Determination of the thermodynamic activities of LiF and ThF₄ in the LiₓTh₁₋ₓF₄₋₃ₓ liquid solution by Knudsen effusion mass spectrometry

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Knudsen effusion mass spectrometry (KEMS) has been used to investigate the vapour pressure over the molten LiF–ThF₄ salt and determine the thermodynamic activity of LiF and ThF₄ in the liquid solution. As part of the study, the vaporization of pure LiF and pure ThF₄ was examined and the results were compared with the literature values finding a good agreement. Next, the vapour pressure of the LiₓTh₁₋ₓF₄₋₃ₓ liquid solution was investigated by measuring four samples having different compositions (X₃LiF = 0.2, 0.4, 0.6, 0.8 mol%). In order to determine the thermodynamic activities, the vapour pressure of LiF and ThF₄ species over the liquid solution, as calculated from our results, were compared with the vapour pressure over the pure LiF(l) and pure ThF₄(l) systems. A strong deviation from the Raoult’s law was observed, more evident in case of LiF species, in agreement with the predictions by our thermodynamic model.

Vapour pressure measurements can be used to determine the activity of a species (such as LiF or ThF₄) in a mixture, which is a measure of the thermodynamic stability of a system. These thermodynamic functions are extremely important in the development of thermodynamic models and they are particularly important in the context of the electrochemistry of the fuel salt. In fact, MSRs design includes a reprocessing of the fuel salt, mainly for separation of fissile material, actinides and fission products. Some of the steps of the global reprocessing scheme are based on the redox processes and thus on the electrochemical properties and the activities of the different elements and the solvent (LiF–ThF₄).

The aim of the present work is to evaluate the vapour pressure over the molten LiF–ThF₄ salt and determine the thermodynamic activities of the end-member species in the liquid solution. The system was investigated using Knudsen effusion mass spectrometry, which is a very well suited technique to measure high-temperature thermodynamic properties of condensed and gaseous phases. As first step, we have studied the vaporization of pure LiF and pure ThF₄ focusing on the liquid phase. Rather good agreement was found between our results and the literature value. Next, the vapour pressure of the LiₓTh₁₋ₓF₄₋₃ₓ liquid solution was investigated by measuring four samples with different compositions (X₃LiF = 0.2, 0.4, 0.6, 0.8 mol%). The vapour pressure of LiF and ThF₄ species over the liquid solutions were compared with the vapour pressure over the pure LiF(l) and pure ThF₄(l). From the observed difference with the ideal behaviour, the thermodynamic activity of LiF and ThF₄ in the LiₓTh₁₋ₓF₄₋₃ₓ liquid solution were determined.

1 Introduction

The binary system LiF–ThF₄ is a key system for various designs of the molten salt reactor (MSR). The MSR is one of the most promising future fission reactor technologies, selected by the Generation IV Forum, in which the fissile and fertile materials are dissolved into a molten salt mixture. Recent designs are based on a fast neutron spectrum reactor and on the thorium fuel cycle, therefore a crucial component is ThF₄ which is based on a fast neutron spectrum reactor and on the thorium dissolved mainly in the 7LiF solvent. In view of this fact, an extensive study is being conducted on the physico-chemical properties of the binary mixture LiF–ThF₄ in order to determine the operation parameters and the safety limit of this technology. With respect to the reactor safety, one of the key parameter to be assessed is the vapour pressure of the salt mixture. A low pressure system offers the advantage of reducing the main driving force of radioactivity release during accidents and it is a beneficial parameter with regard to engineering issues. Furthermore, in a multi-component salt higher evaporation of one component in comparison with the others causes a change in the final composition of the mixture leading to a change in its thermodynamic properties. Since the salt composition is usually optimized to have the lowest liquidus temperature, a change in the concentrations would lead to an increase of the melting temperature and could approach the safety limit.

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2 Experiment

2.1 Sample preparation

All the samples measured in this work were prepared from pure lithium fluoride LiF, obtained from Alfa Aesar, and pure thorium fluoride ThF₄, obtained from Rhodia. Since fluorides are very sensitive to water molecules, the materials were stored in a protective atmosphere and the preparation of the samples was done completely inside an argon glove box, where a low level of oxygen and water is ensured (typically below 5 ppm). Moreover, both compounds have been subjected to pre-treatments to ensure the high purity of the starting materials. In case of LiF compound, it consists of a heating cycle at 623 K for several hours under inert argon flow in order to remove the residual moisture, if present. Different treatment is required for ThF₄ that shows an additional tendency to oxidize and form oxyfluorides. A purification technique was applied using NH₄HF₂ as fluorinating agent as described in detail elsewhere.⁴

The purity of both compounds was then checked by identification of the melting point using the differential scanning calorimeter (DSC), as described in our previous works.⁴,⁵ The samples were encapsulated to prevent possible reactions with water/oxygen and protect the instrument from corrosive fluoride vapours. The results were in close agreement with the literature value, within ±5 K.

