Thermal properties of binary chlorides relevant to molten salt chemistry

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Abstract: Among proposed Generation IV nuclear reactors, the molten salt fast reactor (MSFR) has some of the most promising inherent safety features available. Among these includes the solidification of the molten salt matrix upon loss of external heating, preventing runaway. Other convenient features include online reprocessing and increased fuel variety. A major hurdle for MSFR design is the lack of fundamental data on the component salts, and the resulting fission and corrosion product speciation. While MSFRs are typically designed for use with fluoride salts, chloride salts have shown promise, and have had increased interest in recent years. A better understanding of the fundamental thermodynamic properties of chlorides would aid in the design of more efficient and more precise separations of the spent fuel salt mixture for recycling of fissile isotopes. This review has collected and analyzed existing literature data on the relevant thermochemical and thermophysical properties including: boiling / melting / sublimation points, heat capacity, vapor pressure expressions, enthalpic / entropic / free energy formation and phase change values. The elements of interest include that of fuel salts (actinides), solvent salts (alkali and alkaline earth metals), and fission and corrosion product (main group, transition metal, and rare earth element) chloride salts.

1. Introduction

The current generation of nuclear fission reactors, Generation III (Gen III), primarily use UO_2, PuO_2, or U,PuO_2 (MOX) fuel clad in aluminum, steel, and zirconium alloys with light (H_2O), or heavy (D_2O) water used as coolant. While Gen III reactors are safer than the previous generation, they are not without their disadvantages. The oxide fuel is most commonly in the form of a solid rod covered by the cladding and requires a fine temperature balance.

The reactor becomes more efficient as the operating temperature increases, but if the operating temperature is too high, the reactor can undergo a meltdown event. Reactor temperature is controlled with the coolant. However, if there is a loss in coolant due to excessive heat, melting of the fuel rods and ignition of radiolytically generated hydrogen may occur. These massive hydrogen explosions following meltdown events are the primary source of structural damage in major nuclear accidents such as the Chernobyl and Fukushima disasters.

As part of the fourth generation of nuclear reactors (Gen IV), more robust fuels, and coolants with higher condensed phase ranges are being investigated. This design ethos was presumably chosen to mitigate meltdown possibilities present in Gen II and III reactors. New coolants under examination include: molten salt eutectics, molten sodium, molten lead, or gases.[1] Molten sodium, gas-cooled, and very high temperature reactor (VHTR) designs change the cooling medium while maintaining the use of oxide fuel rods or pebble beds, while molten salt reactors dissolve fuel salts within the coolant solvent.

Although many Gen IV reactors benefit from improved coolants, molten salt reactors (MSRs) have additional safety advantages and solid foundational research. The MSR concept originated in the United States at Oak Ridge National Lab (ORNL) in programs running from the 1940s until the 1970s.[2, 3] The work was focused into two different projects, the Aircraft Reactor Experiment (ARE) and the Molten Salt Reactor Experiment (MSRE). The ARE program investigated the viability of nuclear–powered aircraft while the MSRE was a large scale attempt to run a reactor closely resembling the current MSR concept. Both designs used fluoride salt mixtures as fuel and operated at, ~860 °C (ARE[4]) and ~650 °C (MSRE).[5] The ORNL work demonstrated the viability of the MSR concept but the technology was not developed further due to a myriad of factors, including prioritization of other reactor concepts difficulties with corrosion and incomplete fundamental data.[6, 7]

Over the last two decades, the MSR concept has been revisited with new designs and reactors piloted.[8-10] MSRs have many features that make them more appealing than Gen III and other Gen IV reactor concepts. Notably, in the event of a sudden loss of power, the MSR fuel mixture can be drained into a series of tanks designed to prevent criticality.[11]. When the liquid fuel is emptied into these tanks, it cools and solidifies. The removal of the fuel prevents further damage to the reactor, unintended criticality events, and with the fissile material too diffuse to sustain fission it will remain solid. The salts used in MSRs are less susceptible to radiolytic damage unlike the cladding/water used in most Gen III reactors, requiring less regular replacement. The refueling process for MSRs allows for more flexibility than Gen III reactors even allowing for online refueling. MSRs can also minimize waste processing depending on the neutron spectrum via burn-up.[12] When waste processing is necessary, MSRs lend themselves to pyrochemical and thermophysical separations without much additional treatment.[13, 14] Finally, halide based MSRs have a versatile range of possible designs and fuel selections depending on the application.

All MSRs can use ^{235}U or ^{239}Pu as fissile isotopes in various mixtures, but other isotopes can also be used depending on the neutron spectrum of the reactor. Thermal spectrum reactors can also use ^{232}Th, (99.98% abundant) as a breeder for fissile ^{233}U, while fast spectrum reactors can use ^{238}U. It has also been proposed that MSRs can be used to consume a variety of trans–uranium (TRU) isotopes, based on Pu, Am, Cm, and other heavier actinides (**An**). The TRU–isotopes produced in a nuclear reactor have little practical use and are highly radioactive making them difficult to dispose of beyond permanent deep geologic storage.[15] Therefore, burn reactors offer an opportunity to reduce the amount and radiotoxicity of waste for deep geologic storage.

Chloride based MSR experiments were first reported in the United States in 1952.[16, 17] Further chloride-based experiments appeared in the literature, primarily in France,[18] Switzerland,[19] and other countries.[20] The most common chloride salt eutectics are LiCl–KCl, NaCl–KCl, or NaCl–**An**Cl_x (**An** = Th, x = 4; **An** = Pu, U; x = 3, 4) in varying compositions.[21, 22] Like the fluoride systems, natural ^{23}Na (100 %), and ^{nat}K (^{39}K = 93.2581%, ^{40}K = 0.0117%, ^{41}K = 6.7302%) are used and ^{7}Li is enriched to 100%. ^{9}Be (100 %) is avoided due to issues with the fast neutron spectrum of chloride-based reactors. In all cases ^{37}Cl (24.229% abundance, 0.433±0.006 barns) is enriched to 100 % due to the large neutron cross-section of ^{35}Cl (75.771% abundance, 43.55±0.40 barns) which significantly impacts the neutron economy of the reactor.[23] The actinide trichlorides, **An**Cl_3, (**An** = Pu, U) are used as the actinide source as sole or mixtures of actinides, with isotope ratios appropriate for the reactor design. Molten chloride salts have several advantages over fluoride salts including a harder neutron spectrum than fluoride designs. A harder neutron spectrum allows for heavier, less fissile/non-fissile isotopes to be consumed as part of reactor operation. Chloride salts also have higher elemental solubilities and are less corrosive than fluoride melts, easing design constraints. Chloride-based eutectics also generally have lower melting points (T_M) resulting in lower operating temperatures, typically 560–740 °C, *c.f.*, fluoride-based reactors typically operating at 650–850 °C.[7, 24] In addition to lower operating temperatures, the less acidic nature of the chloride melts reduces operating stress on the containment material, allowing a wider range of materials to be used in reactor construction. Chloride reactors are not the only type of MSR that can achieve these low operating temperatures, but other systems are beyond the scope of this review. All of these factors contribute to the interest in chloride MSRs and position them as a viable competitor to the more traditionally studied fluoride MSRs.

This review draws into focus a wide range of data from across the history of chloride and molten salt chemistry. Much of the data for molten salt reactors has been focused on fluoride salts but compiling similar data for chloride compounds helps support design parameters of molten chloride salt reactors. A sizeable portion of this data was previously unavailable and is only accessible now due to the declassification of governmental reports.

As fundamental data has accumulated we feel it is best to prepare for the spent fuel from a molten chloride reactor, rather than fresh fuel. Although, the properties discussed will also encompass those of fresh fuel. With this approach in mind, the compounds of interest include solvent (alkali and alkaline earth metals), fuel (actinides), and contaminant salts. Where contaminant salts encompass fission (main group transition metals, and lanthanides) and corrosion products (aluminum and transition metals). In reference to these elements, we will focus on both thermophysical and thermochemical properties which are integral parts of reactor design and waste processing.

The properties include: melting (T_M), boiling (T_B), and sublimation points (T_{sub}). These basic properties inform phase diagrams for complex mixtures and assist in simulating different melt compositions. The vapor pressure (V_P) of compounds in different phases (solid, liquid, gas) are critical thermophysical properties for MSR operation. Differences in vapor pressure determine which components of the melt would volatilize and mix with cover gases commonly used within MSRs. Knowledge of possible vapor compositions are needed to prepare proper safety standards. Much like the aforementioned phase change points, heat capacity (C_p) affects critical systems in any MSR, particularly the design of heat exchangers. Because C_p measurements are made alongside thermochemical properties it will be presented alongside those to match literature conventions. The fundamental values related to heats (ΔH), entropies (ΔS), and Gibbs Free Energies (ΔG) of formation, and their corresponding energy/entropy of fusion (fus), or phase change, vaporization (vap), or sublimation (sub) are also presented.

The thermodynamic values provide the some of the most critical information, from the stability of a given compound, the propensity to change phase, or the behavior within a mixture. The collection and presentation of this data will aid in furthering the development of chloride based molten salt reactors and highlight gaps in data. It is worth noting, that nuclear reactors and the products produced can sensitive/specific to the isotopes used/produced. However, the literature presented for stable elements does not specify if a specific isotope was used and presumably the natural isotopes were used. In the case of actinides, some elements perform reactions using specified isotopes, but due to values being collected across several literature references no isotopes are specified in this review. Use of specific isotopes may have small effects on the values of the measurable properties and is worth bearing in mind.

2. Thermodynamic Fundamentals

Before the thermodynamic properties of the species of interest can be interpreted and discussed, it may be wise to review some fundamentals. Thermophysical properties such as the melting (T_M), boiling (T_B), and sublimation points (T_{sub}) are relatively self-explanatory, but they are included for their relevance to separation techniques and reactor operation criteria.

Vapor pressure (V_p) is a more complicated property and is included due to its importance in volatility-based separations. The volatility of any specific compound is governed by several different factors including the degree of intermolecular forces, the presence of extended structures, and the ionic-covalent characteristics of a bond. Strong intermolecular forces typically result in low volatility, as the attractive forces prevent individual molecules from entering the vapor phase. Extended structures inhibit vaporization of molecules due to strong interactions between monomers. For inorganic salts, ionic size is a major factor in extended structure formation, with the relative size of the individual ions determining the maximum coordination number of a given cation and the ability to form bridges between cations. Generally, ionic compounds are less volatile than covalent compounds due to the strong electrostatic interactions. All three of these factors interplay with each other, and each contributes to what conditions are required for volatilization. These effects have implications for industrial applications, *e.g.*, high purity zirconium for fuel cladding is produced through volatilizing hafnium (a strong neutron absorber) out of a salt mixture.[25, 26]

The primary method of quantifying volatility is through the measurement of vapor pressure, V_P. The vapor pressure of a compound is measured over a range of temperatures and analyzed using the Antoine or the Clausius-Clapeyron equations, **eq. 1** and **2**, respectively.

$$\boldsymbol{logV_p = X - \frac{Y}{Z+T}} \tag{1}$$

$$\boldsymbol{lnV_p = -\frac{\Delta H_{vap}}{RT} + W} \tag{2}$$

Where, W, X, Y, and Z are all substance-specific constants, while T = temperature (K), R = gas constant, and ΔH_{vap} = enthalpy of vaporization (kJ/mol). In modern practice, volatility can be measured using manometric or Knudsen effusion techniques where the vapor pressure (V_p) is defined by **eq. 3**.[27] This form is a polynomial fit to the experimental data with unique coefficients (A, B, C) for each species. Certain literature sources expand this expression with a fourth term (D), shown in **eq. 4**.[28]

$$\boldsymbol{logP_{mmHg} = -\frac{A}{T} + B - Clog(T)} \tag{3}$$

$$\boldsymbol{logP_{mmHg} = -\frac{A}{T} + B - Clog(T) + 10^{-3}DT} \tag{4}$$

Because substances can deviate from a single polynomial fit, the experimental constants are often given for a specified temperature range. In some cases, the original values were reported in units of atmospheres or bar, these can be converted to units of millimeters of mercury (mmHg) using **eqs. 5** and **6**, respectively.

$$\boldsymbol{logP_{mmHg} = logP_{bar} + \log(750.062) = -\frac{A}{T} + B - Clog(T)} \quad \textbf{(5)}$$

$$\boldsymbol{logP_{mmHg} = logP_{atm} + \log(760) = -\frac{A}{T} + B - Clog(T)} \quad \textbf{(6)}$$

The isobaric molar heat capacity, specific heat, (C_p) is a critical property in the analysis of molten salts, as it determines how much energy is required to change the temperature of a given substance. In the literature C_p is often reported alongside thermodynamic values as it is experimentally determined as part of thermodynamic measurements. Therefore, heat capacity values will be reported alongside other thermodynamic values.

More in-depth information can be gained from the fundamental thermodynamic properties. Namely the thermodynamic properties related to the changes in heats (ΔH), entropies (ΔS), and Gibbs free energies (ΔG) of various states. Based on the literature, values for the formation (f), fusion (fus), vaporization (vap), and sublimation (sub) of element chlorides are reported at standard state. The Gibbs free energies are related to the enthalpy and entropy *via* the Gibbs function in **eq. 7** where incomplete data can be calculated using the Gibbs function at a given temperature. In some cases, data is available for ΔH° and ΔS°, but no ΔG° are given. Such ΔG° values will be calculated here at a temperature T = 298 K and denoted as such. The measurement of the heat of formation ($\Delta H_f°$) is often accomplished through Hess' Law, **eq. 8** using the $\Delta H_f°$ of certain reactants and products, or the Born-Haber cycle, **eq. 9**, where $\Delta H_{sub\,(M)}$ is the enthalpy of sublimation for metallic elements, ΔH_{bond} is the enthalpy of the bonds, IE_M is the ionization energy of metal atoms, EA_x is the electron affinity for non-metal atoms, and U_L is the enthalpy of the lattice formed. **Eq. 8** is also used in the calculation of ΔH_{sub} using known ΔH_{fus} and ΔH_{vap} values as shown in **eq. 10**.

$$\boldsymbol{\Delta G = \Delta H - T\Delta S} \quad \textbf{(7)}$$

$$\boldsymbol{\Delta H_f^{\circ} = \Delta H_{f,prod}^{\circ} - \Delta H_{f,react}^{\circ}} \quad \textbf{(8)}$$

$$\boldsymbol{\Delta H_f^{\circ} = \Delta H_{sub\,(M)} + \frac{1}{2}\Delta H_{bond} + IE_M - EA_x + U_L} \quad \textbf{(9)}$$

$$\boldsymbol{\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}} \quad \textbf{(10)}$$

3. Solvent Chlorides

While only selected alkali metals (**A** = Li–K) have been the focus of chloride based MSR technology, for the sake of completion and interest in the use of alkaline earth metals (**Ae** = Mg, Ca**)** in reprocessing and cooling loops, data from all elements in groups 1 and 2 are presented. Although some of the elements, e.g., cesium, are not commonly used as solvents, they are important fission products and will be presented with their group 1 and 2 congeners for consistency.

