Determination of Activity Coefficient of Lanthanum Chloride in Molten LiCl-KCl Eutectic Salt as a Function of Cesium Chloride and Lanthanum Chloride Concentrations Using Electromotive Force Measurements

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Abstract

The thermodynamic behavior of lanthanides in molten salt systems is of significant scientific interest for the spent fuel reprocessing of Generation IV reactors. In this study, the apparent standard reduction potential (apparent potential) and activity coefficient of LaCl_3 were determined in a molten salt solution of eutectic LiCl-KCl as a function of concentration of LaCl_3 . The effect of adding up to 1.40 mole % CsCl was also investigated. These properties were determined by measuring the open circuit potential of the La—La(III) redox couple in a high temperature molten salt electrochemical cell. Both the apparent potential and activity coefficient exhibited a strong dependence on concentration. A low concentration (0.69 mole %) of CsCl had no significant effect on the measured properties, while a higher concentration (1.40 mole %) of CsCl caused an increase (become more positive) in

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the apparent potential and activity coefficient at the higher range of LaCl_3 concentrations.

Keywords: Activity Coefficient, Molten Salt Electrochemistry, Lanthanum Chloride, Cesium Chloride, Apparent Potentials

1. Introduction

The behavior of lanthanides in molten salt systems is of great scientific curiosity for the research, development and commercialization of Generation IV reactor candidates. The pyrochemical treatment of spent nuclear fuel (pyroprocessing) also represents a promising alternative to the aqueous processing of oxide fuel[1–3]. In the pyroprocessing scheme, the uranium and transuranics are separated from the bulk of the spent nuclear fuel using an electrolytic cell called an electrorefiner. During electrorefining, the spent nuclear fuel is placed in anode baskets. The cathode is either a steel cylinder or a crucible containing a liquid metal like cadmium. The electrolyte used for pyrochemical reprocessing is eutectic LiCl-KCl molten salt which contains nominally 5 to 10 wt. % UCl_3 . One of the major objectives of recent research in pyroprocessing has been towards understanding how to efficiently recover actinides from the electrorefiner and prevent their loss to waste streams. During normal operations, transuranic actinides and other active metal fission products accumulate in the salt as chlorides. To achieve high levels of actinide recovery in the process, these actinides must be separated from the salt prior to disposal of the salt. This is commonly referred to as actinide drawdown. A promising option for actinide drawdown is electrolytic reduction onto either a solid or liquid cathode coupled with

21 evolution of chlorine gas at an inert anode. In theory, the actinides can be
22 reduced first, due to their higher electrochemical nobility, leaving the rare
23 earths in the salt. However, in some cases, the standard reduction potentials
24 for actinides and rare earths are quite close and may result in co-deposition
25 of unwanted rare earth metals. Standard reduction potentials do not take
26 into account the non-ideal behavior of solutions. Understanding the behavior
27 of these species in molten salt systems will aid in the design and develop-
28 ment of optimized electrolytic systems. It is imperative to be able to predict
29 the reduction potentials of actinides and rare earths at conditions of interest
30 including varying compositions of complex salt mixtures and temperatures.

31 The development of highly accurate, predictive thermodynamic models
32 for the pyrochemical treatment of spent nuclear fuel is critical for many
33 other aspects of commercialization; development of on-line sensors, assess-
34 ment of corrosion processes, and advancement of salt treatment methods
35 to enable waste minimization. For the development of such models, one of
36 the most fundamental yet esoteric quantities of interest are species' activ-
37 ity coefficients. Unlike gases where the fugacity can be calculated from first
38 principles by determining the partition functions, for liquids there presently
39 exists no grand unifying theory to calculate the activities from first princi-
40 ples. Activities have to be determined empirically for a given mixture, and
41 the results are unique to that mixture and its individual constituents. For
42 pyrochemical reprocessing of spent nuclear fuels in molten salts, the empirical
43 determination of activities is further complicated by the quagmire of esoteric
44 thermodynamic formalisms.

45 For LaCl_3 in molten eutectic LiCl-KCl salt, the activity coefficient has

46 been previously measured experimentally by a number of groups over the
47 years [4–8]. Activity coefficient of lanthanides like Gd, Nd, Ce has been mea-
48 sured by a much larger group of authors. A good summary of the data was
49 published by Zhang[9] recently. One of the common themes of the studies
50 to date has been the inherent presumption that the activity coefficients are
51 independent of concentration of analyte present in solution. The activity
52 coefficient of lanthanum chloride has been studied only at single concentra-
53 tion in these studies. There is significant divergence in the data reported in
54 literature. One of the contributing factors for such divergence may be the
55 fact that every study was performed at a different concentration of LaCl_3 .
56 Looking at analogous aqueous chemistry literature, it has been reported [10]
57 that the activity coefficient of metal ions in aqueous solutions varies with
58 concentration. No such study has been performed for La(III) ions in molten
59 chloride salt.

