(i) \geq 0.15$ a different set of equations
 143 is used:

$$\begin{aligned}
 \Delta x_x^{x,y,z} &= (T_x - T_{fus}^{y,z}) \left(\frac{\Delta x_x^{x,y} x_y^{y,z}}{T_x - T_y} + \frac{\Delta x_x^{x,z} x_z^{y,z}}{T_x - T_z} \right), \\
 \Delta x_x^{x,y} &= |0.5 - x_x^{x,y}|, \\
 \Delta x_x^{x,z} &= |0.5 - x_x^{x,z}|, \\
 x_x &= |0.5 - \Delta x_x^{x,y,z}|, \\
 x_y &= (1 - x_x) x_y^{y,z}, \\
 x_z &= (1 - x_x) x_z^{y,z}.
 \end{aligned} \tag{8}$$

144 where (xyz) is the rotation of (ijk) such that $P(x) < P(y) < P(z)$. Trunin et al.
 145 further develop this system for several different eutectics. Among their results,
 146 the root mean square error of composition is less than three, and the melting
 147 point is often calculated within 2%. Application of these equations as presented
 148 leads to errors in composition which, while not as egregious as previous methods,
 149 nevertheless can be improved. For example, the ternary carbonate system yields
 150 a composition which has a RMS error of 5.2%, which is an improvement from

Table 3: Results of method developed by Martynova and Susarev, Eqs.(7),(8)

Eutectic	Experimental Composition	Theoretical Composition	RMS Error
	%mol	%mol	%
$\text{Li}_2\text{CO}_3 + \text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3$	43.5/31.5/25	40.4/34.9/24.7	2.3
$\text{LiF} + \text{NaF} + \text{KF}$	46.5/11.5/42	44.5/12.7/42.8	1.4
$\text{Li}_2\text{SO}_4 + \text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4$	78/13/9	78.4/16/5.6	2.6

151 the 10.3% RMS error of the previous prediction. However, the agreement can
 152 be improved by utilizing Eq. (7) not when $P(i) < 0.15$, but rather in all cases
 153 where the stability of the three elements is similar; i.e, when $|P(x) - P(z)| \leq 1.5$.
 154 In addition, when the element x is the element with the median melting point,
 155 Eq. (8) is modified as such:

$$\begin{aligned}
 x_y &= |0.5 - \Delta x_x^{x,y,z}|, \\
 x_x &= (1 - x_x)x_x^{x,z}, \\
 x_z &= (1 - x_x)x_z^{x,z}.
 \end{aligned}
 \tag{9}$$

156 Eqs. (7), (8), and (9) have been applied to selected systems. The results of
 157 these computations are presented in Table 3. These results are superior to those
 158 of Brunet et al. and Sun et al. as they predict the composition of the eutectics
 159 to within 5%, and to within 3% in most cases. This is in marked contrast to
 160 the methods presented earlier, which usually contain errors of 12% or more in
 161 the predicted composition.

162 Susarev and Martynova[21] extended their equations to apply to the pre-
 163 diction of the composition of quaternary eutectics utilizing binary data and
 164 predicted ternary data. Their results had a maximum error in composition of
 165 2% for reciprocal eutectic mixtures. Non-reciprocal eutectic mixtures do not
 166 contain all the possible combinations of species in the definition, which can lead
 167 to errors in prediction as new species can be formed upon melting. The maxi-

168 mum error for non-reciprocal mixtures wherein the ternary data was predicted
169 based on binary salts was 7%. These results suggest that experimental binary
170 eutectic data can be utilized to predict composition for reciprocal quaternary
171 eutectic mixtures, as these errors are similar in size to the errors in the ternary
172 calculations.

173 Beilmann et al.[23] performed a thermodynamic investigation of the LiF +
174 NaF + CaF₂ + LaF₃ system based on a polynomial estimation of the excess
175 Gibbs free energy. The excess Gibbs free energy is fitted to experimental data
176 with a polynomial equation and this equation is used to compute the Gibbs free
177 energy of higher order systems, which, in turn is used to calculate the phase
178 diagrams. Beilmann et al.[23] experimentally verified their predicted phase dia-
179 grams via differential scanning calorimetry. For three ternary systems and one
180 quaternary system, the experimental solidus and liquidus temperatures varied
181 by about 5% when compared with the theoretical prediction. This is in very
182 good agreement with the theory. However, estimating the Gibbs free energy
183 requires at least one experimental data point for enthalpy of mixing, which
184 Beilmann et al. were required to choose. Existing literature sometimes reports
185 extremely variable enthalpies of mixing for identical samples. The data obtained
186 by Macleod et al.[24] is approximately three times the results obtained by Hong
187 et al.[25] Thus, a careful critic is required of the available enthalpy of mixing
188 data before any further analysis can be completed. Without this enthalpy of
189 mixing data, further analysis would be impossible. However, with just the eu-
190 tectic points of the LiF + CaF₂ and NaF + CaF₂ systems, Eq. (8) yields a
191 eutectic composition for LiF + NaF + CaF₂ of 53.4/34.2/12.4, which compares
192 favorably with Beilmann et al.'s prediction of 51.1/36.5/12.4.