3.1. Thermophysical Properties of Solvent Chlorides

The alkali (**A**) and alkaline earth (**Ae**) metal chlorides represent some of the most basic and prototypical chlorides on the periodic table. Therefore, the **A**Cl and **Ae**Cl_2 data are the most complete in terms of T_M and T_B, with sublimation and triple point data difficult to obtain. The melting points of the alkali metals initially increases from the lowest melting temperature, LiCl (T_M = 610 °C) to the highest melting temperature for NaCl (T_M = 802.18 °C) then decreasing to CsCl (T_M = 646 °C). All the **A**Cl compounds are typically octahedral in the rock salt lattice, although for CsCl this is only true for T > 450 °C, at lower temperature it adopts the primitive cubic CsCl lattice. The T_B of the **A**Cl compounds follow a similar pattern where T_B initially increases from LiCl (T_B = 1383 °C) to KCl (T_B = 1500 °C), decreasing to CsCl (T_B = 1297 °C), the lowest value in the **A**Cl series, see **Table 1**. There are two values of T_M and T_B, each, for FrCl from the same report.[29] These values would make FrCl the lowest melting and lowest boiling of the alkali series. Given the difficulty in working with Fr it is not clear how reliable these values are, and there is little indication of francium's presence as a fission product.

Table 1. Thermochemical properties of alkali (**A**) and alkaline earth (**Ae**) metals

Compound	T_M (°C)	T_B (°C)	Ref
Alkali Metals			
LiCl	610	1383	30
NaCl	802.18	1465	30
KCl	771	1500	30, 31
RbCl	724	1390	30
CsCl	646	1297	30
FrCl	577, 590	1223, 1275	29
Alkaline Earth Metals			
$BeCl_2$	415	482	30
$MgCl_2$	714	1412	30
$CaCl_2$	775	1935	30

$SrCl_2$	874	1250	[30]
$BaCl_2$	961	1560	[30]
$RaCl_2$	~900		[32]

The alkaline earth chloride, **Ae**Cl_2, melting points initially increase starkly from $BeCl_2$ (T_M = 415 °C) to $MgCl_2$ (T_M = 714 °C) then steadily increase to $BaCl_2$ (T_M = 961 °C). The boiling points of the **Ae**Cl_2 compounds display a similarly stark increase from $BeCl_2$ (T_B = 482 °C) to $MgCl_2$ (T_B = 1412 °C) remaining high, but not regular for the rest of the series, see **Table 1**. The irregularity in **Ae**Cl_2 properties could be due to lack of consistent solid-state structural properties, with each compound displaying different coordination modes/modifications. There is an approximate T_M for $RaCl_2$ given (~900°C),[32] similar to francium, it is not clear how accurate this value is and radium is not a typical fission product of focus.

Beryllium chloride is an outlier among the alkaline earth metals, not only for its narrow liquid range but also the T_M and T_B among the [32] and **Ae** elements. This is attributed to the covalent Be–Cl bonding and the small electronegativity difference between Be and Cl. The structure of $BeCl_2$ is a linear polymer, $Be(\mu\text{–}Cl)_2$, rather than the lattice structures seen in the other alkaline-earth metals.[33] The high melting point of sodium chloride compared to the other alkali metals can be attributed to the size-matching between the sodium and chloride ions, giving a more tightly bound lattice, which becomes less well matched with larger cations. The Ae^{2+} charge allows the heavier elements in the series to form more complex lattices which increases the melting point.

3.2. Volatility of Solvent Chlorides

As the operating temperature of molten chloride reactors are 560–740 °C, none of the relevant pure alkali or alkaline earth chlorides would volatilize in the operating temperature range of most reactors. Only $BeCl_2$, would volatilize under reactor conditions. As pointed out in **section 1**, ^{9}Be (100 % abundant), is not used due to issues with the fast neutron spectrum in chloride based MSRs and has not been indicated as a fission product. This makes these salts ideal as solvents, allowing unspent fuel to volatilize off while leaving undesired impurities within the solvent.

The vapor pressure of the **A**Cl and **Ae**Cl_2 compounds have primarily been studied in the gas phase with less data for liquid and solid phase compounds. Some observations have led to claims of dimerization for Li, Na, K, Be, and Mg, with the $(LiCl)_3$ trimer also being reported,[34] see **Table 2**. The presence of these species significantly complicates the analysis of the vapor phase of these compounds. Row 4 and 5 **A**/**Ae** metal chlorides have not been reported to oligomerize, remaining binary compounds into the gas phase with Sr and Ba going through crystal phase transitions rather than gas phase transitions. The data suggests that the vapor pressure of the **A**Cl and **Ae**Cl_2 compounds are all rather low, except for beryllium, which is consistent with the thermochemical properties (T_M, T_B) in **Table 1**.

Table 2. Vapor pressure coefficients of alkali (**A**) and alkaline earth (**Ae**) chlorides in different physical states where coefficients A–C come from **Eq. 3-6**.

Compound	A	B	C	T range (K)	Ref
Alkali Metals – Solid Phase					
NaCl[a]	12,440	14.31	0.90	298-1075	28
KCl	12,230	20.34	3.0	298-1044	28
RbCl[b]	10,920	14.533	2.32	700-996	34
RbCl	11,670	20.157	3.0	298-997	28
CsCl	10,800	19.99	3.02	700-919	28
Alkali Metals – Liquid Phase					
LiCl	10,760	22.30	4.02	883-1656	28
NaCl	11,530	20.77	3.48	1075-1738	28
KCl	10,710	18.91	3.0	1044-1773	28
KCl[c]	11,101	20.83	3.52	1189-1418	35
RbCl[b]	10,004	15.892	3.08	996-1679	34
RbCl	10,300	18.77	3.0	997-1663	28
CsCl	10,052	20.51	3.52	1102-1387	35[c]
CsCl	9815	20.38	3.52	919-1570	28
Alkali Metals – Gas Phase[d]					
LiCl (G_1)[b]	11,620	16.416	2.79	700-883	34
LiCl (G_2)[b]	10,101	11.073	1.56	883-1633	34
$(LiCl)_2$ (G_1)[b]	12,523	23.031	4.68	700-883	34
$(LiCl)_2$ (G_2)[b]	9525	12.653	2.31	883-1633	34
$(LiCl)_2$ (G_3)[b]	5312	4.617	0.37	1633-2000	34
$(LiCl)_3$ (G_1)[b]	10,248	11.131	2.64	900-1633	34
NaCl (G_1)[b]	11,972	17.865	3.26	700-1074	34
NaCl (G_2)[b]	10,661	17.766	3.63	1074-1757	34
$(NaCl)_2$ (G_1)[b]	13,231	26.333	5.69	700-1074	34
$(NaCl)_2$ (G_2)[b]	10,638	26.344	6.49	1074-1757	34
$(NaCl)_2$ (G_3)[b]	8739	21.075	4.87		34
KCl (G_1)[b]	12,151	17.254	2.99	700-1045	34

KCl (G_2)[b]	11,326	20.148	4.21	1045-1714	[34]
$(KCl)_2$ (G_1)[b]	14,592	26.312	5.40	800-1045	[34]
$(KCl)_2$ (G_2)[b]	12,877	31.525	7.67	1045-1714	[34]
$(KCl)_2$ (G_3)[b]	4,849	4.185	0.32	1714-2000	[34]
$CsCl$ (G_1)[b]	10,796	17.327	3.12	700-918	[34]
$CsCl$ (G_2)[b]	10,522	22.717	5.04	918-1569	[34]
$(CsCl)_2$ (G_1)[b]	12,271	25.545	5.41	700-918	[34]
$(CsCl)_2$ (G_2)[b]	11,754	36.567	9.32	918-1569	[34]
$(CsCl)_2$ (G_3)[b]	4610	4.252	0.33	1569-2000	[34]
Alkaline Earth Metals – Solid Phase[d]					
$BeCl_2$	7870	27.15	5.03	298-688	[28]
Be_2Cl_4	8970	37.0	7.65	298-688	[28]
$MgCl_2$[c]	12,820	9.168±0.048		802-985	[36]
$CaCl_2$[b]	17,494	17.772	2.72	1000-1045	[34]
$SrCl_2$ (A)[b]	20,129	30.576	6.38	990	[34]
$SrCl_2$ (B)[b]	21,693	43.420	10.14	990-1146	[34]
$BaCl_2$ (A)[b]	19,689	23.239	4.12	1000-1198	[34]
$BaCl_2$ (B)[b]	20,773	35.811	7.91	1198-1235	[34]
Alkaline Earth Metals – Liquid Phase[d]					
$BeCl_2$	7220	26.28	5.03	688-755	[28]
$MgCl_2$[c]	11,735	20.27	4.076	1208-1413	[35]
$MgCl_2$	10,840	25.53	5.03	987-1685	[28]
$CaCl_2$[b]	17,032	23.760	4.85	1045-2279	[34]
$CaCl_2$	13,570	9.22		1110-1281	[28]
$SrCl_2$[b]	18,381	25.141	5.11	1146-2000	[34]
$BaCl_2$[b]	18,956	28.682	6.08	1235-2000	[34]
Alkaline Earth Metals – Gas Phase					
$BeCl_2$ (G_1)[b]	7404	15.399	2.10	400-688	[34]
$BeCl_2$ (G_2)[b]	8277	32.246	7.59	688-760	[34]
$(BeCl_2)_2$ (G_1)[b]	9334	21.283	3.10	500-688	[34]
$(BeCl_2)_2$ (G_2)[b]	11,028	53.192	13.83	688-760	[34]
$(BeCl_2)_2$ (G_3)[b]	2721	4.791	0.57	760-2000	[34]
$MgCl_2$ (G_1)[b]	13,605	17.819	2.68	800-980	[34]
$MgCl_2$ (G_2)[b]	11,955	19.216	3.71	980-1634	[34]

$MgCl_2$ (G_3)[b]	12,347	3.765	0.18	1634-2000	34
$(MgCl_2)_2$ (G_1)[b]	18,276	25.918	4.42	900-980	34
$(MgCl_2)_2$ (G_2)[b]	14,943	28.441	6.40	980-1634	34
$(MgCl_2)_2$ (G_3)[b]	4476	4.959	0.50	1634-2000	34

[a] D term = -0.46 [b] Converted from bar to mmHg using **eq. 5** [c] Converted from atm to mmHg using **eq. 6** [d] "G_n, A, B" designations as given in the primary literature

3.3. Thermochemical Properties of Solvent Chlorides

For the Alkali (**A**) and Alkaline Earth (**Ae**) metals there is good data for the solid and gas phase compounds, except for the heaviest group members francium and radium. There are two vastly different values reported the enthalpy of formation (ΔH_f^o) for FrCl, -181.6 and -493.3 kJ/mol, both reported in the same source.[29] The gas phase data also includes evidence of oligomerization for multiple species (**A** = Li, Na, K, **Ae** = Be, Mg) which are primarily the lighter members of each series. In general, the data on the solid-state compounds show that ΔH_f^o and Gibbs free energy (ΔG_f^o) trend more negatively down each series. The solid-state data also shows that as the series descends there is a general trend of increasingly positive values for the standard entropy (ΔS^o) and the heat capacity (C_P). The solid-state data also show that the differences between the smallest and largest values are greater for the **Ae** metals than **A** metals. These trends are retained in the gas phase to some degree, but are less pronounced, see **Table 3**.

Table 3. Enthalpy of formation (ΔH_f^o, kJ/mol), standard entropy (ΔS^o, J/molK), free energy of formation (ΔG_f^o, kJ/mol), and heat capacity (C_p, J/molK) thermodynamic data for alkali (**A**) and alkaline earth (**Ae**) metal chlorides.

Compound	ΔH_f^o	ΔS^o	ΔG_f^o	C_p	Ref
		Alkali Metals – Solid Phase			
LiCl	–408.6	59.3	–384.4	48.0	30
LiCl	–408.6	59.3	–426.3	48.1	34
NaCl	–411.2	72.1	–384.1	50.5	30
NaCl	–411.2	72.1	–432.7	66.9	34
KCl	–436.5	82.6	–408.5	51.3	30
KCl	–436.5	82.6	–461.1	51.6	34
RbCl	–435.4	95.9	–407.8	52.4	30
RbCl	–435.1	95.2	–463.5	51.4	34
CsCl	–443.0	101.2	–414.5	52.5	30
FrCl	–181.6, –439.3				29

Alkali Metals – Gas Phase					
LiCl	–195.4	212.9	–258.9	33.3	[34]
$(LiCl)_2$	–593.5	288.8	–679.6	72.2	[34]
$(LiCl)_3$	–962.3	335.8	–1062.4	102.0	[34]
NaCl	–191.7	229.8	–260.2	35.8	[34]
$(NaCl)_2$	–586.7	325.4	–683.7	119.8	[34]
KCl	–214.6	239.1	–285.9	36.5	[34]
$(KCl)_2$	–615.4	350.4	–719.9	80.9	[34]
RbCl	–233.1	241.3	–305.1	36.5	[34]
Alkaline Earth Metals – Solid Phase					
$BeCl_2$	–490.4	75.8	–445.6	62.4	[30]
$BeCl_2$	–496.2	75.8	–518.8	62.4	[34]
$MgCl_2$	–641.3	89.6	–591.8	71.4	[30]
$MgCl_2$	–644.3	89.5	–671.0	71.3	[34]
$CaCl_2$	–795.4	108.4	–748.8	72.9	[30]
$CaCl_2$	–795.4	108.4	–827.7	72.6	[34]
$SrCl_2$	–828.9	114.9	–781.1	75.6	[30]
$SrCl_2$	–828.9	114.9	–863.1	75.6	[34]
$BaCl_2$	–855.0	123.7	–806.7	75.1	[30]
$BaCl_2$	–858.6	123.7	–895.4	75.2	[34]
Alkaline Earth Metals – Gas Phase					
$BeCl_2$	–360.2	252.0	–435.4	51.6	[34]
$(BeCl_2)_2$	–823.2	381.5	–936.9	115.4	[34]
$MgCl_2$	–392.5	277.0	–475.1	57.1	[34]
$(MgCl_2)_2$	–954.4	418.9	–1079.3	123.6	[34]
$CaCl_2$	–470.5	290.3	–557.1	59.4	[34]
$SrCl_2$	–473.2	316.3	–567.5	55.7	[34]
$BaCl_2$	–498.7	325.7	–595.8	56.2	[34]

When turning to thermodynamic, enthalpic (ΔH), and entropic (ΔS), energies of phase transition, fusion (fus), vaporization (vap), and sublimation (sub) of the **A** and **Ae** chloride compounds, the most comprehensive data exists for fusion with some data on **A**Cl vaporization. Data on **Ae**Cl_2 sublimation and vaporization is present, but incomplete. The heat of fusion is highest for the second-row elements, Na and Mg, and decreases down the remainder of the columns, however the lowest ΔH_{fus} are for the first member of each group, Li and Be, indicating that they have the weakest intermolecular forces. Sodium and magnesium have the highest heats of fusion primarily because of their compatible ionic radii, with the heavier metals being too large to allow for the ideal lattice present in NaCl. The heats of vaporization are sparse, but trends can still be drawn from the available data. Aside from the estimated value for LiCl, the heats of vaporization decrease down the alkali metal series, with ΔH_{vap} dropping by approximately 40 kJ/mol between NaCl and KCl, then again for KCl and RbCl. Entropy of vaporization rapidly decreases down the alkali metals, falling by almost 100 J/molK between Na and Rb (**Table 4**). In terms of separations, the data suggests that the heavier elements should be the most volatile, consistent with the T_M and T_B values in **Table 1**.