60 Cesium is an important fission product that can accumulate in the elec-
61 trolyte in the molten salt over time. Large amounts of accumulated cesium
62 in the electrorefiner electrolyte can interfere with the separation process for
63 the uranium and transuranics. This would require the either the eventual re-
64 placement of the electrolyte or the selective extraction of cesium from the salt.
65 One of the proposed flow sheets for the further reduction in total waste is the
66 Rare Earth Drawdown (REDD) process [11]. REDD can be a useful process
67 for minimizing the amount of waste generated by selectively separating rare
68 earth fission products from Group I and II metals in the salt thus enabling
69 recycling of the eutectic LiCl-KCl electrolyte back to the electrorefiner. One
70 of the motivations of this paper is to study the concentrations at which the

71 presence of CsCl will begin to affect the properties of the lanthanides in
72 the molten salts, to enable us to predict and anticipate the levels of CsCl
73 concentrations would be a cause of concern from a reprocessing standpoint.

74 In this study, we present a thermodynamic framework for determining
75 the activities of species in dissolved molten salts and further present experi-
76 mentally determined activity coefficient of LaCl_3 in molten eutectic LiCl-KCl
77 salt. Further, we will look at the effects of concentration of LaCl_3 and the
78 effect of cesium chloride on the activity coefficient of LaCl_3 .

79 2. Experimental

80 2.1. Equipment and Reagents

81 All the experiments were performed inside an ultra-dry argon atmo-
82 sphere (≤ 0.1 ppm O_2 and ≤ 0.1 ppm H_2O) glovebox (Innovative Tech-
83 nologies). A Kerr furnace was used to heat the salts to the desired tempera-
84 ture. The salts were heated in SIGRADUR[®] glassy carbon crucibles (HTW
85 Germany). A two-electrode electrochemical cell was set-up to perform open
86 circuit potential (OCP) measurements. The working electrode was a perfo-
87 rated stainless steel basket into which a lanthanum metal rod was placed.
88 The counter/reference electrode was a 5 mole % Ag/AgCl reference elec-
89 trode. The reference electrode was encased in a Pyrex tube (Wilmad[®] Sigma
90 Aldrich; 100MHz; 10 mm diameter). The temperature of the molten salt was
91 measured using RTD thermocouples (Omega). The OCP was measured us-
92 ing an Autolab potentiostat (MetrohmUSA). Though nominal concentrations
93 were based on mass of salts added to the mixtures, actual concentrations of
94 lanthanum in the salt mixture were determined using an inductively cou-

95 pled plasma - optical emission spectroscopy (ICP-OES) instrument (Spectro
96 Genesis). Actual cesium concentration was determined using an inductively
97 coupled plasma - mass spectrometry (ICP-MS) instrument (Agilent Tech-
98 nologies). All samples were weighed on a precision balance (Mettler Toledo).
99 Precision balances are susceptible to drift due to build-up of static charges
100 which is aggravated with balances placed inside a dry atmosphere glovebox.
101 A vial full of radioactive material (uranium oxide) was always kept inside the
102 precision balance to neutralize the static charges.

103 Reagents used for this study were as follows: Ultra dry 99.99 % LiCl-KCl
104 (Sigma-Aldrich), 99.998 % ultra-dry cesium chloride salt (Alfa Aesar), 99.99
105 % ultra-dry lanthanum chloride salt (Alfa Aesar) and lanthanum metal rod
106 (6.35 mm x 25 mm; 99.9 % Alfa Aesar), silver chloride (99.997 % metals basis;
107 Alfa Aesar), silver wire (1 mm diameter, 99.9 % metal basis; Alfa Aesar).
108 Standards for ICP calibration were procured from Inorganic Ventures.

109 *2.2. Experimental Procedure*

110 A schematic of the experimental set-up is shown in Figure 1. This set-up
111 was used for all of the experiments unless otherwise stated. For studying
112 the activity coefficient as a function of LaCl_3 concentration, pre-weighed
113 quantity of pure LiCl-KCl salt was heated to the desired temperature (773
114 K). Subsequently, pre-weighed quantities of LaCl_3 were added to this molten
115 salt progressively. After every addition of LaCl_3 , the solution was allowed to
116 stand and equilibrate. The stainless steel basket with the lanthanum metal
117 rod was then inserted into the molten salt mixture and open circuit potential
118 (OCP) measurements were made. After such a measurement, LaCl_3 was
119 again added and the process was repeated. After every OCP measurement,

120 a sample was taken using a stainless steel all-thread rod. For tests with
121 CsCl present, the initial melt consisted of LiCl-KCl-CsCl. During the life of
122 the tests, small quantities of CsCl were added to prevent dilution of CsCl
123 concentration. The remaining experimental methodology was similar to the
124 one described above.

125 The glassy carbon crucible is a conductor of electricity. To ensure that
126 there were no mixed potential artifacts between the crucible and working
127 electrode, we ensured that the working electrode was never in physical con-
128 tact with the glassy carbon crucible. The working electrode basket was
129 held suspended in the molten salt with the help of alligator clips, which
130 were resting against the alumina lid used for the experiments. Addition-
131 ally any mixed potential effects associated with the stainless steel basket
132 and La metal rod, we believe should be negligible. Iron (the predominant
133 constituent in stainless steel) is electrochemically nobler than lanthanum in
134 molten LiCl-KCl eutectic salt [12]. For any significant mixed potential ef-
135 fects to be present, the Fe(II)/Fe(0) half-cell reaction must proceed forward,
136 driving the La(III)/La(0) half-cell reaction backwards. In our working elec-
137 trolyte, no significant quantities of Fe(II) are present (apart from impurities),
138 for this to be a cause of concern.