193 Trunin [22] describes the calculation of the melting point for ternary systems
194 as follows. The calculation is broken up into the following four conditions. To

195 begin, let $(\alpha\beta\gamma)$ be the rotation of (ijk) such that $T_\alpha > T_\beta > T_\gamma$. First, if the
 196 binary eutectic with the lowest melting point (e^{lmp}) is not the eutectic formed
 197 by components y and z ($e^{y,z}$), but does contain α , then the ternary eutectic
 198 temperature is the average of the two individual components with the closest
 199 temperatures. If not, the melting point of the ternary eutectic is determined
 200 via:

$$T_{fus}^{i,j,k} = T_\phi - \frac{1 - x_\phi^{i,j,k}}{1 - x_\phi^{\phi,\theta}} (T_\theta - T_{fus}^{\phi,\theta}) \quad (10)$$

201 ϕ and θ are determined via the following three conditionals:

$$\alpha \notin e^{lmp} \text{ and } e^{lmp} \neq e^{y,z}$$

$$\text{then } \phi = \gamma \text{ \& } \theta = \beta$$

$$e^{lmp} = e^{y,z} \text{ and } x \neq \alpha$$

$$\text{then } \phi = \alpha \text{ \& } e^{\phi,\theta} = e^{lmp}$$

(11)

$$e^{lmp} = e^{y,z} \text{ and } x = \alpha$$

$$\text{then } \phi = \beta \text{ \& } \theta = \gamma$$

202 Despite Trunin et al.'s excellent agreement, Eq. (10) yields poor agreement.

203 A new equation for the melting point of the ternary eutectic is developed:

$$T_{fus}^{i,j,k} = T_\gamma - m^\ddagger \cdot (1 - x_\gamma)$$

$$m^\ddagger = \frac{T_\gamma - T_{fus}^{\alpha,\gamma}}{x_\alpha^{\alpha,\gamma}} \frac{x_\beta}{x_\beta + x_\gamma} + \frac{T_\gamma - T_{fus}^{\beta,\gamma}}{x_\beta^{\beta,\gamma}} \frac{x_\gamma}{x_\beta + x_\gamma} \quad (12)$$

204 As shown in Table 4 this yields better agreement, however, the absolute errors

205 are still quite large. Better predictions are necessary.

206 Numerous programs, such as FactsageTM, Thermo-CalcTM, and OpenCalphadTM

Table 4: Calculations of ternary eutectic temperature based on Eqs. (10) and (12).

Eutectic	Experimental Temperature	Theoretical Temperature via Eq. (10)	Error
	K	K	%
Li ₂ CO ₃ + Na ₂ CO ₃ + K ₂ CO ₃	670	1067	37.2
LiF + NaF + KF	727	724	0.4
Li ₂ SO ₄ + Na ₂ SO ₄ + K ₂ SO ₄	785	949	17.3
	Experimental Temperature	Theoretical Temperature via Eq. (12)	Error
	K	K	%
Li ₂ CO ₃ + Na ₂ CO ₃ + K ₂ CO ₃	670	661	1.3
LiF + NaF + KF	727	777	6.9
Li ₂ SO ₄ + Na ₂ SO ₄ + K ₂ SO ₄	785	814	3.7
NaCl + KCl + BaCl ₂	813	874	7.5
LiF + NaF + CaF ₂	880 [22]	825	6.3
NaF + KF + SrF ₂	748 [22]	708	5.3

207 generate phase diagrams based on several geometric methods or mathematical
 208 formalisms. These programs are widely used in research and industry to predict
 209 thermophysical properties based on the properties of the individual components
 210 and single points of experimental data of mixtures. Beilmann et al.'s inves-
 211 tigation of the quaternary fluoride system, discussed earlier, follows the same
 212 formalisms and uses Factsage to complete the calculations. Their accurate re-
 213 sults provide evidence for the efficacy of these systems, however, several recent
 214 studies[13, 17, 14] describe instances where the calculated properties differ from
 215 experimental results.