Table 4. Enthalpic (ΔH, kJ/mol) and entropic (ΔS, J/molK) heats of fusion (fus), vaporization (vap) and sublimation (sub) for the alkali (**A**) and alkaline earth (**Ae**) metal chlorides.

Cmpd	ΔH_{fus}	ΔS_{fus}	ΔH_{vap}	ΔS_{vap}	ΔH_{sub}	ΔS_{sub}	Ref
				Alkali Metals			
LiCl	19.8	23.4	114.1[a]		212.5[b]		30, 37, 38
LiCl	19.5	22.1					34
NaCl	28.16	26.2, 28.0	223.0	277.32 ± 2.8[a]	221.84 ± 2.0[a]	305.3[b]	30, 37, 39-41
NaCl	28.3	26.3					34
KCl	26.28	25.9	187.7	267.53± 1.6[a]	214.01 ± 1.0[a]		30, 37, 41
KCl	26.2	25.0					34
RbCl	24.4	18.4, 24.47					30, 37, 39
RbCl	23.7	23.8	148.5	88.5	172.2[b]	112.3[b]	34
CsCl	20.4	14.6					30, 37
CsCl	20.3	22.1					34
FrCl					181.6		29
				Alkaline Earth Metals			
$BeCl_2$	8.66						30
$BeCl_2$	8.58	12.5					34
$MgCl_2$	43.1		190[b]		233.1[a]		30, 38
$MgCl_2$	39.9	40.8					34
$CaCl_2$	28.05	24.3					30, 37
$CaCl_2$	27.3	26.1		102.9		129.0[b]	34
$SrCl_2$	16.22	15.1					30, 37
$SrCl_2$	16.5	14.4		109.7		124.1[b]	34
$BaCl_2$	15.85	18.4					30, 37

$BaCl_2$	16.0	12.9	34

[a] Value recorded at 800 K. [b] Calculated value using **eq 10**

4. Fuel Chlorides

In the study of the actinides (**An**) the elemental and oxide forms are the most studied types of compounds, presumably due to their utilities in energy and defense applications.[42, 43] The halides also represent a well-studied class of compounds driven by the formation of high valent-volatile compounds, *e.g.*, $U^{VI}F_6$.[44-46] In general, the amount of available literature for actinide halides decreases down the series, F > Cl > Br > I. This is presumably due to the volatility characteristics, industrial use, and environmental aspects. The scarcity and synthetic nature of actinides - except uranium and thorium - coupled to the constraints due to handling radioactive materials means that data can often be difficult to collect.

4.1. Thermophysical Proprieties of Actinide Chlorides

The binary actinide chlorides, **An**Cl_x, have been prepared by a variety of routes, most commonly by chlorination of an oxide. Common chlorinating agents include anhydrous HCl; hexachloropropene, C_3Cl_6; carbon tetrachloride, CCl_4; chlorine, Cl_2; and combinations thereof.[47-49] Scaled up syntheses often use high temperature chlorination of a dioxide, **An**$^{IV}O_2$, with CCl_4 and/or Cl_2. Other preparations employ phosgene, $COCl_2$; thionyl chloride, $SOCl_2$; or phosphorus pentachloride, PCl_5; as chlorination sources.[50-52] Other **An** forms are readily chlorinated including oxalates, hydroxides, hydrides, or metallic actinides.[50-52] One notable exception includes $U^{IV}Cl_4$ where pilot plant scale syntheses use $U^{V,VI}{}_3O_8$ or $U^{VI}O_3$ with C_3Cl_6 at 210 °C.[53, 54] All of the uranium oxides can be chlorinated to UCl_x ($x = 3–6$) depending on the reaction conditions and reagents used.[55-57] The chlorination of $Pu^{IV}O_2$ follows similar routes to that of uranium and other actinides, using CCl_4 at 700 °C to produce $Pu^{III}Cl_3$.[51, 55, 58-60]

In general, these methods produce compounds with formally tri- or tetravalent oxidation states with trivalent preparation data available for Ac, U–Es.[52, 61-64] Attempts have been made to synthesize higher chlorides, but only uranium and protactinium are isolable as penta– or hexavalent chlorides. Work on the chlorination of protactinium oxides suggests that reaction of $Pa^{V}{}_2O_5$ with CCl_4 with or without Cl_2, or only $SOCl_2$ at 300 °C gives $Pa^{V}Cl_5$.[65, 66] The high temperature reaction of $Pa^{V}Cl_5$ with H_2 at 800 °C gives $Pa^{IV}Cl_4$ or the reaction of $Pa^{IV}O_2$ with CCl_4 at 500 °C gives $Pa^{IV}Cl_4$.[65, 67] Work on $Pa^{V}Cl_5$ suggests that it is highly volatile and sublimes well below the reported melting point of 306 °C.[68, 69] Compounds with formally low valence, e.g., $Am^{II}Cl_2$, $Cf^{II}Cl_2$, and $Es^{II}Cl_2$, species have been claimed,[70, 71] but they differ from traditionally divalent lanthanides $Ln^{II}Cl_2$ (Eu^{II}, Sm^{II}, Yb^{II}), and are most likely electronically similar to non-traditional $Ln^{II}I_2$.[72, 73]

In terms of important relevant properties of $AnCl_x$, the highly ionic nature of actinide-halide bonds means that the melting (T_M) and boiling (T_B) points of these compounds are relatively high. The prevalence of the trivalent oxidation state (Ac, U–Es) gives the highest number of values, with the available tetravalent compounds (Th–Np) well characterized, and some data available for $PuCl_4$, see **section 4.3**. The limited availability of higher penta- and hexavalent (Pa, U) oxidation states gives fewer data measurements. Uranium displays the greatest number of oxidation states, from +3 to +6 and thus, has the highest number of isolatable, and well-studied **An**Cl_x.

The melting points of many early actinide (Th, U–Am) chlorides are well characterized, with some data for the high activity, scarce elements such as Pa, Cm–Es, as shown in **Table 5**. In general, the T_M of a compound is most dictated by the oxidation state, which is coupled to the compound's coordination number and ionic radius. When considering the effects of ion size, it is important to compare compounds within the same coordination number (CN). Where CN = six, CN_6, represents the most common CN with values according to Shannon's revised table of ionic radii (iRad).[74] In general, CN_6 may be assumed unless noted otherwise. The melting points generally decrease as the formal oxidation state increases and as the ion becomes smaller. The dependence on oxidation state appears to follow the coordination number, based on the crystal structure, where **An^{III}** (CN_9), **An^{IV}** (CN_8), **An^{V}** (CN_6), and **An^{VI}** (CN_6). The **An^{III}** and **An^{IV}** compounds crystallize as extended structures in the $U^{III}Cl_3$ and $U^{IV}Cl_4$ lattices, respectively. The U^V and U^{VI} compounds are characterized as being bimetallic and monometallic molecules, $U^{V}_2(m\text{–}Cl)_2Cl_8$, and $U^{VI}Cl_6$, respectively.[75, 76] Therefore, $U^{III}Cl_3$, the largest (iRad = 1.025 Å, CN_6) and least charged actinide in the list, displays the highest T_M (835 °C), while $U^{VI}Cl_6$, the smallest (iRad = 0.73 Å, CN_6) and most charged actinide in the list, displays the lowest T_M (177 °C).[74] The dependence on size within a single oxidation state is shown nicely across the trivalent compounds, from $U^{III}Cl_3$ (T_M = 835 °C, iRad = 1.025 Å) to $Cf^{III}Cl_3$ (T_M = 545 °C, iRad = 0.95 Å), with a report that $Es^{III}Cl_3$ melts above a temperature of 450 °C, **Table 5**. A similar trend is observed in the tetravalent series from Th^{IV} to Np^{IV} where the highest value is observed for $Th^{IV}Cl_4$ (T_M = 770 °C, iRad = 1.05 Å, CN_8), and the lowest for $Np^{IV}Cl_4$ (T_M = 517 °C, iRad = 0.98 Å, CN_8), see **Table 5**. Similar trends are observed in the boiling points (T_B), where the influence of size is secondary to oxidation state. T_B, where **An^{III}**Cl_3 > **An^{IV}**Cl_4 > **An^{V}**Cl_5 > $U^{VI}Cl_6$, see **Table 5**. Although all metal halides can sublime, recording the temperature of sublimation, T_{sub}, is often difficult for the actinides and is often best achieved under reduced pressure. The sublimation of several **An**Cl_x compounds has been reported, but the precise T_{sub} are not well defined. In some cases relative temperature ranges over which the compounds can be sublimed are reported, *e.g.*, $Np^{III}Cl_3$ can be purified by sublimation in the range of 750–800 °C.[77] Without knowledge of the pressure, or a consistent study under the same conditions these values can only be taken at face value. Again, oxidation state and ion size appear to affect the reported temperatures. Lastly, the value of the triple point, T_{TP} (temperature), or P_{TP} (pressure), is least reported, with only $U^{IV}Cl_4$[78, 79] (T_{TP} = 590±1 °C; P_{TP} = 18.4 mmHg) and $Np^{IV}Cl_4$[79] (T_{TP} = 538 °C) being reported.

Table 5. Thermochemical properties of actinide (**An**) chlorides

Compound	T_M (°C)	T_B (°C)	T_{sub} (°C)	Ref
Trivalent Actinides				
$AcCl_3$			950	52
UCl_3	835	1657	850	30, 80
$NpCl_3$	800		750-800	55, 81
$PuCl_3$	760±5	1790	800	30, 82, 83
$AmCl_3$	500,[a] 715	1180[a]	750, 850	30, 82, 84, 85
$CmCl_3$	695±10			86
$BkCl_3$	603			86
$CfCl_3$	545			87
$EsCl_3$	>450			64
Tetravalent Actinides				
$ThCl_4$	770	921	815	30, 88
$PaCl_4$	677, 500[a]		400	89
UCl_4	590±5	789	400,[a] 600	30, 90, 91
$NpCl_4$	530	847	500	81, 82, 92
$PuCl_4$	583[b]	837[b]		93
Pentavalent Actinides				
$PaCl_5$	306	420[c]	~200	30, 94, 95
UCl_5	287	527		30, 82
Hexavalent Actinides				
UCl_6	177.5±2.5	277	75-100[a]	30, 31, 47, 82

[a] Under reduced pressure, ca. 10^{-4} mmHg [b] Extrapolated from thermodynamic data on $AnCl_4$ (An = Th, U, Np), [c] Extrapolated from vapor pressure data

4.2. Volatility of Fuel Chlorides

The volatility of **An**Cl_x has been a point of interest for well over seven decades. Volatility-based separations have been considered as viable actinide purification and reprocessing schemes.[96] The interest in **An**Cl_x volatility has produced numerous useful studies quantifying the vapor pressure of actinide chlorides in different oxidation and physical states. Actinide chloride volatility has primarily been studied in the early actinides: thorium, uranium, neptunium, and plutonium, with some data on $Pa^{V}Cl_5$. High temperature chlorination of berkelium metal in a tube furnace showed that some material migrated from the hot zone in a manner similar to Pu. The unexpected migration of Bk lead researchers to suggest the presence of a transient "$Bk^{IV}Cl_4$," reminiscent of $Pu^{IV}Cl_4$, please see **section 4.3**.[97]

In general, measurements of **An**Cl_x vapor pressure are limited to the most available elements, Th, U, Np, and Pu with some available measurements on Pa, where the tetravalent oxidation state has the largest amount of data, **Table 6**. For certain species, multiple values are reported, where more recent measurements typically present a higher precision. Uranium is the only element with documented dimerization in the gas phase with all other species characterized as monomers. Only $U^{IV}Cl_4$ and $U^{V}Cl_5$ have been reported to dimerize in the gas phase. Conflicts exist within the literature regarding the existence of these dimers, with some authors denying the existence of the dimer[98] while others maintain their existence.[55, 99, 100] Comparing the vapor pressures across species shows that $U^{V}Cl_5$ is the most volatile at room temperature, however even a slight elevation in temperature leads to rapid volatilization of $U^{VI}Cl_6$. Broadly, volatility increases with increasing formal oxidation state, $+3 < +4 < +5 < +6$, as observed for other thermochemical properties (T_M, T_B, *etc.*), in **Table 5**. The data for the tetravalent compounds, show a general trend towards increased volatility as the series is traversed, Th < U < Np < Pu. Perhaps the most intriguing data points are those for $Pu^{IV}Cl_4$ (g) considering its difficulty to work with, as discussed in **section 4.3**. The values given for $Pu^{IV}Cl_4$ (g) suggest it is the most volatile tetravalent actinide.

Table 6. Vapor pressure coefficients of actinide (**An**) chlorides in different physical states where s = solid, l = liquid, g = gas, a, b indicate different crystal modifications, the coefficients A–C come from **Eqs. 3-6**.