In total six samples have been prepared as listed in Table 1, in which the exact composition and the liquidus temperature of each sample, as measured by DSC, are reported. Typically, an amount of salt about 30–50 mg was loaded into a nickel crucible and placed in the Knudsen cell for the measurement.

2.2 Setup and measurements

The experimental setup used in this work consists of a Knudsen effusion cell coupled to a quadrupole mass spectrometer, as shown in Fig. 1. The facility is specifically designed for radioactive materials and irradiated fuel samples and it is described in details elsewhere.⁶ The Knudsen cell (cell dimensions: h = 21 mm, ∅ = 11 mm, orifice dimensions: d = 0.25 mm, ∅ = 0.5 mm) is made of tungsten with an inserted internal liner made of pure nickel in order to avoid possible corrosion by the fluoride vapours. Prior the measurement, the chamber is evacuated to high vacuum (10⁻⁸ to 10⁻⁹ kPa) so that no interference between atmosphere and sample gas molecules occurs. The cell is heated to high temperature using a tungsten-coil heating element and seven cylindrical shields, both in tungsten and tantalum, are placed around the cell to provide the required thermal isolation. The molecular beam emerging from the effusion orifice on the top of the cell is ionized by a cross electron beam and then analyzed by a quadrupole mass spectrometer.

Two main signals are measured during an investigation by the KEMS technique: the intensities of ion currents originating from the ionization of the evaporated gaseous species and the Knudsen cell temperature. The latter is measured using a pyrometer, which had been calibrated by determining the melting points (visible on the MS signal) of several standard materials (Zn, Cu, Fe, Pt, Al₂O₃). Furthermore, a calibration of the electron energy was performed prior the measurements by identifying the ionization potential of different gaseous and metal species (Ar, Kr, Xe, Zn, In, Ag).

A standard procedure was used for all the measurements performed, applying an electron ionization energy of 33.5 eV and a temperature ramp of 10 K min⁻¹. The use of a continuous temperature increase, instead of isothermal steps, allows a good description over the widest possible temperature range in a relative short time. Nevertheless, equilibrium conditions are reached during the measurements as suggested by the reproducibility of the literature values for Ag, LiF and ThF₄.

The temperature was increased until both sample and standard material were quantitatively vaporized. Moreover, the possible reaction products between fluorine and tungsten were monitored but none of these masses were detected indicating that no corrosion occurred during the measurements. For the pure substances, appearance potentials measurements were also performed to identify dissociation processes. The intensity of each species was measured during two consecutive runs performed at constant temperature (1250 K for LiF and 1293 K for ThF₄) and increasing the electron energy from 0.9 to 63.4 eV.

Table 1 Composition and liquidus temperature of the samples measured in this work

| Sample       | LiF Molar fraction | ThF₄ Molar fraction | LiF Molar fraction | Liquidus temperature (K) |
|--------------|--------------------|---------------------|--------------------|--------------------------|
| LiF          | 0                  | 1                   | 1                  | 1121.2                   |
| Li₀.₄Th₀.₆F₁.₆| 0.200              | 0.800               | 0.800              | 893.8                    |
| Li₀.₄Th₀.₆F₂.₄| 0.391              | 0.609               | 0.609              | 1044.6                   |
| Li₀.₄Th₀.₆F₃.₄| 0.598              | 0.402               | 0.402              | 1200.0                   |
| Li₀.₄Th₀.₄F₄.₄| 0.796              | 0.204               | 0.204              | 1303.0                   |
| ThF₄         | 1                  | 0                   | 0                  | 1383.2                   |
with step of 0.5 eV. The complete available energy range was
scanned in order to have more information on the ionization
process.