216 3. Density

217 The density of molten salt eutectics is accurately predicted at the melting
 218 point [26, 27, 12, 28]. Artsdalan suggested using a simple mixing model:

$$\rho_{eutectic} = \sum_i^n x_i * \rho_i. \quad (13)$$

219 where ρ_i is the density of the component salt extrapolated to the eutectic
 220 temperature based on the linear trend of the single component, and n is the

221 number of components. Table 5 contains results compiled from several sources
 222 [26, 27, 12, 29, 30]. The theoretical density is calculated from data presented by
 223 Janz et al.[29, 30] and Nasch et al. [31] and the data for zirconium tetrafluoride
 224 is taken from Williams et. al. [12]. The average error is less than 3.5% with only
 225 two instances of greater than 6% error, across a wide variety of measurements
 226 and salts. This indicates excellent agreement with the theory, especially when
 227 considering that the linear extrapolations of salt densities often have errors in
 228 excess of 2%.

Table 5: Calculations of density based on Eq.(13) and single salt data.

Eutectic	Concentration wt%	Temperature K	Literature $\text{g}(\text{cm})^{-3}$	Theoretical $\text{g}(\text{cm})^{-3}$	Error %	Reference
LiCl + KCl + CsCl	29/12/59	573.35	2.337	2.553	9.24	[27]
LiCl + CsCl	27/73	613.55	2.51	2.714	8.13	[27]
LiCl + KCl	45/55	653.85	1.694	1.686	0.47	[27]
$\text{Li}_2\text{CO}_3 + \text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3$	32.1/33.4/34.5	670	2.148	2.085	2.93	[28]
LiF + LiCl + LiBr	9.6/22/68.4	773	2.19	2.283	4.25	[28]
$\text{Li}_2\text{SO}_4 + \text{K}_2\text{SO}_4$	71.6/28.4	860	2.105	2.106	0.05	[28]
LiF + BeF_2	51.7/48.2	733	2.056	1.981	3.6	[12]
LiF + BeF_2 + ZrF_4	42.4 / 35.7/ 21.9	701	2.295	2.375	3.5	[12]
LiF + KF	30.9/ 69.1	765	2.125	2.097	1.3	[12]
LiF+ NaF + KF	29.2/11.7/59.1	727	2.199	2.133	3	[12]
LiF + RbF	15.8/84.2	743	2.886	3.041	5.3	[12]
NaF + BeF_2	54.2/45.8	613	2.144	2.159	0.7	[12]
NaF + ZrF_4	25/75	773	3.21	3.308	3	[12]

229 4. Latent Heat of Fusion

Very little work has been done on the prediction of the latent heat of fusion based on single salt properties. Kosa et al.[32] published a method which is based on the assumption that the entropy of a binary eutectic must be equal to the

entropy of the individual components. They proposed the following equation:

$$\Delta H_{fus} = T_{fus} * (-R * x_1 * \ln(a_1 * x_1) - R * x_2 * \ln(a_2 * x_2) + \Delta S_{f,1} + \Delta S_{f,2}) + T_{fus} * \left(\int_{T_1}^{T_{fus}} \frac{\Delta C_{p,1}}{T} dT + \int_{T_2}^{T_{fus}} \frac{\Delta C_{p,2}}{T} dT \right) + \Delta H_{mix}. \quad (14)$$

230 where T_{fus} is the melting temperature of the eutectic in Kelvin, T_i is the melting
 231 temperature of the i^{th} component, $\Delta S_{f,i} = \frac{\Delta H_{f,i}}{T_i}$ is the entropy of fusion for
 232 the i^{th} component, $\Delta C_{p,i}$ is the difference in heat capacity between the solid
 233 and liquid phase for the i^{th} component, a_i is the activity coefficient of the i^{th} ,
 234 and ΔH_{mix} is the heat of mixing. Kosa et al. further discussed the practicality
 235 of applying this equation to unstudied binary salt combinations. The heat
 236 of mixing is difficult to determine without studying the latent heat, and the
 237 specific heat of the liquid is difficult to determine for temperatures lower than
 238 the melting temperature of the pure substance. Kosa et al. make the following
 239 simplifying assumptions: $\Delta C_{p,i} = 0$, the activity coefficient is one, and ΔH_{mix}
 240 $= 0$ and then they compare their predictions with the literature for the systems
 241 NaF + Na₂SO₄ and KF + K₂SO₄. Their predictions for the above simplifying
 242 conditions are 13% and 0%, respectively, of the literature values. Kosa et al.
 243 further investigate the influence of their simplifying conditions, finding that
 244 there is little effect on the final error with any combination of conditions.