Compound	A	B	C	T range (K)	Ref
Trivalent Actinides – Solid Phase					
UCl_3	12,000	10.0			[55]

UCl$_3$	11,149	8.90		590-790	55
UCl$_3$	11,552	8.97		>790	55
UCl$_3$[a]	15,543	23.436	4.31	800-1114	34
PuCl$_3$[a]	18,270	29.725	5.34	700-1033	34
PuCl$_3$	15,910±120	12.726±0.126		850–1033	58
PuCl$_3$	18,270	32.60	5.34	298-1033	28
Trivalent Actinides – Liquid Phase					
UCl$_3$[a]	13,506	24.778	5.35	1114-1851	34
PuCl$_3$[a]	15,490	28.883	6.45	1033-2065	34
PuCl$_3$	12,356±32	10.237±0.033		1033–1100	58
PuCl$_3$	12,590	9.509			55
PuCl$_3$	15,490	31.76	6.45	1033-2063	28
Tetravalent Actinides – Solid Phase					
ThCl$_4$	12,910	14.30			55
ThCl$_4$	12,900	14.30		974-1043	28
ThCl$_4$ (α)[a]	11,929	20.522	3.27	600-679	34
ThCl$_4$ (β)[a]	11,859	22.146	3.88	679-1042	34
UCl$_4$[b]	7223±15	6.77 ±0.02			98
UCl$_4$	10,427	13.2995			55
UCl$_4$[a]	11,571	23.637	4.01	600-863	34
UCl$_4$	11,350	23.21	3.02	298-863	13
NpCl$_4$	8920	12.17			79
Tetravalent Actinides – Liquid Phase					

$ThCl_4$	7987	9.57			55
$ThCl_4$[a]	10,137	30.514	7.20	1042-1224	34
$ThCl_4$	7980	9.57		1043-1186	28
UCl_4	7205	9.65			55
UCl_4[a]	9720	29.332	6.68	863-1068	34
UCl_4	9950	28.96	5.53	863-1062	13
$NpCl_4$	6220	8.64			79
Tetravalent Actinides – Gas Phase [c]					
$(UCl_4)_2$ (G_1)[a]	12,410	31.646	7.50	700-863	34
$(UCl_4)_2$ (G_2)[a]	8940	41.426	12.20	863-1154	34
$PuCl_4$ (G_1)[a]	9351	17.819	3.47	600-1033	34
$PuCl_4$ (G_2)[a]	6948	21.762	5.55	1033-2000	34
Pentavalent Actinides [c]					
$PaCl_5$ (s)	11,162	23.87			101
$PaCl_5$ (l)	7377	17.27			101
UCl_5 (s)	3307	3.361			13
UCl_5 (s)	6957	23.014	4.04		34
UCl_5 (s - α)[a]	2586	11.356	1.68	298-367	34
UCl_5 (s - β)[a]	2591	11.446	1.71	367-600	34
$(UCl_5)_2$ (G_1)[a]	4587	15.116	3.48	298-600	34
$(UCl_5)_2$ (G_2)[a]	4587	15.116	3.48	600-863	34
$(UCl_5)_2$ (G_3)[a]	1696	30.352	9.81	863-1154	34
$(UCl_5)_2$ (G_4)[a]	5237	8.421	1.14	1154-1700	34

Hexavalent Actinides[c]					
UCl_6 (s)	4000	10.20		298-450	13
UCl_6 (s)	3788	9.52			47
UCl_6 (s)	2422	6.634			47
UCl_6 (s)[a]	4710	19.197	3.96		34
UCl_6 (S_1)[a]	2907	14.417	2.54	298-368	34
UCl_6 (S_2)[a]	2907	14.417	2.54	368-451	34
UCl_6 (G_1)[a]	1958	7.356	2.25	298-863	34
UCl_6 (G_2)[a]	463	14.344	5.22	863-1154	34
UCl_6 (G_3)[a]	4118	6.703	0.69	1154-2000	34

[a] Converted from bar to mmHg using **eq. 5** [b] Converted from atm to mmHg using **eq. 6** [c] "G_n" and "S_n" designations as given in the primary literature

4.3. The $PuCl_4$ Problem

Of the actinide elements available in multi-kilogram quantities, one of the most difficult actinide species to study is $Pu^{IV}Cl_4$. The most common preparation methods for $Pu^{IV}Cl_4$ have been high temperature (>600 °C) chlorination of $Pu^{IV}O_2$ with $Cl_2/CCl_4/Ar$,[58, 97] although other chlorinating agents have been used.[60, 102] $Pu^{IV}Cl_4$ is known to be highly volatile[103] with its existence being proven by the reaction of chlorine gas with $Pu^{III}Cl_3$ and recording high temperature gas phase UV-visible spectrum.[104] However, $Pu^{IV}Cl_4$ is known to decompose to $Pu^{III}Cl_3$ (s) + ½ Cl_2 (g) upon condensation, therefore, high quality data on binary $Pu^{IV}Cl_4$ is sparse in the open literature.[104, 105] Some physical property data on $Pu^{IV}Cl_4$ has been published using extrapolation and computational methods from similar actinide compounds, $Th^{IV}Cl_4$, $U^{IV}Cl_4$, $Np^{IV}Cl_4$, *e.g.*, T_M/T_B.[93, 106] More in-depth data on $Pu^{IV}Cl_4$ is limited presumably due to the high temperatures needed to record these values coupled to the difficulty in working with trans-uranium (TRU) elements.

The instability of binary $Pu^{IV}Cl_4$ is countered by the ability to generate oxidation state pure Pu(IV) in aqueous HCl media.[102] It has also been shown that the neutral Lewis base adduct, $Pu^{IV}Cl_4(DME)_2$ (DME = $H_3COCH_2CH_2OCH_3$) is structurally characterizable.[107] There are also numerous anionic hexachloroplutonate compounds, $[Pu^{IV}Cl_6]^{2-}$.[108-110] The solid state $Pu^{IV}Cl_4L_2$ (L = Cl^{1-}, DME) compounds display some level of room temperature stability lending themselves to study. However, aqueous solutions of Pu(IV) are known to exhibit complicated com- and disproportionation chemistry, where mixtures of oxidation states from +3 to +6 are observed.[111, 112] Similar behavior has been noted for berkelium,[113, 114] however high stability of Bk(III) coupled to the dearth of fundamental Bk data, means that little is known about its behavior in such systems. The small (<50 mg) quantities of Bk produced in nuclear reactors means that most Bk study is performed in the academic realm.[115-118]

As part of the fundamental study of plutonium for use in MSRs, $Pu^{III}Cl_3$ has always been chosen as the plutonium starting material, presumably due to its relative ease in preparation, handling, favorable thermophysical properties, and subsequent salt studies. It is reasonable to assume that in a molten chloride mixture, plutonium would exist as a complex of chloride anions, $[PuCl_x]^{n-}$, most likely $[PuCl_6]^{n-}$. The speciation of uranium in molten chlorides has recently been examined and demonstrates fluxional oxidation states like those expected for plutonium.[119] While molten chlorides have been suggested to stabilize lower oxidation states of metals, some preliminary work in molten salts have suggested the presence of both Pu(III) and Pu(IV), with Pu(III) dominating.[120, 121] The complexity of what oxidation state(s) of plutonium are present in a molten salt system are difficult to study in pure systems and become more complicated in the presence of fission/corrosion products. A strong understanding of the redox/oxidation state chemistry of plutonium in molten salt mixtures will also be key to fine tuning recycling processes, especially on-line recycling and reducing proliferation concerns.

4.4. Thermochemical Properties of Fuel Chlorides

In examining the actinide chlorides, of all the properties, the enthalpy of formation (ΔH_f^o) is by far the most well reported value. A recent updated handbook chapter reports the values of many **An**Cl_x compounds to a high precision,[122] although older values are presented as well. The actinide trichlorides, **An**$^{III}Cl_3$, have the largest number of compounds characterized, primarily for the crystalline phase with a limited amount of gas phase data. Several of the $An^{III}Cl_3$ compounds (Bk–No) use estimated values based on ionic radii, presumably due to lack of material or difficulties of work with TRU elements. The tetravalent compounds are very well characterized for Th–Pu in the crystalline and gas phases. While fewer higher valent compounds are accessible, there is good data for $Pa^{V}Cl_5$, $U^{V}Cl_5$, and $U^{VI}Cl_6$ in the crystalline and gas phases, see **Table 7**. Uranium species provide a unique perspective into the effect of oxidation state, showing that ΔH_f^o, ΔS^o, ΔG_f^o, and C_p all increase with higher oxidation states in both the solid and gas phases. None of the other actinides have data for the same range of oxidation states as uranium, the rest being limited to one or two oxidation states. Only uranium is documented to dimerize within the gas phase, although this could be due to a lack of data on the other elements.

Table 7. Enthalpy of formation (ΔH_f^o, kJ/mol), standard entropy (ΔS^o, J/molK), free energy of formation (ΔG_f^o, kJ/mol), and heat capacity (C_p, J/molK) thermodynamic data actinide (**An**) metal chlorides, where s = solid, l = liquid, g = gas, a, b indicate different crystal modifications.

Compound	ΔH_f^o	ΔS^o	ΔG_f^o	C_p	Ref
Trivalent Actinides – Crystalline Phase					
$AcCl_3$	–1053[a]	148.7±6.0[a]			89
UCl_3	–863.700±2.000	163.900±2.000	–797.832±2.088	102.520±0.500	122
UCl_3	–861.9	159.0	–909.3	102.5	34
$NpCl_3$	–896.800±3.000	160.400±4.000	–829.811±3.237	101.850±4.000	122
$PuCl_3$	–959.600±1.800	161.700±3.000	–891.806±2.024	101.200±4.000	122
$PuCl_3$	–961.5	159.0	–1008.9	102.9	34
$AmCl_3$	–977.800±1.300	146.200±6.000	–905.105±2.290	103.000±10.000	122
$CmCl_3$	–974±4	163±6	–1023[b]		123
$CmCl_3$	–969.6±6.7[a]	163.1±6.0[a]	–1018.2[b]		89
$BkCl_3$	–952±15[a]	164.6±6.0[a]	–1001[b]		89
$CfCl_3$	–965±20[a]	167.2±6.0[a]	–1015[b]		124
$EsCl_3$	–950±24[a]				89
$FmCl_3$	–963±44[a]				89
$MdCl_3$	–864±50[a]				89
$NoCl_3$	–716±50[a]				89
Trivalent Actinides – Gas Phase					
UCl_3	–523.000±20.000	380.300±10.000	–521.652±20.221	82.400±5.000	122
UCl_3	–580.7	357.0	–687.1	76.1	34
$NpCl_3$	–589.000±10.400	362.800±10.000	–582.357±10.822	78.500±5.000	122

$PuCl_3$	–647.400±1.868	368.620±10.000	–641.299±3.598	78.470±5.000	122
Tetravalent Actinides – Crystalline Phase					
$ThCl_4$ (*b*)	–1186.300±1.300	183.500±5.000	–1092.293±1.984	120.3±6.0	125
$ThCl_4$	–1186.8	190.4	–1243.5	120.3	34
$PaCl_4$	–1044.3				126
$PaCl_4$	–1044±13	193.7±4.2	–954±13		127
UCl_4	–1018.800±2.500	197.200±0.800	–929.605±2.512	121.800±0.400	122
UCl_4	–1018.8	197.2	–1077.6	120.8	34
$NpCl_4$	–984.000±1.800	200.000±8.000	–895.562±2.998	122.000±6.000	122
$PuCl_4$	–963.6±7.5				127
$PuCl_4$	–968.700±5.000	201.000±10.000	–879.368±5.826	121.400±4.000	122
Tetravalent Actinides – Gas Phase					
$ThCl_4$	–951.400±5.166	403.400±4.000	–922.956±5.304	101.4±3.0	125
$ThCl_4$	–967.9	397.6	–1086.5	101.6	34
UCl_4	–815.400±4.717	409.300±5.000	–789.442±4.947	103.500±3.000	122
UCl_4	–1018.8	197.2	–1077.6	120.8	34
$(UCl_4)_2$	–1891.6	581.3	–1992.9	165.0	34
$NpCl_4$	–787.000±4.600	423.000±10.000	–765.050±5.487	105.000±5.000	122
$PuCl_4$	–792.000±10.000	409.000±10.000	–764.683±10.438	103.400±5.000	122
$PuCl_4$	–793.7	412.5	–916.7	98.0	34
Pentavalent Actinides – Crystalline and Gas Phase					
$PaCl_5$ (s)	–1147.8±14.4	238.8±8	–1219.0†		89
$PaCl_5$ (g)	–1042±15	440.8			89

UCl_5 (s)	–1039.000±3.000	242.700±8.400	–930.115±3.908	150.600±8.400	122
UCl_5 (s)	–1041.5	246.9	–1115.1	114.6	34
UCl_5 (g)	–900.000±15.000	438.700±10.000	–849.552±15.074	123.600±5.000	122
$(UCl_5)_2$ (g)	–1960.2	707.2	–2171.1	263.4	34
Hexavalent Actinides – Crystalline and Gas Phase					
UCl_6 (s)	–1066.500±3.000	285.500±1.700	–937.120±3.043	175.700±4.200	122
UCl_6 (s)	–1068.2	285.8	–1153.4	175.6	34
UCl_6 (g)	–985.500±5.000	438.000±5.000	–901.588±5.218	147.200±3.000	122
UCl_6 (g)	–987.8	432.7	–1116.9	142.7	34

[a] Estimated Value [**b**] Calculated value using **eq 10**

The thermodynamic data in **Table 7** suggest americium to be the most stable trivalent actinide. This behavior is consistent with the known increase in stability for the trichlorides among heavier actinides and the difficulty in accessing higher oxidation states for those same elements. Computational studies have attributed the subtle decrease in trivalent stability past Am to *f*-electron spin pairing.[128, 129] In viewing the data for the trivalent crystalline phase, the ΔH_f^o ranges from -1053 kJ/mol ($Ac^{III}Cl_3$, an estimated value) to -716 kJ/mol ($No^{III}Cl_3$, an estimated value), with most experimental values in the range of ~ -800 to -1000 kJ/mol. $U^{III}Cl_3$ displays the least negative ΔH_f^o of compounds with reliable experimental values for both the crystalline (-863 kJ/mol) and gas (-523 kJ/mol) phases. The ΔS^o data range from 146.200 ($Am^{III}Cl_3$) to 167.2 ($Cf^{III}Cl_3$) J/molK.