2.3 Mass spectral analysis
Under quasi equilibrium conditions (small ratio between the
orifice cross section and the vaporising surface) and low
pressure conditions, the partial pressure $p_A$ of the species A
at the temperature $T$ results from the following relation:

$$ p_A = KT \frac{1}{\sigma_A} \sum_i \frac{1}{I_i} $$

where $K$ is the calibration factor, $\sigma_A$ is the electron impact
ionization cross section of the species $A$, $\sum (1/I_i)$ is the sum
of intensities of the ion currents $i$ originating from the mole-
cule A considering the efficiency ($\gamma_i$) of the secondary electron
multiplier (SEM) for each ion mass.

The calibration factor $K$ is determined based on the quanti-
tative evaporation of a known amount of a standard material, in
our case silver, placed in the Knudsen cell during the measure-
ments. The mass loss rate of silver $dm/dt$ is given by the Hertz–
Knudsen equation as follows:

$$ \frac{dm}{dt} = p_A \cdot S \cdot C \cdot \sqrt{M_A} \cdot \frac{1}{\sqrt{2\pi R T}} $$

where $p_A$ is the vapour pressure of silver, $T$ is the temperature,
$M_A$ is the molar mass of silver, $S$ is the universal gas constant,
$C$ is the effusion orifice surface and $I$ is the Clausing factor.

The latter term is the correction for an orifice with short but finite channel as
reported by Santeler.\(^7\) By integration over the measurement
time of the Hertz–Knudsen equation combined with eqn (1) for
$p_A$, it is possible to determine the calibration factor $K$.

$$ K = \frac{\sigma_A \cdot \gamma_A \cdot \sqrt{2\pi R T} \cdot \Delta m}{S \cdot C \cdot \sqrt{M_A} \cdot \sum_n (I_{Ag} \cdot T^{1/2}) \cdot \Delta t_n} $$

where $\sigma_A$ is the electron impact ionization cross section of silver,
$\gamma_A$ is the efficiency of secondary electron multiplier for silver, $\Delta m$
is the total mass evaporated and the term $\sum_n (I_{Ag} \cdot T^{1/2}) \cdot \Delta t_n$ is
the integrated product between the intensity of silver ion current and the temperature along the time of the experiments. In
addition to this method, the calibration factor can be determined
using the well-known vapour pressure of silver.\(^8\)

2.3.1 Ionization cross sections and efficiencies of SEM. As
described in the previous section, the determination of the absolute vapour pressure requires the knowledge of the efficiency
of the SEM for each recorded ion and the electron impact
ionization cross section of the molecular species. A detailed
explanation on the estimation of these properties as applied in
this work is given in this section.

The efficiency of the secondary electron multiplier depends
on the mass of the species detected and is usually approximated, as suggested by Grimley,\(^9\) to:

$$ \gamma_i = \delta M_i^{-1/2} $$

where $\delta$ is a constant and $M_i$ is the molar mass of the species $i$.
Using eqn (4) the normalized SEM gains $\gamma_i/\gamma_A$ for the species
Th$^+$, ThF$^+$, ThF$_2^+$, ThF$_3^+$ were determined as 0.68, 0.66, 0.63,
0.61 respectively. However, this approximation is good only for
mass numbers greater than 50 amu and in case of the lighter
species (Li$^+$, LiF$^+$, LiF$^2$) could not be applied. For that reason,
the normalized SEM gains $\gamma_i/\gamma_A$ for the species Li$^+$, LiF$^+$, LiF$^2$ and
LiF$_2^+$ (0.87, 1.47, 1.66 and 2.48) were taken from Yamawaki et al.\(^10\)
and for more details of obtaining these values we refer to that study.

The second important term is the electron impact ionization cross section, which depends on the electron energy. For single
atoms, the ionization cross sections have been computed by
Mann\(^11,12\) and are available for a large range of energy. In this
work, the SIGMA software,\(^13\) which is based on Mann’s values,
has been used for the calculation of the atomic cross sections.

The case of molecules is more complex and the additivity rule
postulated by Otvos and Stevenson\(^14\) is generally used. Follow-
ning this rule, the cross section of a molecule is calculated as
sum of the cross sections of the single components. However,
this “simple” approach is not giving good estimations in case
of complex molecules, such as ThF$_4$ in the present case. If we
consider as an example the similar SiF$_4$ molecule, a clear
contradiction of the additivity rule has been observed. In fact,
for the series SiF, SiF$_2$, SiF$_3$ and SiF$_4$, the ionization cross
section decreases with increasing number of fluorine atoms
($\sigma_{SiF} < \sigma_{SiF_2} < \sigma_{SiF_3} < \sigma_{SiF_4}$). This discrepancy was explained by
Deutsch et al.\(^15\) as an effect of the molecular bonding and
weighting factors have to be introduced to take this effect into
account. A modified additivity rule\(^16\) has been proposed for the
calculation of total electron impact cross sections of molecules
of the form AB$_n$, as given by the following equation:

$$ \sigma_i^{(AB_n)} = [r_A^2/r_B^2 \gamma_A^n/(\xi_A + n\xi_B)]\sigma_A^+ + [n r_A^2/r_A^2 \beta_{th}(\xi_A + n\xi_B)]n\sigma_B^+ $$

where $r_A$ and $r_B$ are the atomic radii, taken from the table of
Desclaux,\(^17\) $\xi_A$ and $\xi_B$ are the effective number of atomic
electrons and $\sigma_A$ and $\sigma_B$ are the atomic ionization cross sections
calculated at the correct ionization energy. The exponents $\alpha$ and
$\beta$ are explicitly dependent on $r_A$, $r_B$, $\xi_A$, and $\xi_B$ and they are
determined empirically (see details in ref. 16).

Since no experimental data on the electron impact ionization
cross section of ThF$_4$ have been found in literature, the
value was calculated based on eqn (5) and using parameters
reported in Table 2. In this case the dependency of the cross
section on energy is expressed solely by the energy dependence
of the individual atomic ionization cross section, as follows:

$$ \sigma_i^{(ThF_4)} = 0.44\sigma_{Th}^+ + 2.08\sigma_{F}^+ $$

This relation gives, for the ionization energy used in
our measurement, a total ionization cross section for ThF$_4$ of
$\sigma_{ThF_4} = 8.9184 \times 10^{-16}$ cm$^2$. In case of the LiF related species,
the ionization cross section normalized to silver $\sigma_i/\sigma_{Ag}$ for
the monomer, dimer and trimer was estimated to be 0.61, 0.71 and
0.85 as reported by Yamawaki et al.\textsuperscript{10} for a similar ionization energy as used in this study.

2.3.2 Thermodynamic calculations. Calculations of thermochemical data for pure LiF and pure ThF\textsubscript{4} were performed using both second law and third law approaches. Second law enthalpies of reaction (vaporization or sublimation) \(\Delta_rH^0\) are obtained based on the equilibrium constant measurement in a certain range of temperature, as given by the equation:

\[
\Delta_rH^0_{\text{eq}} = -R \frac{d \ln K^0_{\text{eq}}}{d(1/T)} \tag{7}
\]

where \(R\) is universal gas constant, \(K^0_{\text{eq}}\) is the equilibrium constant of the vaporization reaction and \(T_{\text{eq}}\) is the mean temperature of the measurement. For a simple vaporization process, such as \(A(s) = A(g)\) or \(A(l) = A(g)\), the equilibrium constant is given by the following equation:

\[
K^0_{\text{eq}} = \frac{a(g) \text{resp.} a(g)}{a(s) \text{resp.} a(l)} \tag{8}
\]

in which \(a(g)\), \(a(s)\) and \(a(l)\) are activities of the gas phase, the solid phase and the liquid phase respectively. Since activities of solids and liquids in equilibrium are equal to unity, \(K^0_{\text{eq}}\) becomes:

\[
K^0_T = \frac{P(g)}{P_0} \tag{9}
\]

where \(P(g)\) is the equilibrium pressure and \(P_0\) is the standard pressure (10\textsuperscript{5} Pa). Thus, a plot of \(\ln(P(g)/P_0)\) versus \(1/T\) gives a linear relation with a slope \(\Delta_rH^0_{\text{eq}}/R\). The reaction enthalpy refers to the average temperature (1/T) of the measurements and it is converted to the reaction enthalpy at the standard temperature \(\Delta_rH^0_{\text{298}}\) by using the reported \(C_p\) function for the different phases. The enthalpy of fusion was also considered to calculate the sublimation enthalpy from the liquid state data.

The third law approach is based on similar equations but requires in addition the knowledge of the standard entropy function \(S^0_T\) for all the phases. The enthalpy of the reaction at the standard temperature is given by the following equation:

\[
\Delta_rH^0_{\text{298}} = -RT \ln K^0_{\text{eq}} + T \Delta fef_T \tag{10}
\]

where \(\Delta fef_T\) is the free energy function which is defined for each phase as:

\[
\Delta fef_T = -\frac{G^0_T + H^0_{\text{298}}}{T} = S^0_T - \frac{H^0_T - H^0_{\text{298}}}{T} \tag{11}
\]

This results in an enthalpy of reaction for each data point and the average is taken from all the data. The thermodynamic functions for the third law calculation were taken from ref. 18 for the LiF and from ref. 19 and 20 for ThF\textsubscript{4} solid and gas phases. In case of the ThF\textsubscript{4} liquid phase, the data have been taken from our previous work\textsuperscript{21} where they have been revised.