139 **3. Theory**

140 *3.1. Experimental Determination of Activity Coefficients*

141 In this section, the theoretical basis for determining the activity coefficient
142 from an electrochemical cell will be presented. Consider a metal M and its
143 dissolved species M^{n+} . An elementary reversible reaction can be written as

144 shown in Equation 1

145 For Equation 1, the Nernst equation can be written as shown in Equation
146 2

$$E^{eq} = E^0 - \frac{RT}{nF} \ln \left(\frac{a_{M^0}}{a_{M^{n+}}} \right) \quad (2)$$

147 In Equation 2, R is the universal gas constant, T is the temperature
148 in Kelvin, n is the number of electrons transferred in Equation 1 and F is
149 Faraday's constant. a_{M^0} and $a_{M^{n+}}$ are the activities of M^0 and M^{n+} . E^{eq}
150 is the equilibrium potential and E^0 is the standard reduction potential. In
151 general, E^0 is defined as the potential when a pure metal M is in equilibrium
152 with its pure dissolved ion M^{n+} at the temperature of interest. We know
153 from thermodynamics that $a_{M^0} = 1$, since it is a pure solid. Hence Equation
154 2 can be re-written as follows:

$$E^{eq} = E^0 + \frac{RT}{nF} \ln (a_{M^{n+}}) \quad (3)$$

but,

$$a_{M^{n+}} = \gamma_{M^{n+}} X_{M^{n+}} \quad (4)$$

155 where $\gamma_{M^{n+}}$ and $X_{M^{n+}}$ represent the activity coefficient and mole fraction
156 of species M^{n+} respectively. Substitute Equation 4 in Equation 3,

$$E^{eq} = E^0 + \frac{RT}{nF} \ln (\gamma_{M^{n+}} X_{M^{n+}}) \quad (5)$$

157 Re-arranging the terms,

$$E^{eq} = E^0 + \frac{RT}{nF} \ln (X_{M^{n+}}) + \frac{RT}{nF} \ln (\gamma_{M^{n+}}) \quad (6)$$

Equation 6 can be re-written as follows:

$$E^{eq} - \frac{RT}{nF} \ln (X_{M^{n+}}) = E^0 + \frac{RT}{nF} \ln (\gamma_{M^{n+}}) \quad (7)$$

In deriving Equation 7, Equation 4 is used which defines the activity of the solute as a product of activity coefficient and mole fraction. The Nernst equation can be written correctly for any of the three concentration scales of molarity, molality and mole fraction[13, 14]. Depending on the concentration scale used, the standard states for each of these concentration scales must be defined adequately. Hence each of the concentration scales there will be unique values of standard reduction potential (E^0) designated as E_M^0 , E_m^0 and E_X^0 for molarity, molality and mole fraction respectively [13, 14]. For this study, the standard state used is the Pure Supercooled Liquid LaCl_3 i.e. $X_{\text{LaCl}_3} = 1$. The mole fraction scale is more convenient to use for molten salt systems than the molarity scale as it is independent of density and temperature. This is also the scale most widely used in the molten salt literature hence comparable thermodynamic data is more easily available. Density of salts is extremely hard to measure accurately due to solute effects. Hence we derive the Nernst equation on the mole fraction scale.

All of the terms on the left hand side (LHS) of Equation 7 are known. We would measure E^{eq} in an electrochemical cell (as the OCP). Knowing the concentration of the species present, $X_{M^{n+}}$ can be calculated. Thus, using Equation 7 we can calculate the Apparent Potential ($E^{0'}$). $E^{0'}$ is defined as shown in Equation 8. Bard and Faulkner[15] call the term $E^{0'}$ as the *Formal*

179 *Potential.*

$$E^{0'} = E^0 + \frac{RT}{nF} \ln (\gamma_{M^{n+}}) \quad (8)$$

180 The right hand sides (RHS) of both Equations 7 and 8 are the same. Hence we
 181 can equate the left hand sides of the aforementioned equations and obtain
 182 the value of $E^{0'}$. Knowing $E^{0'}$, we can determine the value of $\gamma_{M^{n+}}$ from
 183 Equation 8 if we know the value of the only other unknown quantity; E^0 .
 184 As mentioned earlier, in the purist sense, E^0 for the La(0)—La(III) system,
 185 will be the equilibrium potential when pure La metal is in equilibrium with
 186 pure La(III) (lanthanum chloride) at the temperature of interest (773 K).
 187 The electrorefining of the spent fuel in eutectic salt is carried out at 773
 188 K. Pure lanthanum chloride melts at 1131 K, hence it is not possible to
 189 obtain a true value of E^0 for lanthanum chloride for molten eutectic salt
 190 mixtures. This is also true for other lanthanides and actinides that have the
 191 melting temperature of the pure salt above the working temperature of an
 192 electrorefiner. Due to this conundrum, there is clearly a need to define the
 193 activity of La(III) versus a different standard state. For that we delve into
 194 the most basic definition of activities for real solutions. In general, activity
 195 of any species ' i ' can be defined as shown in Equation 9.