245 Kosa et al. only examined binary systems, however, so in order to examine
 246 n-component eutectics a generalized Eq.(14) for n-component mixtures is given:

$$\Delta H_{fus} = T_{fus} * \sum_i^n \left(\Delta S_{f,i} + \int_{T_i}^{T_{fus}} \frac{\Delta C_p}{T} dT - R * x_i * \ln(a_i * x_i) \right) + \Delta H_{mix}. \quad (15)$$

247 As shown in Table 6, applying Eq.(15) to the system NaCl + Na₂SO₄ yields
 248 a latent heat of 266 J/g, which compares very favorably with the literature
 249 results. Results that correlate within 9% of literature values for most salts can

250 be calculated by using the assumptions that a_i can be determined via Eq. (1),
 251 $\Delta C_{p,i} = 0$, and $\Delta H_{mix} = 0$. These assumptions are difficult to justify, however,
 252 as they produce extremely inaccurate results for some salts, such as the ternary
 253 system LiF + NaF + KF.

254 Misra et al.[33] have developed another method to determine the latent heat
 255 of fusion. Their method is based on the assumption that the heat of fusion for
 256 the eutectic is given by the heat of fusion of the individual components, Eq.
 257 (16), plus the heat of mixing of the liquid and solid phases.

258 The latent heat of the component at the melting point of the eutectic
 259 (ΔH_i^{fus}) is given by:

$$\Delta H_i^{fus} = \Delta H_i + \int_{T_i}^{T_{fus}} \Delta C_p dT. \quad (16)$$

260 thus, the latent heat of fusion is given by:

$$\Delta H_{fus} = \sum_i^n \Delta H_i^{fus} + \Delta H_{mix}^{i,j,k}. \quad (17)$$

261 Misra et al. do not consider the heat of mixing to be able to be approximated
 262 as zero, and thus develop very explicitly the relationship between the heat of
 263 mixing of binary mixtures and the heat of mixing of ternary components:

$$\Delta H_{mix}^{i,j,k} = (1-x_3)^2 (H_{mix}^{1,2}) \left(\frac{x_1^{1,2}}{x_2^{1,2}} \right) + (1-x_2)^2 (H_{mix}^{1,3}) \left(\frac{x_1^{1,3}}{x_3^{1,3}} \right) + (1-x_1)^2 (H_{mix}^{2,3}) \left(\frac{x_2^{2,3}}{x_3^{2,3}} \right). \quad (18)$$

264 where $H_{mix}^{i,j}$ is the heat of mixing of the binary eutectic, and $x_i^{i,j}$ is the con-
 265 centration of component i in the binary eutectic of components i and j . This
 266 explicit relationship allows for the calculation of the heat of fusion to be cal-
 267 culated for ternary mixtures where the heat of mixing is unknown. Systems
 268 where the binary heats of mixing are unknown must use a different method to
 269 determine the latent heat. Misra et al. develop an approximation of the entropy

Table 6: Latent heat as determined by Eq. (15) with $\Delta C_{p,i} = 0$ and $\Delta H_{mix} = 0$, and by Eq.(17)

Eutectic	Experimental J(g) ⁻¹	Eq.(15) J(g) ⁻¹	Eq.(15) Error %	Eq.(17) J(g) ⁻¹	Eq.(17) Error %
Li ₂ CO ₃ + Na ₂ CO ₃ + K ₂ CO ₃	276	288	4.3	257	6.9
NaCl + Na ₂ SO ₄	268	266	0.7		
NaCl + KCl + BaCl ₂	221	230	4.1	286	29.4
LiF + NaF + KF	402	666	65.7	790	96.5
NaNO ₃ + NaCl + Na ₂ SO ₄	177	193	9		
NaF + CaF ₂ + MgF ₂	512	676	32	574 ²	12.1

270 of mixing based on binary eutectics:

$$\Delta S_{mix}^{i,j} = -R(x_i \ln(x_i^{i,j}) + x_j \ln(x_j^{i,j})) = \frac{\Delta H_{mix}^{i,j}}{T_{fus}^{i,j}}. \quad (19)$$

271 The results of Misra et al.'s method as applied to selected salts are also
 272 given in Table 6. This method is not as accurate as Kosa et al. Both methods
 273 fail for the mixture LiF+NaF+KF, and if experimental binary heats of mixing
 274 are used, Eq.(15) yields 441 g⁻¹J and Eq.(17) yields 541 g⁻¹J. Eq. (17) still
 275 has unacceptable error. However, Eq. (15) only overestimates the results by
 276 10% as compared to experimental values[12]. This may be acceptable for some
 277 applications, however, the lack of extensive heat of mixing data makes this of
 278 limited applicability.