3 Results

3.1 Vapour pressure of pure LiF

The lithium fluoride vaporization has been studied by different authors during the past years using different techniques, such as the Miller and Kusch method\textsuperscript{22} (re-plotted by Scheffee et al.\textsuperscript{23}), the KEMS technique\textsuperscript{10,24–26} a double-oven apparatus\textsuperscript{27} and the torsion-effusion method.\textsuperscript{28} As established by all the authors, the LiF vapour system contains monomer, dimer, and trimer species but some discrepancies on their relative amounts have been found owing to assumptions concerning the electron-impact ionization cross section and the ion–neutral precursor assignment.

In this work, four main ions were observed in the mass spectrum, namely \(\text{Li}^+\), \(\text{LiF}^+\), \(\text{Li}_2\text{F}^+\), \(\text{Li}_3\text{F}_2^+\), in accordance with the literature works. The attribution of the measured molar mass to the respective ion was confirmed by the identification of the correct isotopic ratio (natural abundance: \(^7\text{Li}\) 92.41% and \(^6\text{Li}\) 7.59%). For each ion species, the ionization efficiency curve at fixed temperature was also recorded as illustrated in Fig. 2. Based on these results, the appearance energies of the ions were determined and they are listed in Table 3 in which the measured values are compared with literature. As mentioned before, although the LiF vapour system has been the subject of numerous investigations, there is disagreement in literature on the identity of the neutral precursors of each ions. In particular, the ions \(\text{Li}^+\) and \(\text{LiF}^+\) could be produced by different mechanisms from monomer, dimer or from both species. Since our measurements showed no clear inflection in the linear portion of the ionization efficiency curves, thus indicating no dissociation of molecules, as first attempt we considered that both ions

![Fig. 2](Image)

**Fig. 2** Ionization efficiency curves measured for the ions \(\text{Li}^+\), \(\text{LiF}^+\), \(\text{Li}_2\text{F}^+\), \(\text{Li}_3\text{F}_2^+\). The intensity of the signal is reported as function of the calibrated energy in the range between 0 and 35 eV.
mental results when considering that most of the processes
This fragmentation path is not in disagreement with our experi-
et al.26
Using a phase-sensitive mass spectral analysis, they report for
similar ionization energy the following ion–precursor combina-
tions: Li’ [90.4% LiF–9.6% Li3F3], LiF’ [18% LiF–71% Li2F2–
11% LiF], LiF’ [99.5% LiF–2% Li3F3 Li2F2 [100% LiF].
This fragmentation path is not in disagreement with our experi-
mental results when considering that most of the processes
(i.e. for LiF’: simple ionization LiF + e− → LiF+ + 2e−
and fragmentation Li2F2 + e− → LiF+ + LiF+ + 2e− ) are probably
within few eV (ref. 29) and a better energy resolution is needed
to identify the slope changes. Applying the precursor partition
as reported by Bonnell et al.,26 the best agreement with litera-
ture was observed for both monomer and dimer pressure, thus
it was considered in all the calculations in this work. It is
important to notice that although there are some uncertainties
in the assignment of the neutral precursors to the ions, the
different assumptions do not strongly influence neither the
total vapor pressure of the salt (mainly given by the monomer)
nor the activities (providing a consistent analysis for all the
measurements).

The experimental data measured in this work are shown in
Fig. 3, where the vapour pressure of all the gaseous species LiF,
Li2F2, Li3F3 are reported. Two LiF samples were measured under
the same experimental conditions and the comparison confirms
the reproducibility of the measurement. The results have been
compared with the data calculated from the FactSage software32
based on the JANAF tables18 and the agreement is very good except
for the trimer species. Such a discrepancy may arise from the low
ion currents of the trimer, but we must note that our result is in
line with the results obtained by other authors. The vapour
pressure data of liquid phase of LiF (from 1121 K to 1352 K) were
fitted using a least-square method and the following equations
were found to represent the monomer, dimer and trimer pressure:

Monomer:

\[
\ln(P/Pa) = (25.893 \pm 0.124) - (28 064 \pm 159)/T(K)^{-1} \quad (12)
\]