$$\bar{G}_i = \bar{G}_i^0 + RT \ln a_i \quad (9)$$

196 In Equation 9, $\bar{G}_i$ is the partial molar Gibbs free energy (chemical po-
 197 tential) of the species ' i ' and $\bar{G}_i^0$ is the partial molar Gibbs free energy of
 198 the species ' i ' at the standard state (equivalent to the molar Gibbs free en-
 199 ergy of the pure species). We can choose to define the standard state with

the most appropriate conditions of extensive thermodynamic properties. For molten salt systems, if we want to measure the deviation from ideal behavior, $\bar{G}_i^0$ must be defined as the chemical potential of the 'Pure Supercooled Liquid Salt'[16]. This is the reference that has been used by various authors that have experimentally determined the activity coefficient of lanthanum chloride. Some authors have mistakenly used the value of Gibbs free energy of formation of pure crystal as the reference/standard state. Such a standard state has no physical meaning and is inherently inaccurate. The 'Pure Supercooled Liquid LaCl_3 ' standard state will be used in this work.

Converting potential to Gibbs free energies using the relationship $\Delta G = -nFE$ and replacing the value of ΔG^0 with ΔG^{SC} , the Gibbs free energy of Pure Supercooled Liquid. Now, Equation 8 can be re-written as follows:

$$\Delta G^{SC} - \Delta G^{0'} = RT \ln (\gamma_{M^{n+}}) \quad (10)$$

The term $\Delta G^{SC} - \Delta G^{0'}$ is also known as the Gibbs Excess Free Energy (ΔG^{Excess}). The term ΔG^{Excess} captures the deviation from ideal behavior of a liquid mixture[17]. For ideal solutions, ΔG^{Excess} is zero. Equation 10 can be re-written as follows:

$$\boxed{\Delta G^{Excess} = \Delta G^{SC} - \Delta G^{0'} = RT \ln (\gamma_{M^{n+}})} \quad (11)$$

Using Equation 11, the activity coefficient (and by extension the activity) of a species can be calculated. The only unknown in this equation is the value of ΔG^{SC} . A detailed discussion on how to determine this value is provided in the next subsection.

220 3.2. Determination of ΔG^{SC}

221 In general, we can define a change in Gibbs free energy of fusion (ΔG_{Fusion})
 222 in Equation 12, where $G_{PureLiquid}$ and $G_{PureSolid}$ are the chemical potentials
 223 of pure liquid and pure solid respectively.

$$\Delta G_{Fusion} = G_{PureLiquid} - G_{PureSolid} \quad (12)$$

224 If we are at temperatures below the melting point of the species, as is the
 225 case for LaCl_3 at 773 K here, then ΔG_{Fusion} is the hypothetical free energy of
 226 fusion, $G_{PureLiquid}$ is equal to the chemical potential of the pure supercooled
 227 liquid (G^{SC}), our desired standard state for determination of activity coef-
 228 ficients, and $G_{PureSolid}$ is equal the Gibbs free energy of formation of pure
 229 crystal ($G_{Formation}$) at the temperature of interest (T_i). Hence Equation 12
 230 can be re-written as follows:

$$\Delta G_{Fusion}^{Hypothetical}(T_i) = G^{SC}(T_i) - G_{Formation}(T_i) \quad (13)$$

231 In Equation 13, ' T_i ' represents the temperature (in Kelvin) for which the
 232 calculations are performed. For Equation 13 to be true as written, $T_i < T_M$,
 233 where T_M is the melting point of the pure solid (For LaCl_3 , $T_M = 1131$
 234 K). In Equation 13, the value of $G_{Formation}$ can be found in thermodynamic
 235 databases[18] or sources like the NIST-JANAF Thermochemical Tables. G^{SC}
 236 is the unknown value of the "Pure Supercooled Standard State" we are trying
 237 to determine. In the next subsection, we will look at the method to determine
 238 the value of $\Delta G_{Fusion}^{Hypothetical}$.

239 3.2.1. Determination of $G_{Fusion}^{Hypothetical}$

240 In this section, we will look briefly at a general method to calculate the
 241 value of $G_{Fusion}^{Hypothetical}$. Figure 2 shows a schematic of the H vs. T diagram. T_i
 242 and T_M denote the temperature of interest for which the value of $G_{Fusion}^{Hypothetical}$
 243 (hereafter denoted as G_{Fusion}) needs to be calculated and the melting tem-
 244 perature of the substance respectively. On an H vs. T diagram, the slope
 245 of the lines is the $C_{p(S)}$ and $C_{p(L)}$, which denote the specific heat capacity of
 246 solid and liquid at temperatures lower and higher than T_M respectively. The
 247 value of ΔG_{Fusion} , can be determined as follows[19]:

248 At $T = T_M$,

$$\Delta G_{Fusion} = \Delta H_{Fusion} - T_M \Delta S_{Fusion} = 0 \quad (14)$$

249 The values of ΔH_{Fusion} and ΔS_{Fusion} at $T = T_M$ can be found in thermo-
 250 dynamic databases. At any other temperature of interest (T_i), the values
 251 of $\Delta H_{Fusion}(T_i)$ and $\Delta S_{Fusion}(T_i)$ which are needed to calculate the value of
 252 $\Delta G_{Fusion}(T_i)$ can be calculated as shown in Equation 15 and 16, respectively.