279 Misra et al. go on to describe more detailed methods for computing the heats
 280 of mixing. These methods depend heavily on phase diagrams of constituent par-
 281 tial mixtures, which are difficult to acquire for complicated mixtures. Acquiring
 282 these phase diagrams and heats of mixing is more difficult than experimentally
 283 measuring the latent heat of the desired eutectic.

284 Thus, no robust solution has been indentified which can be applied to predict
 285 the latent heat of eutectics from single salt data. All of these methods either

286 require extensive additional experimental data, or have unacceptable errors.

287 **5. Thermal Conductivity**

288 The many methods of thermal conductivity measurement have yielded a
289 very large spread in the reported values for single salt species [34]. This makes
290 estimating the thermal conductivity of eutectics more difficult. To establish
291 a basis for the prediction of eutectics, the state of the literature for thermal
292 conductivity values of single salts must first be examined.

293 Nagasaka et al. [34] suggested an equation for the thermal conductivity of
294 molten NaNO_3 based on an extensive critical review of published results, tak-
295 ing into account the weaknesses of many methods in controlling for convection.
296 Close to the melting point, this correlation differed from the published data by
297 up to 10%. Further from the melting point, the drift became more pronounced,
298 with up to 20% error at larger temperatures. This error was attributed to
299 weak results from techniques which did not properly take into account convec-
300 tion or electrical conductance of the molten salt. Nagasaka, Nakazawa, and
301 Nagashima[35, 36, 37, 38] have also published a critic of the standard methods
302 for measuring thermal conductivity. They suggested that the forced Rayleigh
303 scattering method is the preferred method for measuring thermal conductiv-
304 ity, as this reduces the contribution of convection and radiative heat transfer.
305 Their results for the measurement of molten chlorides[35], bromides[37], and
306 iodides[38] are all on the low end of the results reported previously in the liter-
307 ature. Their results are often as low as 50% of the maximum result reported in
308 the literature. In addition, they have measured a decline in thermal conductivity
309 as temperature increases for every molten salt. This observation is counter to
310 the majority of the experimental literature, but in line with theoretical results

²Misra et al.[33] utilized experimental heats of mixing to predict this.

311 based on first principles[39, 40] This gives little reason to doubt the validity of
312 their results, despite the large observed differences and the large experimental
313 uncertainty in their results.

314 Otsubo et al.[41] published an experimental study on the thermal conductiv-
315 ity of molten carbonates and their eutectic mixtures. They have also used the
316 forced Rayleigh scattering method and report results significantly below those
317 presented elsewhere in the literature. Of note here is that they suggest a thermal
318 conductivity of 0.567 W(mK)^{-1} for the ternary eutectic of lithium, sodium and
319 potassium carbonate. Maru et al. [42] have estimated the thermal conductivity
320 of this salt as 2.041 W(mK)^{-1} ; this not an atypical variance in literature values
321 for the thermal conductivity of eutectic salts[39, 40]. This large variance makes
322 assessing the accuracy of predictions difficult, and greatly complicates design
323 and selection work for molten salt mixtures, as there is little consistency in the
324 data for single salts. This issue must be resolved before selection of molten salts
325 can be effectively conducted.

326 Hossain et al.[39] have developed further a theory for the prediction of the
327 thermal conductivity of single salts. They base their model on Chandler's theory
328 of molten salts as being a collection of hard spheres. Characteristic properties of
329 the salts can be derived from a single specimen of a species of salts and applied
330 to the other members of said species via the constant C_λ . The hard sphere
331 model for thermal conductivity of molten salts is written in a similar fashion
332 to the relationship of viscosity discussed by Chandler. Essentially, the thermal
333 conductivity, λ , relates to temperature via the same function as a reference, in
334 this case liquid argon, with respect to the reduced volume:

$$\lambda(t) = C_\lambda * (0.68285 - 0.84286x + 0.66370x^2 - 0.21015x^3). \quad (20)$$

335 where, C_λ is the characteristic property of the salt, $x = (V - V_m)/V_s$ is the re-