Dimer:

\[
\ln(P/Pa) = (24.886 \pm 0.055) - (27 707 \pm 69)/T(K)^{-1} \quad (13)
\]

Table 3 Appearance energy of the ion species detected by the mass spectrometer

| Reaction | Appearance energy (eV) |
|----------|------------------------|
| Measured | Literature |
| LiF + e− → LiF+ + F− + 2e− | 11.5 ± 0.5 | 11.5,27 11.825 and 11.410 |
| LiF + e− → LiF+ + 2e− | 11.8 ± 0.5 | 11.3,27 11.825 and 11.110 |
| Li2F2 + e− → Li2F+ + F− + 2e− | 11.3 ± 0.5 | 11.5,27 13.025 and 11.710 |
| Li3F3 + e− → Li3F+ + F− + 2e− | 12.3 ± 0.5 | 12.325 and 11.410 |
| ThF4 + e− → Th+ + 4F− + 2e− | 33.0 ± 0.5 | 3930 |
| ThF4 + e− → ThF3+ + 3F− + 2e− | 29.1 ± 0.5 | 3630 |
| ThF4 + e− → ThF2+ + 2F− + 2e− | 21.1 ± 0.5 | 23.230 and 21.013 |
| ThF4 + e− → ThF+ + F− + 2e− | 13.4 ± 0.5 | 14.530 and 13.513 |

\[ \ln(P/Pa) = (19.305 \pm 0.161) - (24 566 \pm 203)/T(K)^{-1} \quad (14) \]

In addition, the enthalpy of sublimation have been calculated for
all the LiF gaseous species using the second and third law methods, as described in Section 2.3.2. The results are
summarized in Table 4. A very good agreement between second
and third law calculations was observed for the monomer while
a slightly higher discrepancy was observed for dimer and
trimer. Moreover, the results fit very well within the literature
values.

3.2 Vapour pressure of pure ThF4

There are three studies on the vapour pressure of ThF4(s)
and ThF4(l), performed by Darnell et al.,33 Lau et al.,31 and
Nagarajan et al.36 The composition of the vapour phase is very
simple, consisting of only ThF4(g) in the monomeric form.
The observed ions in the mass spectrum of the vapour effusing
from the cell were Th+, ThF+, ThF2+ and ThF3+ and the appearance
potentials of these ions, as measured in this work (Fig. 4), are

Table 4 Enthalpy of sublimation \( \Delta H_{f,\text{sub}}^0 \) (kJ mol\(^{-1}\)) of LiF(s) at 298.15 K for the three found gaseous species

| Researchers | \( \Delta H_{f,\text{sub}}^0 \) (LiF) | \( \Delta H_{f,\text{sub}}^0 \) (Li3F3) |
|-------------|-------------------------------|-------------------------------|
| Yamawaki et al.10 (1982) \(^a\) | 284.5 ± 6.7 | 309.6 ± 7.1 |
| Yamawaki et al.10 (1982) \(^b\) | 283.3 ± 7.1 | 301.2 ± 7.1 |
| Grimeley et al.25 (1978) \(^c\) | 272.2 ± 3.1 | 308.1 ± 1.7 |
| Snelson et al.33 (1969) \(^d\) | 285.2 ± 4.6 | 337.2 ± 5.4 |
| JANAF tables18 (1968) | 276.1 | 291.1 |
| Glushko tables19 (1982) | 277.4 ± 3 | 333.6 |
| Present work \(^a\) | 277.9 ± 1.5 | 316.6 ± 1 |
| Present work \(^b\) | 277.48 ± 2 | 301.6 ± 8.2 |

\(^a\) Second law calculation. \(^b\) Third law calculation.
listed in Table 3. No evidences were found during the measurement for the presence of ThO$_2$ or ThOF$_2$ impurities in the salt.

The measurements were performed from 1000 K to 1457 K when the complete evaporation of the sample was reached. Fig. 5 shows the results obtained, which are in good agreement with the literature. The total vapor pressure of solid and liquid ThF$_4$ can be represented by the following equations:

**Solid**

$$\ln(P/\text{Pa}) = (36.045 \pm 0.101) - (43.493 \pm 124)(T/K)^{-1}$$

**Liquid**

$$\ln(P/\text{Pa}) = (29.386 \pm 0.124) - (34.858 \pm 180)(T/K)^{-1}.$$ (15)

Also in the case of ThF$_4$ compound, the enthalpy of sublimation was determined by second and third law. The calculations gave $\Delta H_{298}^0 = 359.25 \pm 2.6$ kJ mol$^{-1}$ from second law method and $\Delta H_{298}^0 = 353.8 \pm 2.5$ kJ mol$^{-1}$ from third law method, similar to the selected literature value$^{17}$ of $\Delta H_{298}^0 = 349.3 \pm 2$ kJ mol$^{-1}$.