$$\Delta H_{Fusion}(T_i) = \Delta H_{Fusion}(T_M) + \int_{T_M}^{T_i} (C_{p(Liquid)} - C_{p(Solid)}) dT \quad (15)$$

$$\Delta S_{Fusion}(T_i) = \Delta S_{Fusion}(T_M) + \int_{T_M}^{T_i} \frac{C_{p(Liquid)} - C_{p(Solid)}}{T} dT \quad (16)$$

253 For the above calculations, the value of $C_{p(L)}$ is extrapolated below the
 254 melting point to the temperature of interest. Using Equations 15 and 16,
 255 the values of $\Delta H_{Fusion}(T_i)$ and $\Delta S_{Fusion}(T_i)$ can be calculated. The value of

$\Delta G_{Fusion}(T_i)$ can then be calculated simply by using the standard thermo-
dynamic relationship $\Delta G_{Fusion}(T_i) = \Delta H_{Fusion}(T_i) - T\Delta S_{Fusion}(T_i)$. After
having calculated the values of $\Delta G_{Fusion}(T_i)$, the value of $\Delta G^{SC}(T_i)$ can be
calculated using Equation 13. If $T_i < T_M$, then the value calculated using
the above described method will be equal to ΔG^{SC} . The value of ΔG^{SC} can
now be used to calculate the activity coefficient from Equation 11.

In Equation 13, the value of $G_{Formation}$ at any desired temperature can be
obtained readily from thermodynamic databases, software or from previously
published literature. The accuracy with which the value of $G_{Formation}$ can
be calculated is generally $\pm 10 \text{ kJ/mole}$. A survey of literature showed that
at 773 K, the reported values from Gibbs free energy of formation for a pure
crystal LaCl_3 , were found to be -880.9 kJ/mole (HSC Chemistry Software
v. 7.11), -896 kJ/mole [7], -882.8 kJ/mole [18] and -900.8 kJ/mole [20].
Depending on the choice of reference for the Gibbs free energy of formation
that was selected, the value of the activity coefficient would change by over
three orders of magnitude. This is because as shown in Equation 11, the
activity coefficient is an exponential function of the Gibbs free energy of
formation. Rather than consider this as a source of error in the calculation of
activity coefficients, it should be seen as the compelling reason why the data
and methods used to calculate the standard state free energy of formation
must be cited along with the values of the activity coefficients. Without
such specific information, the activity coefficients are of no value as they are
not uniquely defined. Using the theory presented above, we calculated the
 ΔG^{SC} values for LaCl_3 as shown in Table 1. For these calculations, we used
Thermochemical Data of Pure Substances [18] as the source.

281 4. Results

282 In general, we observed that the OCP values recorded using the po-
 283 tentiostat were very stable to the third decimal place (which is the limit
 284 for the instrument) with fluctuations non-existent. Statistical analysis per-
 285 formed on a random sample of 17 independent OCP measurements yielded
 286 an average standard deviation of 0.120 mV in the measurements. Using
 287 that data set, within a 95% confidence interval the average margin of error
 288 for the OCP measurement was calculated to be 0.04 mV. These statistical
 289 calculations help us perform error propagation analysis through the entire
 290 calculations. All the potentials reported in this paper are reported versus
 291 a Cl^-/Cl_2 reference electrode unless otherwise stated. Data reported by
 292 Yang and Hudson[21] was used to convert the potentials from the 5 mole %
 293 Ag/AgCl reference electrode we used to the Cl^-/Cl_2 scale. In this section,
 294 we will now present results from the experiments for activity coefficient of
 295 LaCl_3 first as a function of LaCl_3 concentration. Next data will be presented
 296 on the effect of CsCl on the activity coefficient of LaCl_3 .

297 Figure 3 shows a cyclic voltammogram (CV) of lanthanum chloride present
 298 in molten eutectic salt. The CV was performed at four scan rates of 200,
 299 300 400 and 500 mV/s. The $\text{La(III)}/\text{La(0)}$ peak can be observed clearly in

Table 1: Calculated values of Gibbs Free Energy of Pure Supercooled LaCl_3 .

Temperature	ΔH_{Fusion}	ΔS_{Fusion}	ΔG_{Fusion}	$\Delta G_{\text{Formation}}$	ΔG^{SC}
(Kelvin)	(kJ/mole)	(J/K-mole)	(kJ/mole)	(kJ/mole)	(kJ/mole)
773	41.813	34.507	15.139	-882.767	-867.628

the CV and has been labeled. As expected, it is observed that the current increases with the scan rate. The main take away from the CV is that there is no other analyte species present in the molten salt electrolyte. Any Cs(I) present introduced in the form of CsCl, will reduce at a potential more negative than the reduction potential of Li^+/Li peak[12]. Hence Cs^+/Cs reduction cannot readily be observed in the cyclic voltammetry scans.