Both entropy and heat capacity, C_p, follow an inverse trend, decreasing across the series for $\mathbf{An^{III}}Cl_3$ while increasing for $\mathbf{An^{IV}}Cl_4$ in both the solid and gas phases. When viewing the $\mathbf{An^{IV}}Cl_4$ compounds, $Th^{IV}Cl_4$ displays the most negative ΔH_f^o and ΔG_f^o values and the least positive ΔS^o value. The gas phase data for $Pu^{IV}Cl_4$ is an outlier, with ΔH_f^o increasing slightly and ΔS^o being almost identical to that of $U^{IV}Cl_4$. This is in line with previously noted anomalous chemistry of $Pu^{IV}Cl_4$.[102] The data for the penta– and hexavalent compounds display values similar to their tetra– and trivalent analogs, except the trivalent gas phase compounds which all show ΔG_f^o values much closer to zero than any other form. In general, when comparing crystalline to gas phase data; the gas phase data displays a more positive ΔS^o and less negative ΔH_f^o and ΔG_f^o values. This is due to entropy playing a much larger role for gaseous species, while enthalpy dominates in the crystalline phase.

The C_p, data (in J/molK) show an approximate trend of increasing C_p with increasing formal oxidation state. The heat capacity trend is best displayed uranium, where the crystalline phase values are: $U^{III}Cl_3$ (102.5) < $U^{IV}Cl_4$ (121.8) < $U^{V}Cl_5$ (150.6) < $U^{VI}Cl_6$ (175.7), this trend is also observed in the gas phase data: $U^{III}Cl_3$ (82.4) < $U^{IV}Cl_4$ (103.5) < $U^{V}Cl_5$ (123.6) < $U^{VI}Cl_6$ (147.2), please see **Table 7**.

Similar to the standard thermodynamic data, the heats and entropies of phase change come from a wide variety of sources with sometimes wildly different values. The differences can be accounted for by differences in technique/equipment for the given data point. UCl_4 in particular has a very wide range of data, with sometimes decades between sources. The most well reported values are for enthalpy of fusion, ΔH_{fus}. The existing data shows that ΔH_{fus} for $\mathbf{An}^{III}Cl_3$ increases when going from U–Pu but becomes less exothermic for Am and Cm. In the $\mathbf{An}^{IV}Cl_4$ data Th–Np display increasing enthalpies of vaporization and decreasing enthalpy of sublimation as the series is traversed. There is just one entry for a formally divalent compound, $Am^{II}Cl_2$, with ΔH_{fus} values of 17.2 and 15.8 kJ/mol for the α– and β–phases, respectively. The $Am^{II}Cl_2$ data are significantly lower than any other compound except UCl_6 (20.9 kJ/mol) which supports the instability of $Am^{II}Cl_2$.

Uranium gives the best view of oxidation state effects on phase transition energies, although there are several data points for $U^{III}Cl_3$ and $U^{IV}Cl_4$. In viewing data from a single source for ΔH_{fus} and ΔS_{fus} values, $U^{III}Cl_3$ is typically less than $U^{IV}Cl_4$, but the sheer number of different values for $U^{IV}Cl_4$ make it difficult to parse. $U^{V}Cl_5$ has values greater than $U^{VI}Cl_6$, but less than those of $U^{IV}Cl_4$.[34] Any real trends regarding the entire series are rather tenuous due to the inconsistency in the data.

Table 8. Enthalpic (ΔH, kJ/mol) and entropic (ΔS, J/molK) heats of fusion (fus), vaporization (vap) and sublimation (sub) for the actinide (**An**) metal chlorides.

Cmpd	ΔH_{fus}	ΔS_{fus}	ΔH_{vap}	ΔS_{vap}	ΔH_{sub}	ΔS_{sub}	Ref
			Trivalent Actinides				
UCl_3	49	43.7	225.9	205.0	263.6	238.5	55, 130
UCl_3	48.6	43.7	175.9	95.0	224.5[a]	138.7[a]	34
$NpCl_3$	50						130
$PuCl_3$	63.6	61.5	241.0	241.8	304.6	263.6	30, 34, 55
$PuCl_3$	49, 55						89, 130

$AmCl_3$	48.1 ±0.4						89
$CmCl_3$	47.9 ±0.4						89
Tetravalent Actinides							
$ThCl_4$	43.9		146.4		190.4[a]		30
$ThCl_4$	94.2[a]	80.7[a]	152.7	151.9	246.9	232.6	55
$ThCl_4$			146.4	122.6			55
$ThCl_4$	61.5	59.0	120.8	98.7	182.3[a]	157.7[a]	34, 89
$ThCl_4$	94.14	90.8	152.7	127.6	246.9	218.4[a]	56
UCl_4	44.8, 49.8						30
UCl_4	49.8	49.8†	150.6	174.5	193.7	224.3	55, 89
UCl_4	54.4	63.0	126.8	118.7	181.2†	181.7[a]	34
UCl_4	61.5		138.1		199.6		56
$NpCl_4$	59.6	82.1[a]	123.5±0.8	176.1 ±7.1	189.5 ±1.7	258.2 ±2.1	89, 131
$NpCl_4$	55.5[a]		115.2±3.3		170.7 ±3.4		79
Pentavalent Actinides							
$PaCl_5$	31.5	54.7[a]	61.29	88.3	92.76	143	89, 101
UCl_5	35.6	59.3		192.9		252.2[a]	34, 89
Hexavalent Actinides							
UCl_6	20.9	46.4					34, 89

[a] Calculated value using **eq 10**

5. Contaminant Chlorides

As MSR reactor design matures, it is appropriate to plan for the resulting fission products (**FPs**) and corrosion products (**CorPs**), which can be grouped together as contaminant products (**ConPs**). The exact composition of spent nuclear fuel is difficult to precisely predict,[132] and heavily reliant on several factors including but not limited to: reactor run time, neutron spectrum intensity and fuel identity. Regardless of these factors, many lanthanides (**Ln**) and elements from row five of the periodic table (Rb–Xe) are predicted as **FP**s. Here focus will be paid to elements from the main group/*p*-block (**MG**), transition metal series (**TM**), and the rare earths (**RE**), the group I (Rb), group II (Sr) data are presented in **section 3**. **CorP**s are leeched from the containment casing and largely consist of **TM**s and aluminum. All compounds are presumed to be present as chlorides. These comprise the largest number of compounds within this review, therefore the data has been limited to the most stable/commonly available binary chloride compounds.

5.1. Thermophysical Properties of Fission Product Chlorides

Of the fission products, melting point (T_M) is the most well characterized thermophysical property, followed by boiling point, (T_B) data. Although all compounds have sublimation (T_{sub}) and triple point (T_{TP}) values, they are not well reported for the compounds of interest. The only documented sublimation points are $Zr^{IV}Cl_4$ (T_{sub} = 331 °C[30]) and $Mo^{IV}Cl_4$ (T_{sub} = 281 °C[34]), while the triple point is only documented for $I^{III}Cl_3$ (T_{TP} = 101°C, 16 atm[30]) and $Zr^{IV}Cl_4$ (T_{TP} = 437 °C[30]). Starting from the **MG** data, five of the ten binary chlorides are liquids at ambient temperature (T_M = ~22 °C, 295 K), SCl_2 (-122 °C), S_2Cl_2 (-77 °C), $Sn^{IV}Cl_4$ (-34 °C), $Sb^{V}Cl_5$ (4 °C), and $I^{I}Cl$ (27.4 °C), see **Table 9**. The remaining **MG** compounds all have moderate to low melting points, being $I^{III}Cl_3$ (63 °C), $Sb^{III}Cl_3$ (73.4 °C), $Te^{II}Cl_2$ (208 °C), $Te^{IV}Cl_4$ (224 °C), and $Sn^{II}Cl_2$ (247 °C), with the latter being the highest of the selected **MG** elements. The boiling points (T_B) vary widely with three compounds reportedly decomposing upon boiling $I^{III}Cl_3$ (97 °C), $I^{I}Cl$ (97 °C), and $Sb^{V}Cl_5$ (140 °C). The former two compounds have the lowest T_B of the selected **MG** elements, with $Sn^{II}Cl_2$ (623 °C) being the highest. Of the **MG** elements selected and ignoring any possible speciation from interacting with the molten chloride solvent, only $Sn^{II}Cl_2$ may be in a condensed phase under reactor operating temperatures. The tin chlorides are also of note due to the drastic difference in boiling and melting point, $SnCl_2$ (T_M = 247 °C) vs. $SnCl_4$ (T_M = -34 °C), and $SnCl_2$ (T_B = 623 °C) vs. $SnCl_4$ (T_B = 114.15 °C), demonstrating the importance of oxidation state. It has been noted that basic salt melts such as fluoride melts stabilize high oxidation states while acidic melts such as chlorides stabilize low oxidation states.[133, 134] The relatively acidic nature of chloride melts would likely cause the **MG FP**s to exist in their lower oxidation states.

Table 9. Thermophysical properties of relevant binary fission product chlorides

Compound	T_M (°C)	T_B (°C)	Ref
	Main Group		
SCl_2	–122	59.6	[30]
S_2Cl_2	–77	137	[30]

$SnCl_2$	247.0	623	30
$SnCl_4$	–34.07	114.15	30
$SbCl_3$	73.4	220.3	30
$SbCl_5$	4	140 (dec)	30
$TeCl_2$	208	328	30
$TeCl_4$	224	387	30
ICl	27.38	97.0 (dec)	30
ICl_3	63	97 (dec)	30
Transition Metals			
$ZrCl_2$	722	1291	30, 34
$ZrCl_3$	627		30
$ZrCl_4$	437[a]		30, 34
$MoCl_2$	500 (dec)		30
$MoCl_3$	400 (dec)		30, 56
$MoCl_4$	317	322	30, 34, 56
$MoCl_5$	194	268	30
$TcCl_4$		300	31
$TcCl_5$		232	82
$RuCl_3$	~500 (dec)		30, 82
$RhCl_3$	~450	717	30
$PdCl_2$	679		30
AgCl	455	1547	30
$CdCl_2$	568	964	30
Rare Earths			
$ScCl_3$	967	1086	30, 34
YCl_3	721	1482	30
$LaCl_3$	858	1750	30, 56
$CeCl_3$	807	1730	30, 82
$PrCl_3$	786	1700	30, 31
$NdCl_3$	759	1600	30
$PmCl_3$	655	1670	30, 56
$SmCl_2$	858	1960	34
$SmCl_3$	682		30
$EuCl_2$	731		30

$EuCl_3$	623	(dec)	[30, 31]
$GdCl_3$	602	1580	[30, 31]
$TbCl_3$	582	1596	[30, 34]
$DyCl_3$	718	1530	[30]
$HoCl_3$	720	1500	[30]
$ErCl_3$	776	1477	[30, 34]
$TmCl_3$	845	1527	[30, 34]
$YbCl_2$	721	~1927	[30, 34]
$YbCl_3$	854	>1300 (dec)	[30, 34]
$LuCl_3$	925	~1477	[30, 34]

[a]Under increased pressure, 17.9 bar; dec = decomposes

Of the period five **TM** elements from Zr–Cd, only Nb is not considered a major fission product, but will be included for completeness. In general, the T_M of the **TM**s is higher than the **MG** compounds, presumably due to the highly covalent character of the **MG**–Cl bond. Similar to the actinides, compounds with higher formal oxidation states have lower T_M and T_B values, while compounds with lower formal oxidation states have higher T_M/T_B values. Presumably the oxidation state dependence is due to increased coordination number and the presence of extended structures.[135] The lowest T_M being Mo^VCl_5 (194 °C), and the highest being $Zr^{II}Cl_2$ (722 °C). While the lowest T_B is reported for Tc^VCl_5 (232 °C) and the highest for Ag^ICl (1547 °C), the latter being significantly higher than other reported **TM**–Cl_x, see **Table 9**. When viewing **TM**–Cl_x from a reactor operation standpoint the compounds can be divided into volatile and non-volatile products. The formally mono– and divalent chlorides would remain within the melt while the higher order chlorides *e.g.*, M^{IV} would all volatilize.

Control of oxidation states is more important for the transition metals than any other component of the mixture beyond the actinides, as they have the widest range of available oxidation states. It has been reported that within a LiCl–KCl eutectic, zirconium primarily exists as Zr^{IV}, with small amounts of Zr^{II} that increases with temperature.[136] Considering the trend noted earlier, Mo, Tc, Ru, and Rh will most likely exist in their lower stable oxidation states within the melt (**TM**$^{III/IV}$) due to the acidity of the solution. *In-situ* spectroscopic investigations of $Tc^{IV}O_2$ chlorination within LiCl–KCl, NaCl–KCl, and NaCl–CsCl melts demonstrated that regardless of eutectic composition, $\mathbf{A}_2Tc^{IV}Cl_6$ (**A** = Li, Na, K, Cs) was formed almost exclusively.[137] Determining Tc speciation within the melt is of crucial importance for long-term waste storage, as the oxidized pertechnetate ion, $(Tc^{VII}O_4)^{1-}$ is known to be a highly radiotoxic and a mobile environmental hazard.[138-140] The remainder of the **TM FPs**, Pd, Ag, and Cd primarily exist as mono– or divalent ions, relegating them to remain dissolved within the melt.

Moving to the rare earth (**RE**) elements, Sc, Y, and the lanthanides (**Ln**) La–Lu. Despite Sc and Y formally being **TMs**, their (geo)chemical/physical behavior is similar to that of the lanthanides and will be grouped and discussed together as the rare earth elements. all of the **RE**s have highly stabile trivalent oxidation states. Although, formally divalent compounds can be prepared for Sm, Eu, and Yb[72, 141] only Eu^{II} and possibly Yb^{II} are reasonable under molten salt conditions.[142] Coupled to the chemical similarity of the **RE**s means that the **RE**-chlorides have the most consistent properties of the **FPs** examined. In terms of the thermophysical properties of the **RE**s, their highly ionic nature means their T_M and T_B values are significantly higher than the **MG**, **TM**, and **An** compounds and are most similar to the **A** and **Ae** elements, see **Tables 9**, **5**, and **1**, respectively. The highest reported T_M is $Sc^{III}Cl_3$ (967 °C), while the lowest is $Tb^{III}Cl_3$ (582 °C). There is a regular decrease in T_M from La^{III} (858 °C) to Tb^{III}, where the T_M increases to the end of the series at Lu^{III} (925 °C), please see **Table 9**. Where many of the **RE** from La^{III}–Gd^{III} are characterized in the nine-coordinate $U^{III}Cl_3$ structure type,[76] Tb^{III} is characterized in the eight-coordinate $Pu^{III}Br_3$ structure type,[143] while Dy^{III}–Lu^{III} are characterized in the distorted octahedral $Al^{III}Cl_3$ structure type.[144] The structural changes are due to the decreasing ionic radius of the elements, and has also been claimed for high temperature behavior of $Cf^{III}Cl_3$ and $Es^{III}Cl_3$[75] It is worth noting that $Eu^{II}Cl_2$ (731 °C) melts at a higher temperature than $Eu^{III}Cl_3$ (623 °C), but $Yb^{II}Cl_2$ (721 °C) melts a temperature lower than $Yb^{III}Cl_3$ (854 °C). The T_B data is much less complete with nine values for the 17 elements. The available T_B data ranges from T_B = 1482 °C (Y^{III}) to 1450 °C (La^{III}). In reactor conditions, all of the REs would exist within the solution and are unlikely to volatilize out. This problem of solidified rare-earth fission products is easily remedied by the eutectic nature of the solvent salt, which lowers the melting point of the overall mixture.