### 3.3 Vapour pressure of the Li$_x$Th$_{1-x}$F$_4$ liquid solution

The vapour pressure of the Li$_x$Th$_{1-x}$F$_4$ liquid solution was studied in this work for the first time. In order to understand the behaviour in the whole composition range, four binary mixtures were prepared with concentration step of 0.2 mol% and they were measured under the same experimental conditions as the end-members. The mass spectrum of all the samples showed the presence of the same ions, Li$^+$, LiF$^+$, Li$_2$F$^+$, Th$^+$, ThF$^+$, ThF$_2^+$, ThF$_3^+$ in addition to the reference signal Ag$^+$, with different relative intensities. The LiF$_2^+$ signal was too low to be detected in most of the cases and no evidences for formation of Li–Th molecules in the gaseous phase were found by scanning the complete range of molar masses. We note here that as reported in literature,$^{38}$ the formation of an intermediate compound in the gas phase has been observed for several ionic halide systems and often the main ion formed after electron impact is Li$^+$. In this case, it is not straightforward to separate the contribute to the ion signal from Li$_x$Th$_{1-x}$F$_4(y=g)$ and from LiF(g), respectively. In absence of any experimental evidence on the formation of such compounds, none was consider in our analysis.

As an example, the temperature function of the mass spectrum of Li$_{0.4}$Th$_{0.6}$F$_{2.8}$ is shown in Fig. 6, in which the major isotopes are reported for clarity reasons. Since our method does not allow the determination of the background signal and the sample signal simultaneously, no background treatment has been performed. However, background intensities are very small in comparison to the overall signal in the temperature range considered for the analysis. It is important to notice that all the signals, except the reference, dropped after the complete vaporization at the same temperature/time giving a strong **Fig. 4** Ionization efficiency curves measured for the ions Th$^+$, ThF$^+$, ThF$_2^+$, ThF$_3^+$. The intensity of the signal is reported as function of the calibrated energy in the range between 0 and 60 eV.

**Fig. 5** Vapour pressure of thorium tetrafluoride ThF$_4$. (○) Data measured in this work. (■) Data from Nagarajan et al.$^{36}$ (●) Data from Darnell et al.$^{35}$ (▲) Data from Lau et al.$^{31}$

**Fig. 6** The ion intensities versus temperature obtained for the intermediate composition Li$_{0.4}$Th$_{0.6}$F$_{2.8}$. The main species recorded are: Li$^+$, LiF$^+$, Li$_2$F$^+$, Th$^+$, ThF$^+$, ThF$_2^+$, ThF$_3^+$ plus the reference signal Ag$^+$. Only the intensities of the most intensive isotope is given in each case.
indication of the complete mixing between the end-members LiF and ThF₄. The maximum temperature reached is around 1450 K, determined by complete vaporization of the salt in very low pressure conditions. In different conditions, for instance at ambient pressure, the salts are far from their boiling points and the complete vaporization would occur at higher temperatures.

The vapour pressure of the liquid mixtures was calculated in the range of temperature between the liqudus temperature of the binary mixture and the maximum temperature reached (complete vaporisation of the sample). All the data have been analysed using the same approach and the equations obtained for the partial pressure of the major species, LiF and ThF₄, are summarized in Table 5. The plot of the vapour pressure measured as function of the composition of the liquid is shown in Fig. 7 for the LiF and ThF₄ species.