336 duced volume at temperature t , V is the volume at the temperature, V_m is the
 337 volume at the melting temperature, $V_s = N_a \sigma^3 2^{-1/2}$, N_a is avagadro's number
 338 and σ is the molecular radius. In particular, Hossain et al. predicted C_λ based
 339 on the relationship between C_λ determined from the literature and the molecular
 340 weight of the cation. They claimed to find agreement in predicting the thermal
 341 conductivity of sodium, potassium, and cesium iodides based on the linear rela-
 342 tionship between C_λ and the molecular mass of several chlorides. Their results
 343 are only tabulated in graph form, which makes precise analysis difficult, but
 344 their results appear to suggest error between the theory and experimental data
 345 of about 25%, which is larger than the experimental uncertainty of Nagasaka
 346 et al. In addition, applying this technique to the prediction of bromides fails.
 347 Bromides follow a pattern wherein C_λ increases as molecular mass increases.
 348 Thus, applying Hossain et al.'s technique directly results in an error for CsBr
 349 on the order of 100%, as compared to the experimental results that Hossain et
 350 al. use to justify their theory. For this reason, this theory is not considered
 351 robust for further prediction of salt mixtures.

352 Gheribi et al.[40] utilize the Boltzmann transport equation and hard sphere's
 353 theory to derive an expression for the thermal conductivity at the melting point
 354 which depends on the volumetric specific heat, the speed of sound in the molten
 355 salt, and the phonon mean free path. They then assert that the phonon free
 356 path is proportional to the average of the sum of the anionic and cationic radii,
 357 and inversely proportional to the number of atoms per molecule. Their results
 358 suggest a prediction of thermal conductivity given by:

$$\lambda_{fus} = rK \frac{C_{v,fus} U_{fus}}{3 * n * V_{fus}}. \quad (21)$$

359 where K is a proportionality constant, C_v is the volumetric specific heat at the
 360 melting point, U is the speed of sound at the melting point, V is the molten

361 volume at the melting point, and r is the sum of the average radii. The molten
362 salt LiCl was used to obtain a proportionality constant of 4.33.

363 This equation proves to be quite robust, as Gheribi's predictions for the
364 iodides LiI, RbI, and CsI fall within experimental error, despite the speed of
365 sound data being extrapolated from entropy data. For salts with reliable exper-
366 imental thermal conductivity data, all of Gheribi's predictions fall within the
367 experimental uncertainty.

368 Tufeu et al.[43] measured the thermal conductivity of molten KNO_3 , NaNO_3 ,
369 and NaNO_2 , as well as some mixtures of these salts. They used the coaxial cylin-
370 der method, however, their results for pure NaNO_3 match closely the correlation
371 suggested by Nagasaka et al.[34], so their results can be considered precise. In
372 particular, Tufeu et al. recorded the thermal conductivity of HITECTM, a
373 mixture of all three salts. The following equation has been proposed[44] for
374 estimating the thermal conductivity of salt mixtures:

$$\lambda_{eutectic} = \sum_i^n x_i \lambda_i \quad (22)$$

375 Table 7 compares the predictions of Eq. (22) utilizing the results of Gheribi
376 et al. and experimental data obtained by Tufeu et al.[43] and Otsubo et al.[41].
377 For the nitrate mixtures, the experimental and theoretical results differ by less
378 than 7%. For the carbonate mixtures, the results of Otsubo et al. differ consid-
379 erably from the expected results. However, the experimental results of Otsubo
380 et al. are positively correlated with temperature, which Nagasaka et al.[34] have
381 described as typical of experiments which do not properly take into account con-
382 vection. Thus, Table 7 does not provide a definitive indication of the efficacy of
383 Eq. (22). Multiple temperatures are included as the thermal conductivity varies
384 with temperature, and comparing the variance between experiments and theory
385 demonstrates whether the error is constant or potentially related to experimen-

Table 7: Results of Eq (22).