4.1. Effect of LaCl_3 Concentration

The calculation of activity coefficients from OCP measurements is an exponential mathematical relationship as described earlier. Even small errors in the measurements of the open circuit potentials will not only propagate through the calculations but indeed gets magnified as we go through our calculations. Hence we decided to smooth the open circuit potential measurements at this initial stage using a suitable function to prevent the further propagation and magnification of these errors. Matlab was used to generate this function, of the form $y = ae^{bx} + ce^{dx}$, from the experimental data.

The average difference between the measured and modeled values is observed to be about 2 mV with a standard deviation of 1.4 mV. Such small errors are well within the realm of experimental error associated with physical measurements. Figure 4 shows the experimental values of OCP plotted along with the model fit. The coefficient of determination for the fit to function was greater than 0.99. For all further calculations, the values obtained from the best-fit functions were used rather than discrete measured data points.

Using the values obtained, we can calculate the apparent potential and activity coefficients of LaCl_3 in the molten salt. Figure 5 shows a plot of the apparent potential ($E^{0'}$) plotted as a function of concentration. It can

325 be observed that the value of the apparent potential is not a constant value
 326 as previously assumed and is indeed a function of concentration. The value
 327 of $E^{0'}$ initially increases (becomes more positive) reaching its most posi-
 328 tive value at about 0.55 mole % La. It then proceeds to decrease (becomes
 329 more negative) and beginning to taper off at higher concentrations of LaCl_3
 330 towards a constant value. Within the concentration range tested, the elec-
 331 trochemical potential for the reduction of La(III) to La(0) varies by about
 332 25 mV. Previously, Shirai et al.[22], Kuznetsov et al.[23] & Tang and Pesic[6]
 333 independently reported the apparent potential of the La(III) — La(0) couple
 334 at 773 K to be -3.137 V, -3.079 V, and -3.072 respectively. These values are of
 335 course outside of the potential window that reported in this paper. However,
 336 a closer look at the experimental methods employed by each of these authors
 337 likely explains why that is the case. Shirai et al.[22] used cyclic voltamme-
 338 try (CV) to determine the reduction potentials of the La(III) — La(0) couple.
 339 The use of CV's is not necessarily an optimal technique to determine equilib-
 340 rium reduction potentials since the potentials measured during CV include
 341 overpotentials associated with nucleation and growth of the metal crystals
 342 on the cathode[24, 25]. Kuznetsov et al.[23] performed their experiments
 343 in a mixture of $\text{LiCl-KCl-UCl}_3\text{-LaCl}_3$ mixture. In such a scenario, there is
 344 likely to be other effects at play between the two analytes present. Tang and
 345 Pesic[6] meanwhile used equilibrium measurements. The only difference was
 346 that they used a molybdenum working electrode. They deposited some La
 347 metal on to the working Mo electrode and measured the OCP. This allowed
 348 for a very short time to study the open circuit potentials.

349 The activity coefficient of LaCl_3 (γ_{LaCl_3}), can now be calculated for each

350 concentration of lanthanum chloride for which the open circuit potential mea-
 351 surements were performed using Equation 11. The standard state used for
 352 such calculations was the "Pure Supercooled Liquid Standard State," the
 353 calculations for which have been shown in the Table 1. Figure 6 shows a
 354 plot of activity coefficient as a function of LaCl_3 concentration. We see that
 355 the activity coefficient of LaCl_3 varies with concentration, initially increasing
 356 and subsequently decreasing, a function that is similar to the variation of
 357 apparent potential.

358 Previously from reports in the literature, the value of γ_{LaCl_3} has been as-
 359 sumed to be independent of concentration, presumably based on an assump-
 360 tions regarding pseudo-ideal behavior of dilute solutions. Results reported
 361 here clearly show that the activity coefficient is a function of concentration of
 362 LaCl_3 even at low concentrations of LaCl_3 . Previously various authors [4–7]
 363 have calculated the activity coefficients of LaCl_3 from experimental measure-
 364 ments. From the above studies, Tang and Pesic[6] used values of ΔG^{SC} that
 365 are different from the ones used in this paper. They used HSC Chemistry
 366 software to perform these calculations. They report values which are three
 367 orders of magnitude greater than the ones we report here. Masset et al.[4] re-
 368 ported the value of γ_{LaCl_3} as 0.0057 at a concentration of 20×10^{-5} mole/cm³.
 369 That value is within the range of data reported here. Without knowledge
 370 of the density of the salt, it would be hard to convert that concentration to
 371 mole fraction accurately, for comparison. Castrillejo et al.[7] reported values
 372 at 723K and 823 K, not at 773 K as reported here. At 723 K, they reported
 373 a value of 0.0053 for the activity coefficient of LaCl_3 .

374 4.2. *Effect of Cesium Chloride*

375 The behavior of lanthanum chloride in the presence of Group I element
376 Cs was also studied since it is a major fission products that accumulate
377 in electrorefiner salt. For this study, CsCl was added to the salt at two
378 concentrations– 0.69 mole % (Standard Deviation: 0.04 mole %) and 1.40
379 mole % (Standard Deviation: 0.04 mole %). We followed the same method-
380 ology for analysis as reported in the previous section including the fitting of
381 OCP data to an interpolating function. The average difference between the
382 experimentally measured values and modeled values was again found to be
383 less than 2 mV. Figure 7 shows a plot of open circuit potentials for tests with
384 three concentrations of CsCl; 0, 0.69 and 1.40 mole % CsCl as a function of
385 LaCl_3 concentration. It can be observed that there is not much difference
386 between the open circuit potentials for La/La(III) for the tests with the two
387 lowest concentrations of CsCl i.e. 0 and 0.69 mole %. However, the equilib-
388 rium potentials for the La/La(III) couple show a notable positive shift in the
389 presence of 1.40 mole % CsCl. This is only true at higher concentrations of
390 LaCl_3 . At low concentrations of LaCl_3 , the equilibrium potentials for all of
391 the three tests are fairly similar.