5.2. Volatility of Fission Product Chlorides

The low melting point of many **MG**Cl_x makes it difficult to access the vapor pressure for the solid phase of these compounds, with only data on the high valent $Te^{IV}Cl_4$ and the lower valent $Sn^{II}Cl_2$, $Sb^{III}Cl_3$, and $Te^{II}Cl_2$ compounds available. However, there is good **MG**Cl_x data on the liquid and gas phase of the. The vapor pressure data indicates that even at room temperature several species such as SCl_2, S_2Cl_2, and $Sb^{V}Cl_5$ display appreciable vapor pressure. This high volatility is apparent by the low values for the A, B, and C coefficients of **eq. 3**. This is in line with the other thermophysical data for these compounds, which shows they will readily vaporize under reactor operating conditions, see **Table 10**.

Table 10. Vapor pressure coefficients of fission product chlorides in different physical states where coefficients A–C come from **Eqs. 3-6**.

Compound	A	B	C	T range (K)	Ref
Main Group – Solid Phase					
$SnCl_2$[a]	7335	19.781	3.67	400-520	34

$SbCl_3$[a]	4161	20.495	4.26	298-346	34
$SbCl_3$[b]	3460	2.81	-3.88	298-346	28
$TeCl_2$[a]	4539	17.421	3.40	298-448	34
$TeCl_4$[a]	6846	25.915	5.35	400-497	34
Main Group – Liquid Phase					
SCl_2[a]	2306	18.846	4.72	298-332	34
S_2Cl_2[a]	2917	22.530	5.90	298-410	34
$SnCl_2$[a]	6925	23.120	5.19	520-885	34
$SnCl_4$[a]	3262	32.036	9.10	298-382	34
$SnCl_4$	1925	7.865		298-387	28
$SbCl_3$[a]	3644	21.741	5.34	346-496	34
$SbCl_3$	3770	29.48	7.04	346-493	28
$SbCl_5$[a]	2779	19.861	5.02	298-413	34
$SbCl_5$	2530	8.56		277-350	28
$TeCl_2$[a]	4163	19.472	4.49	448-593	34
$TeCl_2$	3350	8.51		481-601	28
$TeCl_4$[a]	8211	58.025	16.24	497-687	34
Main Group – Gas Phase[c]					
SCl_2 (G_1)[a]	783	-5.841	-1.61	332-717	34
SCl_2 (G_2)[a]	2831	2.003	0.04	717-2000	34
S_2Cl_2 (G_1)[a]	587	-11.537	-3.37	410-717	34
S_2Cl_2 (G_2)[a]	3868	4.714	0.50	717-2000	34
$SnCl_2$[a]	1967	8.386	1.24	885-2000	34
$SnCl_4$[a]	7251	6.435	0.73	600-2000	34
$SbCl_5$ (G_1)[a]	1017	-10.387	-4.34	413-496	34
$SbCl_5$ (G_2)[a]	2349	5.929	0.58	496-1000	34
$TeCl_2$[a]	6562	0.899	-0.21	700-2000	34
$TeCl_4$[a]	2452	3.434	0.05	687-2000	34
Transition Metals – Solid Phase					
$ZrCl_2$[a]	12,761	17.490	2.66	700-1000	34
$ZrCl_2$	8500	16.61	1.50	298-995	28
$ZrCl_3$[a]	6979	23.644	4.86	400-714	34
$ZrCl_4$[a]	6134	17.869	2.80	400-609	34
$MoCl_2$[a]	10,792	31.381	7.30	600-1219	34

$MoCl_3$[a]	12,630	55.648	14.16	500-926	34
$MoCl_4$[a]	6279	20.785	3.73	400-603	34
$MoCl_5$[a]	4978	22.315	4.79	298-470	34
$MoCl_5$	5210	13.1		298-467	28
$RuCl_3$[a]	8870	15.800	2.59	500-1123	34
$RuCl_3$	16,750	30.53	4.63	298-1000	28
$RhCl_3$[a]	10,151	18.377	3.26	500-1221	34
$PdCl_2$[a]	9418	15.215	2.37	600-952	34
AgCl[d]	11,830	12.39	0.30	298-455	28
$CdCl_2$[a]	10,179	17.689	2.79	600-842	34
$CdCl_2$	9270	17.46	2.11	298-842	28

Transition Metals – Liquid Phase

$ZrCl_2$[a]	10,851	17.831	3.41	1000-1564	34
$ZrCl_2$	8440	26.37	5.03	995-1564	28
$PdCl_2$[a]	8765	16.819	3.14	952-1232	34
AgCl[a]	10,750	13.332	2.29	730-1835	34
AgCl	11,320	17.34	2.55	455-1547	28
$CdCl_2$[a]	9335	25.579	5.83	842-1236	34
$CdCl_2$	9183	25.907	5.04	842-1236	28

Transition Metals – Gas Phase[c]

$ZrCl_2$[a]	12,637	7.429	0.93	1564-2000	34
$ZrCl_3$ (G_1)[a]	10,369	18.859	2.96	600-714	34
$ZrCl_3$ (G_3)[a]	6681	2.898	0.10	1564-2000	34
$ZrCl_4$[a]	17,718	3.328	-0.37	1400-2000	34
$MoCl_2$ (G_1)[a]	20,008	21.784	3.93	1100-1219	34
$MoCl_2$ (G_2)[a]	16,089	14.465	2.60	1219-2000	34
$MoCl_3$ (G_1)[a]	16,243	38.973	9.23	800-926	34
$MoCl_3$ (G_3)[a]	7357	3.979	0.51	1219-2000	34
$MoCl_4$ (G_1)[a]	4237	30.870	8.20	603-926	34
$MoCl_4$ (G_2)[a]	11,183	2.538	–0.51	1219-2000	34
$MoCl_4$ (G_3)[a]	7280	3.636	0.42	1219-2000	34
$RuCl_3$ (G_1)[a]	16,502	32.048	6.15	800-1123	34
$PdCl_2$ (G_1)[a]	15,653	18.146	2.50	800-952	34
$PdCl_2$ (G_2)[a]	15,024	19.898	3.31	952-1232	34

$PdCl_2$ (G_3)[a]	6303	3.579	0.32	1232-1825	34
Rare Earths – Solid Phase[c]					
$ScCl_3$[a]	13,490	20.350	3.24	700-1240	34
$ScCl_3$	14,200	14.37		1065-1233	28
YCl_3[a]	16,208	19.289	2.77	900-994	34
$LaCl_3$[a]	18,843	27.350	5.04	900-1131	34
$LaCl_3$	19,040	36.20	7.05	298-1131	28
$CeCl_3$[a]	18,142	25.358	4.54	900-1080	34
$CeCl_3$	18,750	36.38	7.05	298-1080	28
$PrCl_3$[a]	18,151	28.097	5.39	900-1059	34
$PrCl_3$	18,490	36.31	7.05	298-1059	28
$NdCl_3$[a]	17,856	26.563	4.90	900-1032	34
$NdCl_3$	18,220	36.27	7.05	298-1032	28
$SmCl_2$[a]	17,205	22.728	4.34	1000-1013	34
$SmCl_3$[a]	5362	13.153	2.98	400-950	34
$EuCl_3$[a]	15,213	23.117	3.85	800-897	34
$GdCl_3$[a]	16,949	22.850	3.77	875	34
$TbCl_3$ (B)[a]	16,247	25.385	4.78	800-855	34
$DyCl_3$[a]	17,297	21.583	3.22	900-924	34
$HoCl_3$[a]	15,695	19.188	2.79	800-993	34
$ErCl_3$[a]	15,816	21.658	3.57	800-1049	34
$TmCl_3$[a]	15,992	19.386	2.90	900-1101	34
$YbCl_3$[a]	17,268	19.980	2.58	900-1148	34
Rare Earths – Liquid Phase					
$ScCl_3$[a]	12,104	31.467	7.20	1240-1359	34
YCl_3[a]	17,157	38.319	8.80	994-1757	34
$LaCl_3$[a]	17,750	38.476	9.00	1131-2045	34
$CeCl_3$[a]	17,705	37.481	8.67	1080-1997	34
$PrCl_3$[a]	15,442	25.266	5.30	1059-1982	34
$NdCl_3$[a]	16,105	30.893	6.90	1032-1976	34
$SmCl_2$[a]	16,807	24.709	5.13	1013-2000	34
$EuCl_3$[a]	13,395	27.498	6.02	897-1300	34
$GdCl_3$[a]	15,971	30.648	6.80	875-1919	34
$TbCl_3$[a]	15,664	30.596	6.79	855-1869	34

$DyCl_3$[a]	16,585	32.586	7.19	924-1810	34
$HoCl_3$[a]	15,270	31.917	7.18	993-1780	34
$ErCl_3$[a]	15,605	34.537	7.90	1049-1750	34
$TmCl_3$[a]	16,009	34.611	7.90	1101-1800	34
$YbCl_3$[a]	14,971	24.283	4.64	1148-1300	34

[a] Converted from bar to mmHg using **eq. 5** [b] D term = -5.6 [c] "G_n" and "B" designations as given in the primary literature [d] D term = -1.02

The vapor pressures of the **TM**Cl_x are more subdued relative to the **MG**Cl_x, indicating that most species will only volatilize at higher temperatures. While there is good data on the solid and gas phase **TM**Cl_x, there is less data for the liquid phase. In line with the higher T_M and T_B most vapor pressure data on **RE** chlorides are focused on the solid phase with limited liquid phase data and no gas phase data available. Only $Sc^{III}Cl_3$ demonstrated an appreciable vapor pressure, but the minimum temperature (1240 K) was far above operational temperatures (973K).

5.3. Thermochemical Properties of Fission Product Chlorides

For the fission product (**FP**) chlorides, there are several compounds with conflicting data values. While some of these reports are similar in value, there are instances of significant difference. For example, liquid tin(IV) chloride, $Sn^{IV}Cl_4$, where ΔH_f^o, ΔS^o, and ΔG_f^o are given as -511.3, 258.7, -588.4, respectively in one source[34], and -511.29, 258.74, and -440.12, respectively in another[145]. The two references give nearly identical heat capacities (C_p) of 165.3[34] and 165.27[145] (J/molK), **Table 11**. The differences could be due to simple copy/computation error or could indicate a issues with the source.

The trends in the data are best analyzed by grouping the fission products according to their location on the periodic table. Across all reported values ΔH_f^o and ΔS^o the values follow a trend towards lower enthalpy and higher entropy when moving from the solid phase to the gas phase. The ΔH_f^o values are smallest in magnitude for the gas phase and largest in magnitude for the solid phase. Some outliers and exceptions include: gas phase $Mo^{II}Cl_2$ features a positive DH_f^o (+83.1 kJ/mol), and a barely negative DG_f^o (-4.5 kJ/mol) [34], while gas phase $I^{I}Cl$, $Pd^{II}Cl_2$ and $Ag^{I}Cl$ are given with positive DH_f^o and DG_f^o values [34], **Table 11**. The data on gas phase $Ru^{III}Cl_3$ also illustrate literature differences where DH_f^o and DG_f^o are reported as +56.1 and -62.5 kJ/mol, respectively,[34] and +79.1 and +89.4 kJ/mol respectively.[146] The DS° values of $Ru^{III}Cl_3$ are comparable to one another at +397.6 [34] and +328.4 J/molK.[146] All of the **RE**Cl_3 are reported with strongly negative ΔH_f^o values regardless of phase. Across all trivalent **RE** chlorides, the ΔH_f^o and ΔS^o values were nearly identical, with only $Lu^{III}Cl_3$ having a noticeably higher crystalline phase ΔS^o (352.4 J/molK) than any of the other **RE**Cl_3 (121.3 to 159.0 J/molK). Crystalline

$Yb^{II}Cl_2$ is the only formally divalent **RE** with any documented thermodynamic values, having ΔH_f^o closer to the gas-phase trichlorides than to any crystalline trichloride, see **Table 11**. All three element groups of **FP** chlorides demonstrate that the heat capacity, C_p, is generally higher for compounds with higher formal oxidation states, regardless of physical state.

Table 11. Enthalpy of formation (ΔH_f^o, kJ/mol), standard entropy (ΔS^o, J/molK), free energy of formation (ΔG_f^o, kJ/mol), and heat capacity (C_p, J/molK) thermodynamic data for main group (**MG**), transition metal (**TM**), and rare earth (**RE**) element fission product chlorides.