Salt Mixture	Concentration mol%	Temperature K	Experimental	Theoretical	Error %
			Thermal Conductivity $W(mK)^{-1}$	Thermal Conductivity $W(mK)^{-1}$	
NaNO ₃ + KNO ₃	30/70	543.3	0.433	0.453	4.6
		566.7	0.425	0.448	5.4
		589.5	0.429	0.444	3.5
NaNO ₃ + KNO ₃	46/54	526.2	0.4675	0.475	1.6
		541.5	0.465	0.472	1.5
		557.5	0.4579	0.469	2.4
		572.4	0.4543	0.466	2.6
		588	0.4484	0.463	3.3
NaNO ₃ + KNO ₃	50/50	497.5	0.462	0.485	5
		509.4	0.46	0.483	5
		545.3	0.457	0.476	4.2
		573.7	0.446	0.471	5.6
		592.2	0.446	0.467	4.7
NaNO ₃ + KNO ₃	75/25	546.4	0.479	0.505	5.4
		569.6	0.471	0.501	6.4
		587.3	0.465	0.497	6.9
		592.8	0.47	0.496	5.5
Li ₂ CO ₃ + Na ₂ CO ₃	53.3/46.7	792	0.527	0.831	57.7
		1062	0.573	0.786	37.2
Li ₂ CO ₃ + K ₂ CO ₃	62/38	795	0.542	0.848	56.5
		1072	0.55	0.802	45.8
Li ₂ CO ₃ + Na ₂ CO ₃ + K ₂ CO ₃	43.5/31.5/25	679	0.568	0.779	37.1
		1030	0.612	0.725	18.5

386 tal difficulties, such as improper accounting of the effects of convection. The
387 nitrate salts in Table 7 demonstrate relatively constant error across tempera-
388 ture, suggesting that the difference is related to the experimental uncertainties
389 in values used in the prediction. However, the carbonate salts tend to decrease
390 in error very rapidly with temperature, casting doubt on the validity of the
391 experimental results.

392 More recently, work has been done utilizing the transient hot-wire method to
393 thermal conductivity. Zhang and Fujii[45] conducted experiments wherein they
394 were able to measure the thermal conductivity NaNO_3 with an alumina sputtered
395 platinum wire. Their results were within expected uncertainty of the suggested
396 correlation, giving validity to their other results. The sputtered alumina coating,
397 which has been confirmed to have a negligible effect on measurement accuracy
398 [46], prevents reaction between the salt and the hot wire and prevents current
399 leakage through the conductive molten salt. Zhang and Fujii's experiments
400 also included measurement of the same $\text{Li}_2\text{CO}_3 + \text{Na}_2\text{CO}_3$ eutectic as Otsubo,
401 and their results provide an average thermal conductivity of 0.876 W(mk)^{-1}
402 between 837 and 967 K. This compares much more favorably to the theory, which
403 predicts an average thermal conductivity of 0.812 W(mk)^{-1} between those same
404 temperatures.

405 Finally, the Rayleigh scattering method measures thermal diffusivity, and
406 then thermal conductivity is calculated from this. The transient hot-wire method
407 measures thermal conductivity directly. This, along with the more recent re-
408 sults via Zhang and Fujii, suggests that the hot-wire technique may be more
409 accurate, however, further work is required to validate the method for a variety
410 of eutectics. Despite this, there is some evidence to suggest Eq. (22) is a valid
411 method for predicting the thermal conductivity of salt mixtures.

412 6. Economic Analysis

413 As the cost of the system is an important parameter in the feasibility of
414 the latent heat storage systems (LHTESS), a thorough cost analysis should be
415 performed prior to any experimental analysis. Current cost analyses of LHTESS
416 are based on experimental or fictional values of PCMs [47, 48, 49, 50], however
417 as previously mentioned experimental values are only available for a fraction of
418 the possible PCMs and thus many potential cost-effective PCMs are overlooked.
419 Using the cost method described below a comparison of theoretical encapsulated
420 LHTESS system costs using the predicted PCM properties can be performed. For
421 cost analysis procedure of other LHTESS systems readers are directed to [48].

422 The direct cost of an encapsulated LHTESS system is made of three major
423 components; the cost of encapsulation, the cost of the tank and the cost of the
424 storage material. The installed cost is assumed to be twice the direct cost. The
425 cost of encapsulation is based on costs produced by Nithyanandam et al.[47] for
426 the cost of encapsulating a PCM in a shell based on the size of the capsule using
427 a fluidised bed coating method. We extend the validity of Nithyanandam et al.'s
428 estimation by using the following equation, as it takes into account the size of
429 the capsule and the cost of the shell material. This allows a more thorough cost
430 analysis to be performed for various shell materials.

$$CE = (m_s * C_s) + \frac{r_{cap}^{0.3}}{0.005} * C_{pro} * m_p \quad (23)$$

431 where C_E is the cost of encapsulation, m_s is the mass of the total required shell
432 material, C_s is the cost of the encapsulation material, r_{cap} is the capsule radius,
433 C_{pro} is the processing cost, and m_p is the mass of the PCM to be encapsulated.