Using the data obtained in this study for pure compounds and binary mixtures, the thermodynamic activities of both species in the liquid solution were determined. In general, the activity of one species is given by the relation:

\[ a_i = \frac{P_i(\text{soln})}{P_i(\text{end-member})} \]  

(16)

where \( P_i(\text{soln}) \) is the vapour pressure of the species \( i \) in the solution and \( P_i(\text{end-member}) \) is the vapour pressure of the end-member species \( i \). Following this relation, the activities of LiF and ThF₄ have been calculated as function of the molar fraction and temperature. The reference state for pure ThF₄ is the supercooled liquid, as derived by extrapolation from the equation of the vapour pressure of the liquid phase (eqn (15)). The results are plotted for three selected temperature 1200 K, 1300 K and 1400 K in Fig. 8. In case of the LiF species, an alternative method to calculate the thermodynamic activity was also applied. In fact when both monomer and dimer are present in the salt vapor, the activity can be calculated directly from ion intensities, as given by the following equation:

\[ a_i = \frac{I_{\text{Li}^+} / I_{\text{LiF}_2^+}}{(I_{\text{Li}^+} / I_{\text{LiF}_2^+})_{\text{mixt}}} \]  

(17)

where \( I_{\text{Li}^+} \) and \( I_{\text{LiF}_2^+} \) are the intensities of the ion \( \text{Li}^+ \) and \( \text{LiF}_2^+ \) for the pure component and for the mixed samples. This method, which is in principle applicable only when the ion intensities \( \text{Li}^+ \) and \( \text{LiF}_2^+ \) result solely from the LiF and Li₂F₂ respectively, offers the advantage to give the value of the thermodynamic activities without necessity of pressure calibration. The results obtained with this method are in fair agreement with the activities calculated from absolute vapour pressure and the comparison between the two methods was used to estimate the uncertainty on the activity determination. For each measurement, the average deviation of the two methods was calculated and the maximum of those values (about 18%) was considered, in a first approximation, as the error of the thermodynamic activities of LiF and ThF₄.

The results on the activity of the end members LiF and ThF₄ in the LiₓTh₁₋ₓF₄₋ₙₓ liquid solution are shown in Fig. 8. The dashed lines in the figure represent the behaviour of the activities for an ideal solution which is given by the Raoult’s law:

\[ a_i = X_i \]  

(18)

where \( X_i \) is the molar fraction of the gaseous species \( i \). The results clearly show a strong deviation from the ideality of the LiₓTh₁₋ₓF₄₋ₙₓ liquid solution, more evident in case of LiF species. There is a strong connection between the microscopic structure and the deviation of the vapour pressure from the ideality. In ideal mixtures, the assumption is that at the
microscopic level the intermolecular forces between two different molecules (LiF–ThF₄) are equal to those between similar molecules (LiF–LiF and ThF₄–ThF₄, respectively). The lesser the extent to which these criteria are true the greater the deviations of the partial pressures from their linear dependency on the mole fractions. The significant deviation from ideality of the studied system has been observed also for the enthalpy of mixing, as reported in our previous work. For comparison, the solid lines in Fig. 8 represent predictions from the thermodynamic model developed for the LiF–ThF₄ system. This assessment was performed considering the available experimental data on the binary system, that were the phase diagram temperatures, the enthalpy of fusion of the Li₁,Th₁,Th₂,₃,F₄,₄–₃x compound and the enthalpy of mixing of the liquid solution. Considering this fact, the agreement obtained between predictions and experiments is rather good. An higher discrepancy is observable in case of the LiF species, especially with increasing temperature, but the agreement is very good for the ThF₄ species. It can thus be concluded that the model correctly predicts the general behaviour of the thermodynamic activities as function of composition and this confirms that the thermodynamic model predicts the mixture properties correctly.

As mention in the introduction, these type of the data are of great interest to evaluate the safety and the performance of the MSR fuel as well as to evaluate the reprocessing scheme. The experimental results confirm that the Li₁,Th₁,Th₂,₃,F₄,₄–₃x liquid solution has low vapour pressure and it is therefore compatible with a low operating pressure of the reactor. Moreover, the experimental results fit well with the predictions based on the previously published thermodynamic model, confirming the reliability of the developed database.

4 Conclusions

This work presents the determination of the thermodynamic activities of LiF and ThF₄ in the Li₁,Th₁,Th₂,₃,F₄,₄–₃x liquid solution. Knudsen effusion mass spectrometry has been successfully applied to measure fluoride samples at high temperatures. First the end-members LiF and ThF₄ were investigated and next some selected intermediate compositions. The results for the end-members were found to be in very good agreement with the literature data for appearance potential, vapour pressure and enthalpy of sublimation. Afterwards, the same experimental procedure was applied to four different compositions of the Li₁,Th₁,Th₂,₃,F₄,₄–₃x liquid solution and its vapour pressure was determined for the first time. Based on these measurement the thermodynamic coefficients of LiF and ThF₄ in the Li₁,Th₁,Th₂,₃,F₄,₄–₃x liquid solution were determined.

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