392 Figure 8 shows the plot of apparent potential ($E^{0'}$) as a function of LaCl_3
393 concentrations, for three distinct concentrations of 0, 0.69 and 1.40 mole %
394 CsCl. From the figure, we can observe that the nature of the graphs for all of
395 the three tests is similar. All the three tests demonstrate that the apparent
396 potential does indeed follow a pseudo Gaussian function, with a maximum at
397 some concentration followed by a decline. Lower concentration (0.69 mole %)
398 of Cs does not seem to have a substantial impact on the apparent potential.

399 However the presence of 1.40 mole % Cs does seem to move the curve to the
400 right and make the apparent potential of LaCl_3 more positive. An additional
401 observation is that, both without any CsCl and with the presence of 0.69 mole
402 % CsCl, the apparent potential for LaCl_3 reaches its most positive value at
403 about 0.55 mole % LaCl_3 .

404 Figure 9 shows the graph of activity coefficient of lanthanum chloride for
405 the three concentrations of CsCl. It is observed that the activity coefficient
406 of LaCl_3 increases in the presence of 1.40 mole % CsCl. The interaction
407 of the lanthanum and cesium ions in the molten salt changes the activity
408 coefficients of the ions. We presume that this is caused by the influence Cs
409 ions have on the complexation and coordination chemistry of lanthanum ions
410 dissolved in the molten salt.

411 It is important to consider if the effects of CsCl observed and reported here
412 are statistically significant. For this purpose, the Student's t-test was em-
413 ployed. Analyzing the apparent potential data using the t-test indicates that
414 we can say with at least 95% confidence that the difference in the apparent
415 potentials of the tests with 0 & 0.69 mole % CsCl are statistically insignif-
416 icant. Further, the difference in the apparent potentials of the tests with
417 0.69 & 1.40 mole % CsCl is statistically significant (within a 95% confidence
418 interval) A similar conclusion can be made about the activity coefficients
419 of the three data sets where there is observed to be a statistical difference
420 between the activity coefficients of the tests with 1.40 % CsCl and the other
421 two tests.

422 5. Discussion

423 From the data presented above, it is evident that the activity coefficient of
 424 LaCl_3 dissolved in molten eutectic LiCl-KCl salt is dependent on the concen-
 425 tration of LaCl_3 dissolved in solution and not just a single value as previously
 426 reported. Recently Wang et al.[26] published a very detailed study looking
 427 into the activity coefficient and apparent potentials of LaCl_3 as a function
 428 of concentration of LaCl_3 using Molecular Dynamic Simulations (MDS). The
 429 results presented here differ only meaningfully from the ones presented by
 430 Wang et al.[26] at the higher concentrations of LaCl_3 where in we report a
 431 decline in both the apparent potential and activity coefficient wheres they re-
 432 port a linear dependence throughout the concentration range of up to 3 mole
 433 % LaCl_3 . Additionally, there is extensive documentation of such concentra-
 434 tion dependence of activity coefficient within the more vigorously researched
 435 field of aqueous chemistry which necessitated the need to develop sophisti-
 436 cated models like the ones developed by Kenneth Pitzer [27–31].

437 The concentration dependence of activity coefficients is most likely de-
 438 pendent on the local complexation structure of LaCl_3 in the molten eu-
 439 tectic electrolyte. Quite a few studies using various experimental tech-
 440 niques like Raman Spectroscopy[32, 33], neutron diffraction[34–37] and x-ray
 441 diffraction[38–40] has demonstrated that for LaCl_3 , there exists a multitude
 442 of complexes that can be formed by LaCl_3 with lanthanum ions capable
 443 of having variable coordination numbers. In 2010, Okamoto et al.[41] con-
 444 ducted XAFS tests and MDS studies of a LiCl-KCl-LaCl_3 molten salt mix-
 445 ture. They studied mixtures containing from 1 to 100 mole % LaCl_3 . They
 446 demonstrated that the coordination number and inter-ionic distance increase

447 with increasing concentration of LaCl_3 . This and other data available in that
448 paper clearly demonstrate that the coordination chemistry of the dissolved
449 La species is dependent on the concentration of the total La present in the
450 mixture. This concentration dependence of complexation reactions of LaCl_3
451 and ability of LaCl_3 to have a multitude of coordination numbers likely ex-
452 plains the observed trends for apparent potentials and activity coefficients
453 reported here.