434 The estimation of the cost of the tank is based on previous research[51, 52, 53]
435 on the actual cost of storage tanks for a two-tank molten salt system. The cost
436 of the tank is broken into three main costs, namely; the tank material, the

Table 8: Properties of the NaCl + KCl + BaCl₂ eutectic from the literature and predicted via Eqs. (7), (15), and (13). Note that † is calculated via Eq. (13) but uses the literature composition.

Property	Theory	Literature
Composition (%mol)	40.1/33.2/26.7	34/39.3/26.7 [1]
Latent Heat of Fusion (J/g)	233	221 [1]
Solid Density (g/cm ³)	2.96	3.01†
Heat Capacity (J/gK)	–	0.63

437 insulation and the foundation:

$$C_t = [\rho_{TM}h_t(\pi(r_t + w)^2 - \pi r_t^2)]C_{TM} + \pi r_t^2 C_f + 2\pi r_t h_t C_i \quad (24)$$

438 where ρ_{TM} , h_t , r_t , w , and C_{TM} are the density of the tank material, the height,
 439 radius, thickness of the storage tank, and the cost of the tank material respec-
 440 tively. C_f and C_i are the cost of the foundations (\$1210/m²) and insulation
 441 (\$235/m²) respectively. Using the design methodology described in[49], the size
 442 of the storage tank and the mass of the storage materials for the theoretical and
 443 measured PCM is calculated.

444 The cost estimation for the storage material is based on the bulk price of
 445 the PCM and HTF multiplied by the mass of each. As most storage systems
 446 require large quantities of material the assumption that bulk prices can be used
 447 is valid. However it must be noted that additional costs may be associated due
 448 to transportation and further processing which is not explored here. The cost
 449 of some common PCMs and HTFs are shown in [54] and [50].

450 Table 8 lists the properties determined by the methods described previously,
 451 as well as experimental results from the literature. The total cost, as per the
 452 method described previously, is 33.26 \$/kWh for the costs based on theoretical
 453 properties, and 33.66 \$/kWh for costs based on experimental properties. This
 454 indicates excellent agreement between the theory and the literature.

455 7. Conclusions

456 In this paper, several methods for evaluating properties of eutectic salts
457 have been critically evaluated. The melting point and concentration can be
458 effectively evaluated using several methods, although some disagreement exists
459 between experimental work and the theory. Of these, the geometric method
460 proposed by Martynova and Susarev, and modified here and by Trunin, yields
461 good results despite requiring little experimental data.

462 The density of molten salt mixtures at the melting point can be predicted
463 by Eq. (13), which is simply a mass mixing model.

464 The thermal conductivity of molten salts is difficult to predict accurately.
465 This stems from large experimental uncertainties in the properties of the in-
466 dividual salts. Recent work has described theoretical predictions of single salt
467 thermal conductivities. These predictions fall within the experimental uncer-
468 tainty, for the most part, and using these theoretical predictions and a mixing
469 model, Eq. (22), yields results close to experiments for salt mixtures. Recent
470 research has also been undertaken to understand the applicability of the tran-
471 sient hot-wire method to measure directly the thermal conductivity of molten
472 salts. The few results from this technique correlate well to the aforementioned
473 predictions.

474 The last property whose prediction has been reviewed is the latent heat of fu-
475 sion. Two methods were evaluated, entropy or enthalpy balance. Both yielded
476 predictions which deviated less than 10% for salts that did not contain fluo-
477 rine. For fluorine salts, enthalpy balance predictions required precise enthalpy
478 of mixing data to be accurate. This enthalpy of mixing data can be difficult to
479 obtain, or can be incorrect, making this a difficult method by which to predict
480 properties of large numbers of eutectics.

481 Finally, a the properties of the eutectic $\text{NaCl} + \text{KCl} + \text{BaCl}_2$ were pre-

482 dicted and used to perform an economic analysis. This analysis suggests that
483 using the predicted properties to estimate the cost of the eutectic yields a cost
484 which deviates only 2.5% from the cost estimated from experimentally measured
485 properties. This is in excellent agreement.

486 In conclusion, the following gaps have been identified: Firstly, the measure-
487 ment of the latent heat has uncertain correlation to the theory, especially for
488 a few key salt species, such as common fluoride mixtures. Secondly, there is
489 little reliable data to corroborate a mixing model for the thermal conductivity
490 of multi-component eutectics. This is partially due to experimental difficulties
491 in measuring this property. However, despite these difficulties, component con-
492 centration and density for n-component mixtures can be predicted, with some
493 degree of accuracy.

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