Compound	ΔH_f^o	ΔS^o	ΔG_f^o	C_p	Ref
Main Group – Crystalline Phase					
$SnCl_2$	–325.1	134.1	–365.1[a]		30
$SnCl_2$	–328.0	134.1	–368.0	78.0	34
$SnCl_2$	–328.026	78.047	–286.222	78.047	145
$SbCl_3$	–382.2	184.1	–323.7	107.9	30
$SbCl_3$	–382.2	184.1	–437.1	107.5	34
$TeCl_2$	–190.2	161.4	–238.3	83.7	34
$TeCl_4$	–326.4			138.5	30
$TeCl_4$	–323.8	203.0	–384.4	138.5	34
$TeCl_4$	–323.8	200.8	–235.9	138.5	147
ICl	–35.4	97.9	–14.049	55.229	148
ICl_3	–89.5	167.4	–22.3		149
Main Group – Liquid Phase					
SCl_2	–50.0	183.7	–104.8	91.0	30, 34
S_2Cl_2	–57.9	224.4	–124.8	124.3	34
S_2Cl_2	–58.2	223.8	–39.26	124.29	150, 151
$SnCl_4$	–511.3	258.7	–588.4	165.3	34
$SnCl_4$	–511.29	258.74	–440.12	165.27	145
$SbCl_5$	–440.2	301.2	–350.2	159.0	34, 152
ICl	–23.9	135.2	–14.0	102.8	148
Main Group – Gas Phase					
SCl_2	–17.6	281.3	–101.4	50.9	34
S_2Cl_2	–16.7	327.2	–114.3	73.0	34
$SeCl_2$	–33.5	295.7	–121.6	53.7	34
$SeCl_2$	–33.5	295.7	–42.5	53.5	150

$SnCl_2$	–197.9	305.9	–289.1	54.6	[34]
$SnCl_2$	–197.945	305.855	–207.350	54.632	[145]
$SnCl_4$	–471.5	365.0	–580.3	98.4	[34]
$SnCl_4$	–471.54	364.95	–432.04	98.45	[145]
$SbCl_3$	–313.1	339.1	–412.2	76.8	[34]
$SbCl_3$	–313.8	337.7	–301.2	76.7	[152]
$SbCl_5$	–399.4	401.8	–519.2	112.6	[34]
$SbCl_5$	–388.82	401.77	–328.73	120.92	[150]
$TeCl_2$	–113.0	305.7	–122.822	54.346	[147]
ICl	+17.1	247.6	–5.7	35.5	[148]

Transition Metals – Crystalline Phase

$ZrCl_2$	–502.0				[30]
$ZrCl_2$	–431.0	110.0	–463.8	72.6	[34, 148]
$ZrCl_2$	–431.0	110.0	–385.7	72.6	[148]
$ZrCl_3$	–711.9	145.9	–755.4	96.2	[34]
$ZrCl_3$	–714.2	145.8	–646.3	96.2	[148]
$ZrCl_4$	–980.5	181.6	–889.9	119.8	[30]
$ZrCl_4$	–980.5	181.6	–1034.7	119.9	[34]
$MoCl_2$	–279.7	116.3	–314.4	74.6	[34]
$MoCl_3$	–428.1	124.7	–465.3	94.8	[34]
$MoCl_4$	–494.7	182.9	–549.2	124.4	[34]
$MoCl_4$	–477.0	223.8	–402.2	129.7	[148]
$MoCl_5$	–527.1	238.5	–598.2	155.5	[34]
$MoCl_5$	–527.2	238.5	–423.5	155.6	[148]
$MoCl_6$	–523.0	255.2	–391.0	175.3	[148]
$RuCl_3$	–205.0				[30]
$RuCl_3$	–246.7	121.9	–283.1	115.1	[34]
$RuCl_3$	–230.1	127.1	–159.7	92.2	[146]
$RhCl_3$	–299.2	126.8	–227.8	92.2	[30, 146]
$RhCl_3$	–274.6	122.1	–311.1	92.2	[34]
$PdCl_2$	–173.2	104.5	–204.3	75.3	[34]
$PdCl_2$	–198.7	104.2	–152.0	75.3	[153]
AgCl	–127.0	96.3	–109.8	50.8	[30]
AgCl	–127.1	96.2	–155.8	53.0	[34]

$CdCl_2$	–391.5	115.3	–343.9	74.7	[30]
$CdCl_2$	–391.5	115.3	–425.9	74.6	[34]

Transition Metals – Liquid Phase

$ZrCl_2$	–411.6	122.5	–370.0	91.0	[148]
$MoCl_4$	–462.8	245.5	–394.5	146.4	[148]
$MoCl_5$	–510.1	273.8	–416.9	175.7	[148]

Transition Metals – Gas Phase

$ZrCl_2$	–195.1	292.6	–282.3	57.7	[34]
$ZrCl_2$	–186.2	292.6	–195.3	57.7	[148]
$ZrCl_3$	–522.0	339.3	–623.2	76.0	[34]
$ZrCl_3$	–524.3	339.3	–514.1	76.0	[148]
$ZrCl_4$	–870.0	367.7	–979.7	98.2	[34]
$ZrCl_4$	–870.0	367.7	–835.0	98.2	[148]
$MoCl_2$	+83.1	294.0	–4.5	67.4	[34]
$MoCl_3$	–149.6	332.5	–248.8	76.1	[34]
$MoCl_4$	–384.1	371.8	–494.9	98.1	[34]
$MoCl_4$	–384.9	371.9	–354.3	98.1	[148]
$MoCl_5$	–447.3	398.2	–566.0	121.2	[34]
$MoCl_5$	–447.7	397.8	–391.5	119.5	[148]
$MoCl_6$	–461.4	419.8	–586.6	142.7	[34]
$MoCl_6$	–439.3	419.7	–356.4	144.1	[148]
$RuCl_3$	+56.1	397.6	–62.5	55.8	[34]
$RuCl_3$	+79.1	328.4	+89.4	55.2	[146]
$RuCl_4$	–79.9	374.2	–49.9	63.4	[146]
$PdCl_2$	+117.6	307.0	+26.1	60.6	[34]
AgCl	+89.0	246.1	+15.6	35.8	[34]
$CdCl_2$	–205.2	294.7	–293.0	58.1	[34]

Rare Earths – Crystalline Phase

$ScCl_3$	–925.1	127.2	–852.9	91.6	[30, 150]
$ScCl_3$	–918.8	121.3	–955.0	92.1	[34]
YCl_3	–1000.0				[30]
YCl_3	–1000.0	140.2	–1014.8	92.0	[34]
YCl_3	–973.6	137.7	–1014.7	92.0	[154]
$LaCl_3$	–1072.2			108.8	[30]

$LaCl_3$	–1070.7	137.7	–1111.7	98.1	34
$CeCl_3$	–1060.5	151.0	–984.8	87.4	30
$CeCl_3$	–1053.5	150.6	–1098.4	87.8	34
$PrCl_3$	–1056.9			100.0	30
$PrCl_3$	–1056.9	153.3	–1102.6	98.9	34
$PrCl_3$	–1056.9	153.3	–980.8	98.97	30, 153
$NdCl_3$	–1041.0			113.0	30
$NdCl_3$	–1041.8	153.5	–1087.6	99.2	34
$NdCl_3$	–1041.0	143.9	–1083.9	96.2	154
$NdCl_3$	–1041.8	153.4	-966.6	99.1	155
$SmCl_3$	–1025.9	150.1	–950.2	99.5	30, 145
$SmCl_3$	–1025.9	147.7	–1070.0	99.5	34
$EuCl_3$	–936.0				30
$EuCl_3$	–936.0	144.1	–978.9	107.0	34
$EuCl_3$	–922.2	125.5	–959.6	98.3	154
$GdCl_3$	–1008.0			88.0	30
$GdCl_3$	–1008.0	151.5	–1053.5	97.8	34
$GdCl_3$	–1008.0	151.4	–993.1	88.0	156
$TbCl_3$	–997.0	153.1	–921.1	97.5	30, 147
$TbCl_3$	–997.0	153.1	–1042.7	97.5	34
$DyCl_3$	–1000.0				30
$DyCl_3$	–998.3	150.8	–1043.3	97.1	34
$DyCl_3$	–989.9	154.0	–913.7	97.1	157
$HoCl_3$	–1105.4			88.0	30
$HoCl_3$	–1005.4	154.0	–1051.3	96.2	34
$HoCl_3$	–1005.4	154.0	–929.2	96.2	158
$ErCl_3$	–998.7			100.0	30
$ErCl_3$	–994.5	154.8	–1040.7	98.1	34
$ErCl_3$	–994.5	152.7	–918.5	98.1	157
$TmCl_3$	–986.6	146.9	–908.5	97.7	30, 159
$TmCl_3$	–988.1	159.0	–1035.5	97.7	34
$YbCl_2$	–799.1	122.6	–835.7	74.2	34
$YbCl_2$	–799.6	130.5	–754.1	82.9	160
$YbCl_3$	–959.8	147.7	–886.2	95.3	30, 160

$YbCl_3$	–961.1	135.1	–1001.4	95.4	34
$LuCl_3$	–945.6				30
$LuCl_3$	–987.1 ±2.5	352.4	–1092.2[a]		161, 162
Rare Earths – Gas Phase					
YCl_3	–698.2	351.5	–802.9	77.8	34
$LaCl_3$	–730.3	364.5	–838.9	78.4	34
$CeCl_3$	–723.0	370.7	–833.5	78.4	34
$PrCl_3$	–731.0	374.0	–842.5	78.4	34
$NdCl_3$	–719.1	374.4	–830.7	78.3	34
$NdCl_3$	–718.8	374.4	–709.5	78.3	155
$EuCl_3$	–658.1	363.7	–766.6	88.0	34
$GdCl_3$	–696.6	371.5	–807.4	78.2	34
$TbCl_3$	–691.2	375.3	–803.1	78.2	34
$TbCl_3$	–691.2	375.3	–681.5	78.2	147
$DyCl_3$	–677.4	379.9	–790.1	78.2	34
$DyCl_3$	–677.4	376.5	–667.5	78.1	157
$HoCl_3$	–712.9	363.6	–821.3	78.2	34
$HoCl_3$	–682.4	377.4	–672.8	78.2	158
$ErCl_3$	–703.9	363.6	–812.3	78.1	34
$ErCl_3$	–674.0	376.2	–664.6	78.1	157
$TmCl_3$	–691.1	364.6	–799.8	78.1	34
$TmCl_3$	–665.7	374.1	–655.4	78.1	159
$YbCl_3$	–638.9	370.0	–749.2	78.1	34
$YbCl_3$	–638.9	370.0	–631.6	78.1	160
$LuCl_3$	–626.3	352.5	–731.4	78.1	34

[a] Calculated values using **eq. 7** with T = 298 K

Turning to the heats of phase change there are significant gaps in the data similar to other elements; however, some trends can still be drawn. The **MG** ΔH_{fus} values are consistent across almost all compounds, only differing by 7.6 kJ/mol at most. As a sizeable portion of **MG** chlorides of interest are liquids at room temperature, ΔH_{vap} and ΔS_{vap} values provide the clearest trends. Higher valent compounds feature lower ΔH_{vap} values, implying ready evaporation, see **Table 12**. The majority of the sublimation was estimated using eq. **10** and may not accurately represent experimental values and has been noted in the table. The **TM**Cl_x data is the most sparse amount of data for the **FP** element group, see **Table 12.** Experimental ΔH_{sub} values for $Zr^{IV}Cl_4$ and $Mo^{IV}Cl_4$ suggest that they are the most volatile species within the **TM FP** group. All of the lower valence **TM** compounds of interest have much higher ΔH_{sub} values, indicating a higher energy requirement for volatilization. In molten salt reactors, this energy can be provided thermally, with the heat of the reactor driving the volatilization, but some compounds may not volatilize completely. The nearly universal trivalent state of **RE** chlorides aids in comparisons, but trends are limited. The light and heavy **$RECl_3$** have the highest ΔH_{fus} values of the **FP** elements, particularly Sc^{III}, La^{III}, and Yb^{III}. The single formally divalent **RE** species, $Sm^{II}Cl_2$, has a significantly lower ΔH_{fus} than any of the trivalent **RE**'s, resembling **MG**Cl_x and **TM**Cl_x species. This demonstrates again the importance of oxidation state control within the molten chloride melts during separations. The lower oxidation states promoted by the acidic nature of the chloride solvent salt inhibit the volatilization of fission products, and suggests that if **FP** volatilization is desired, the basicity of the mother liquor may need to be increased to better volatilize fission products.

Table 12. Enthalpic (ΔH, kJ/mol) and entropic (ΔS, J/molK) heats of fusion (fus), vaporization (vap) and sublimation (sub) for selected main group (**MG**), transition metal (**TM**), and rare earth (**RE**) element fission product chlorides.

Cmpd	ΔH_{fus}	ΔS_{fus}	ΔH_{vap}	ΔS_{vap}	ΔH_{sub}	ΔS_{sub}	Ref
			Main Group				
SCl_2			31.0	93.4			34
S_2Cl_2			35.8	87.3			34
$SnCl_2$	14.6	28.2	93.7	105.9	$108.3^{\dagger}$	134.1[a]	34
$SnCl_4$		38.2	33.5	87.7		125.9[a]	34
$SbCl_3$	13.0	37.5	47.8	96.3	$60.8^{\dagger}$	133.8[a]	34
$SbCl_5$			36.1	87.3			34
$TeCl_2$	11.3	25.2	57.6	97.1	$68.9^{\dagger}$	122.3[a]	34
$TeCl_4$	18.9	38.0	64.4	93.8	$83.3^{\dagger}$	131.8[a]	34
			Transition Metals				
$ZrCl_2$	42.7	42.7	163.6	104.6	$206.3^{\dagger}$	147.3[a]	34
$ZrCl_4$					103.1	169.2	34
$MoCl_4$					101.5	168.4	34
$MoCl_5$		40.2					34
$PdCl_2$	18.4	19.3					34
AgCl	13.2	18.1	171.7	93.6	$184.9^{\dagger}$	111.7[a]	34
$CdCl_2$	37.3	44.3	118.9	96.2	$156.2^{\dagger}$	140.5[a]	34
			Rare Earths				
$ScCl_3$	67.4	54.3	150.4	110.6	$217.8^{\dagger}$	164.9[a]	34

YCl_3	31.5	31.7	200.1	113.7	231.6†	231.8[a]	34
$LaCl_3$	58.0	51.3		91.2		142.5[a]	34
$CeCl_3$	45.2	41.8		97.8		139.6[a]	34
$PrCl_3$	50.6	47.8		105.1		152.9[a]	34
$NdCl_3$	50.2	48.7		98.7		147.4[a]	34
$SmCl_2$	14.2	14.0		101.3		115.3[a]	34
$SmCl_3$	46.0	48.4					34
$EuCl_3$	51.0	56.9					34
$GdCl_3$	40.7	46.5		102.9		149.4[a]	34
$TbCl_3$	25.0	29.3	194.9	104.3	219.9†	133.6[a]	34
$DyCl_3$	43.9	47.5	209.5	115.7	253.4†	163.2[a]	34
$HoCl_3$	44.3	44.6	186.2	104.6	230.5†	149.2[a]	34
$ErCl_3$	41.7	39.8	183.8	105.0	225.5†	144.8[a]	34
$TmCl_3$	45.3	41.2	188.3	104.6	233.6†	145.8[a]	34
$YbCl_3$	63.6	55.4					34

[a] Calculated value using **eq. 10**

5.4. Thermophysical Properties of Corrosion Product Chlorides

Although molten chlorides are less corrosive than molten fluorides, considerations must still be taken. Therefore, the corrosion products (**CorP**s) of structural materials must be considered. The leeching of elements from alloys such as Hastelloy-N, Inconel 625, and Haynes 230 are of particular interest for their use as high-temperature alloys with high resistance towards corrosion. Elements of note include: **MG** (Al), 1st row **TM** (Ti–Cu), 2nd row **TM** (Nb), and 3rd row **TM** (Ta, W). As the molten salts corrode the containment materials, it is presumed that the metals will be chlorinated.[163] Some corrosion products, namely molybdenum chlorides and select lanthanide chlorides are already present in **Table 9**.