454 A graph of OCP vs. $\text{Ln}(X_{\text{LaCl}_3})$ for the three main tests reported here is
455 shown in Figure 10. As expected, a linear relationship is observed between
456 the two plotted quantities. The slope of the line is equal to RT/nF . Equating
457 the slope to its expected value of RT/nF and calculating n , we obtain the
458 following values; $n = 2.70, 2.80$ and 2.21 for tests with 0, 0.69 and 1.40 mole
459 % CsCl respectively. Now for the first two cases, the value of $n = 2.70$ and n
460 $= 2.80$ is relatively close to the expected value of the expected value of $n =$
461 3 . In the presence of 1.40 mole % CsCl, the value of $n = 2.21$ is significantly
462 lower than the value than the one expected. This perceived trend broadly
463 reflects the trends observed in the measured properties. Properties of LaCl_3 ,
464 tests with 0 and 0.69 mole % CsCl are fairly similar. However the case with
465 1.40 mole % CsCl shows much lower value of n , which implies that $n = 2$.
466 This evidence indicates that the presence of higher concentrations of CsCl
467 does indeed seem to affect the local coordination structure of LaCl_3 .

468 The effect of CsCl on the coordination chemistry of LaCl_3 is much harder
469 to determine theoretically based on previously published open literature.
470 While there has been no study to date of the LiCl-KCl-CsCl- LaCl_3 systems.
471 There is some evidence in the literature of alkali metals play a role in altering

the local coordination structure in molten salts with an increased efficiency going from Li to Cs[42]. These perturbations in the local coordination chemistry of molten salt most likely translate into the effects of CsCl reported in this paper.

In molten salt systems, for LaCl_3 , an initial increase in the activity coefficient in the species can be attributed to the increase in the concentration of the lanthanum. It is likely that at these low concentrations, the concentration of lanthanum is not high enough to engender the formation of higher order complexes as the coordination number of lanthanum is very low. The reduction in the activity coefficient can certainly be attributed to the formation of higher order complexes as reported in literature. We know from thermodynamic literature for both aqueous and molten salt chemistry, the existence of "interaction parameters" that heavily influence the activity coefficients. The presence of other lanthanum ions and Cs ions most certainly influence the coordination chemistry of LaCl_3 , manifesting itself as a systematic variation in the activity coefficients and apparent potentials.

6. Conclusions

This paper sheds new light on our experimental understanding of the behavior of lanthanum chloride in molten eutectic LiCl-KCl salt. Experimental studies are reported in this paper on the behavior of the activity coefficient and apparent potential of the LaCl_3 in molten LiCl-KCl eutectic salt. Experimental evidence indicates that both the activity coefficient of LaCl_3 and the apparent potential exhibit a dependence on the concentration of LaCl_3 present in the solution. Both of the properties are observed to first increase

496 and subsequently decrease with the concentration of LaCl_3 .

497 In addition, we observed that the presence of an alkali metal like CsCl does
498 seem to affect the aforementioned two properties. While a low concentration
499 of CsCl does not seem to affect the LaCl_3 present, a higher concentration
500 of Cs present does indeed seem to affect both the apparent potential and
501 activity coefficient of LaCl_3 . This influence of higher concentrations of CsCl
502 on the electrochemical and thermodynamic properties of LaCl_3 is determined
503 to be statistically significant. Further work may be needed to examine the
504 effects of high concentrations of CsCl on the activity of LaCl_3 .

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Figure 1: Schematic of the experimental set-up used for this work

Figure 2: Schematic representation of a H vs. T Diagram

Figure 3: Cyclic voltammogram at four scan rates of 200, 300, 400 and 500 mV/s for LaCl_3 (0.46 mole %) in molten LiCl-KCl eutectic salt performed at 773 K. Working Electrode: Glassy carbon rod ($\phi = 2$ mm), Counter Electrode: La metal rod, Reference Electrode: 5 mole % Ag/AgCl. Potentials reported vs. Cl^-/Cl_2 couple.

Figure 4: Experimental and modeled values of open circuit potential (vs. Cl^-/Cl_2) for $\text{La}/\text{La(III)}$ couple, plotted as a function of LaCl_3 concentration at 773 K.

Figure 5: Apparent potential (vs. Cl^-/Cl_2) for La/La(III) couple plotted as a function of LaCl_3 concentration at 773 K.

Figure 6: Activity Coefficient (γ_{LaCl_3}) of LaCl_3 plotted as a function of LaCl_3 concentration at 773 K.

Figure 7: Open Circuit Potential (vs. Cl^-/Cl_2) for La/La(III) couple plotted as a function of LaCl_3 concentration for three independent concentrations of CsCl; 0, 0.69 and 1.40 mole % CsCl at 773 K.

Figure 8: Apparent Potentials (vs. Cl^-/Cl_2) for La/La(III) couple plotted as a function of LaCl_3 concentration for three independent concentrations of CsCl; 0, 0.69 and 1.40 mole % CsCl at 773 K.

Figure 9: Activity Coefficient of LaCl_3 (γ_{LaCl_3}) plotted as a function of LaCl_3 concentration for three independent concentrations of CsCl; 0, 0.69 and 1.40 mole % CsCl at 773 K.

Figure 10: Figure of Open Circuit Potential (vs. Cl^-/Cl_2) plotted as a function of $\ln(X_{LaCl_3})$. Figure shows plots for three independent concentrations of CsCl; 0, 0.69 and 1.40 mole % CsCl at 773 K respectively.