The majority of the **CorP**s are transition metals like those in **Table 9**. Where a higher formal oxidation state correlates with decreases in both melting and boiling point, showing once again that the highest order chlorides are the most volatile. The T_M range from $V^{IV}Cl_4$ (-28 °C) and $Ti^{IV}Cl_4$ (-24.1 °C) being liquid at ambient temperature to several compounds melting above typical reactor temperatures, including: $Nb^{IV}Cl_4$ (800 °C, decomposes), $Cr^{II}Cl_2$ (824 °C), $Cr^{III}Cl_3$ (827 °C), $V^{II}Cl_2$ (1027 °C), $Ni^{II}Cl_2$ (1031 °C) and $Ti^{II}Cl_2$ (1035 °C). The T_B values are available for many of the corrosion products ranging from $Ti^{IV}Cl_4$ (136.4 °C) to $Ti^{II}Cl_2$ (1500 °C) with about half of the compounds boiling above the temperature of typical reactor operations, see **Table 13**. The sublimation temperature is the least well characterized thermophysical property, despite evidence that many of the compounds can be purified by sublimation, typically under reduced pressure.

Table 13. Thermophysical properties of relevant corrosion product metal chlorides

Compound	T_M (°C)	T_B (°C)	T_{sub} (°C)	Ref
		Main Group		
$AlCl_3$	192.6	181	180	30, 34
		Transition Metals		
$TiCl_2$	1035	1500		30
$TiCl_3$	425 (dec)	960		30
$TiCl_4$	-24.12	136.45		30
VCl_2	1350		910	30
VCl_3	500 (dec)			30
VCl_4	-28	151		30
$CrCl_2$	824	1120		30
$CrCl_3$	827	1300 (dec)		30
$MnCl_2$	650	1190		30
$FeCl_2$	677	1023		30
$FeCl_3$	307.6	~316		30
$CoCl_2$	737	1049		30
$NiCl_2$	1031		985	30
CuCl	423	1490		30
$CuCl_2$	598	993		30
$NbCl_4$	800 (dec)		275[a]	30
$NbCl_5$	205.8	247.41		30
$TaCl_3$	440 (dec)			30
$TaCl_4$	300 (dec)			30
$TaCl_5$	216.6	239		30
WCl_2	500 (dec)			30
WCl_3	550 (dec)			30
WCl_4	450 (dec)			30
WCl_5	253	286		30
WCl_6	282	337		30

[a] Under reduced pressure, ca. 10^{-4} mmHg; dec = decomposes

Investigations on the oxidation states of Ni and Cr in $Zn^{II}Cl_2$ and KCl–$MgCl_2$ melts showed that Ni^{II} and Cr^{III} are primarily present in melts, with a small amount of Cr^{II}. It was postulated that Cr^{II} was generated in early stages of corrosion, oxidizing to Cr^{III}.[163] Other studies on elements spanning the transition metal series found that the oxidation state of the **CorP**s was highly dependent on the anion used. Where higher oxidation states were only observed in mixed chloride/fluoride and oxyfluoride eutectics, while lower oxidation states were observed in molten chloride mixtures.[133] Overall, the oxidation states in chloride melts trend toward the lowest stable oxidation state for each metal, *e.g.*, $\mathbf{An}^{III}$. Of the metals the authors investigated, the heavier group five metals Nb and Ta displayed oxidation states at or above tetravalent within the chloride melt. The characterization of +4 and +5 compounds was attributed to the high stability of the pentavalent state for those metals. The behavior of tungsten within molten salt systems has been studied by several different groups, not just for corrosion but also to better understand molten salt extractions. A series of studies tested a variety of tungsten sources within a variety of eutectics, ranging from pure **A**Cl mixtures to chloride/fluoride **AX** (X = F, Cl) eutectics.[164-168] The authors found that W^{IV} was maintained within the chloride melts.[164-168] Studies on iron found that $Fe^{III}Cl_3$ was only partially stable within a KCl/LiCl/NaCl melt, noting significant amounts of Fe^{II} species within the mixture.[169] Titanium appears to be more sensitive to melt composition than most of the other metals. Where in the presence of titanium metal, the primary species were $Ti^{II/III}$ and noting that Ti^{IV} species were unstable in a NaCl/$CaCl_2$ melt.[170, 171] The primary Ti^{III} species in CsCl melts was characterized as $Cs_3Ti^{III}Cl_6$.[172] Addition of LiCl to the CsCl mixes promoted formation of $[Ti^{III}{}_2Cl_9]^{3-}$. These studies indicate that most **RE**s and row one **TM** (Ti–Cu) leeched into molten salts *via* corrosion would be present in lower oxidation states, +3 to +1, preventing their volatilization and keeping them within the melt. While the **MG** metal Al^{III} and the rows two and three **TM** (Ta, Nb, Mo, W) will likely be present in higher oxidation states +4, +5 and +6 which are more volatile, see Tables **9** and **13**. The stability of higher formal oxidation states for the row two and three **TM**s means that even within the acidic conditions of the melt, the +4 and +5 oxidation states are likely to be the most favored. The accessibility of $W^{VI}Cl_6$ compared to the hexavalent chlorides of the other metals means it is the most likely exception.

5.5. Volatility of Corrosion Product Chlorides

As previously noted, **CorP** chlorides are almost entirely transition metals aside from aluminum, and as such follow the same trends as **TM** chlorides from **Sections 5.1 and 5.2**. As expected, the vapor pressure increases with temperature and is greater for liquids than for solids. Due to the lack of consistent oxidation states across groups, only limited trends can be drawn. For Group 5, the pentavalent solids have nearly identical vapor pressures while the liquid phase vapor pressure differs by over 100 mmHg at equivalent temperatures.

Table 14. Vapor pressure coefficients of corrosion product chlorides in different physical states where *a*, *b* indicate different crystal modifications, the coefficients A–C come from **Eqs. 3-6**.

Compound	A	B	C	T range (K)	Ref
Main Group[a]					
Al_2Cl_6[b]	6360	9.66	-3.77	298-453	28
$AlCl_3$ (G_1)[c]	6720	19.415	2.97	400-454	34
$AlCl_3$ (G_2)[c]	11,177	4.206	0.16	900-2000	34
$(AlCl_3)_2$ (G_1)[c]	6642	25.842	4.22	298-454	34
$(AlCl_3)_2$ (G_2)[c]	3433	6.927	1.00	454-2000	34
Transition Metals – Solid Phase[a]					
$TiCl_2$ (S_1)[c]	12,980	21.437	3.56	700-1166	34
$TiCl_2$ (S_2)[c]	13,299	23.489	4.14	1166-1246	34
$TiCl_2$	15,230	19.36	2.51	298-1308	28
$TiCl_3$	9620	21.47	3.27	298-698	28
VCl_2[c]	9720	5.735		800-1620	34
VCl_3[c]	9659	20.260	3.28	500-916	34
$CrCl_2$[c]	14,005	17.727	2.53	800-1088	34
$CrCl_2$[d]	14,000	15.14	0.62	298-1097	28
$CrCl_3$[c]	15,876	23.851	3.83	800-1088	34
$CrCl_3$[e]	13,950	17.49	0.73	298-1218	28
$MnCl_2$[c]	11,792	17.628	2.81	700-923	34
$FeCl_2$	9890	11.10		670-740	28
Fe_2Cl_6	9540	45.53	9.5	298-580	28
$CoCl_2$	14,150	30.10	5.03	298-1010	28
$NiCl_2$[c]	12,715	17.305	2.25	700-1228	34
$NiCl_2$	13,300	21.88	2.68	298-1258	28
$CuCl_2$ (S_1)[c]	8419	9.044	-0.12	500-683	34
$CuCl_2$ (S_2)[c]	8940	8.984	-0.41	683-709	34
$CuCl_2$ (S_3)[c]	9569	9.017	-0.71	709-862	34
$NbCl_4$[c]	6870	9.425		400-602	34
$NbCl_4$[c]	6800	17.845	2.91	400-602	34
$NbCl_4$	6870	12.30		577-631	28
$NbCl_5$	5296	18.617	2.99	298-479	34
$NbCl_5$	4370	11.51		403-479	28

$TaCl_3$[c]	8877	19.414	3.27	500-912	[34]
$TaCl_4$[c]	5622	18.905	3.22	298-559	[34]
$TaCl_5$[c]	5288	18.359	2.88	298-490	[34]
$TaCl_5$	6275	34.305	7.04	298-490	[28]
WCl_2[c]	13,493	18.300	3.33	800-862	[34]
WCl_4[c]	7287	25.764	5.65	400-771	[34]
WCl_4	3253	8.195		555-598	[28]
WCl_4 (α)	3996	9.615		458-503	[28]
WCl_4 (β)	3588	8.795		503-554	[28]
WCl_5	3670	9.50		413-526	[28]
WCl_6 (A_1)[c]	5867	23.653	4.87	298-450	[34]
WCl_6 (A_2)[c]	6029	29.293	6.86	450-503	[34]
WCl_6 (B)[c]	4629	19.377	4.22	503-555	[34]
WCl_6 (α)	4580	10.73		425-503	[28]
WCl_6 (β)	4080	9.73		503-555	[28]
Transition Metals – Liquid Phase					
$TiCl_2$	13,110	17.93	2.51	1308-1773	[28]
$TiCl_4$[c]	2915	22.641	5.94	298-409	[34]
$TiCl_4$	2919	25.129	5.788	298-410	[28]
VCl_4[c]	3255	26.458	7.16	298-427	[34]
$CrCl_2$[c]	12,501	22.449	4.54	1088-1576	[34]
$CrCl_2$	13,800	27.70	5.03	1097-1575	[28]
$MnCl_2$[c]	10,257	19.226	3.91	923-1509	[34]
$MnCl_2$	10,606	23.68	4.33	923-1463	[28]
$CoCl_2$	11,050	27.06	5.03	1010-1322	[28]
$CuCl$	10,170	8.04		1000-1922	[28]
Cu_3Cl_3	3750	4.90		900-1800	[28]
$NbCl_5$[c]	5147	39.053	10.73	479-519	[34]
$NbCl_5$	2870	8.37		479-520	[28]
$TaCl_5$[c]	5124	39.007	10.68	490-506	[34]
$TaCl_5$	2975	8.68		490-512	[28]
WCl_5	2760	7.72		526-559	[28]
WCl_6[c]	4619	23.229	5.63	555-613	[34]
WCl_6	3050	7.87		555-610	[28]

Transition Metals – Gas Phase[a]

$TiCl_2$ (G_1)[c]	15,633	22.129	3.82	800-1246	34
$TiCl_2$ (G_2)[c]	6471	4.694	0.57	1246-1939	34
$TiCl_3$ (G_1)[c]	9851	16.393	2.42	600-1017	34
$(TiCl_3)_2$ (G_1)[c]	10,772	20.681	3.40	600-1017	34
$(TiCl_3)_2$ (G_2)[c]	4458	5.855	0.69	1017-2000	34
$TiCl_4$[c]	9043	3.389		800-2000	34
$CrCl_3$ (G_1)[c]	12,631	19.538	3.11	700-1279	34
$FeCl_2$ (G_1)[c]	10,901	17.819	2.83	600-950	34
$FeCl_2$ (G_2)[c]	9422	21.831	4.70	950-1293	34
$(FeCl_2)_2$ (G_1)[c]	13,914	26.033	4.73	700-950	34
$(FeCl_2)_2$ (G_2)[c]	10,978	34.198	8.51	950-1293	34
$(FeCl_2)_2$ (G_3)[c]	3876	4.393	0.35	1293-2000	34
$FeCl_3$ (G_1)[c]	8141	21.485	3.80	400-577	34
$FeCl_3$ (G_2)[c]	6502	25.492	6.28	577-604	34
$(FeCl_3)_2$ (G_1)[c]	8047	29.026	5.52	400-577	34
$(FeCl_3)_2$ (G_2)[c]	4776	37.136	10.51	577-604	34
$(FeCl_3)_2$ (G_3)[c]	4109	6.874	1.01	604-2000	34
$CoCl_2$ (G_1)[c]	11,865	18.509	2.92	700-994	34
$CoCl_2$ (G_2)[c]	9985	19.525	3.89	994-1354	34
$(CoCl_2)_2$ (G_1)[c]	15,153	26.775	4.94	700-994	34
$(CoCl_2)_2$ (G_2)[c]	11,436	29.150	6.98	994-1354	34
$(CoCl_2)_2$ (G_3)[c]	4212	4.628	0.31	1354-2000	34
$CuCl$ (G_1)[c]	11,765	16.471	3.22	800-1482	34
$(CuCl)_3$ (G_1)[c]	8584	27.024	6.20	500-683	34
$(CuCl)_3$ (G_2)[c]	7864	27.862	6.85	683-709	34
$(CuCl)_3$ (G_3)[c]	6942	28.044	7.37	709-1482	34
$(CuCl)_3$ (G_4)[c]	9429	7.003	0.73	1482-2000	34
$TaCl_3$ (G_1)[c]	12,581	20.733	3.55	700-912	34
$TaCl_4$ (G_1)[c]	7568	18.463	2.92	400-559	34
$TaCl_5$ (G_1)	4889	4.561		506-2000	34
WCl_5 (G_1)[c]	5963	25.427	5.34	298-526	34
WCl_5 (G_2)[c]	5124	26.771	6.42	526-558	34
$(WCl_5)_2$ (G_1)[c]	9304	38.321	8.16	400-526	34

$(WCl_5)_2$ (G_2)[c]	7670	41.691	10.54	526-558	34
$(WCl_5)_2$ (G_3)[c]	1248	5.467	1.01	558-2000	34
WCl_6[c]	2862	4.644	0.44	613-2000	34

[a] "G_n, S_n, A_n, B_n" designations as given in the primary literature [b] D term = -6.12 [c] Converted from bar to mmHg using **eq. 5** [d] D term = -0.58 [e] D term = -0.77

5.6. Thermochemical Properties of Corrosion Product Chlorides

In parallel to the data on **TM FP**s most corrosion products (**CorP**s) are composed of transition metals from all three rows. For these species, all of the properties share similar trends to the **TM**Cl_x **FP**s. The data on the **CorP**s was obtained primarily from two sources that are rather consistent to one another. Similar to the **TM FP**s, the **CorP TM**s have a wide range of oxidation states available to them with the higher oxidation states exhibiting more negative DH_f° and DG_f° and more positive DS° and C_p values, see **Table 15**. The majority of the data is for crystalline solids and gas phase compounds, where some oligomerization is characterized in the gas phase. The only liquid phase data on **CorPs** are for $Ti^{IV}Cl_4$ and $V^{IV}Cl_4$, which are both liquids at room temperature and do not have crystalline phase data. Comparing the crystalline phase to the gas phase compounds, the latter have less negative ΔH_f^o and less positive C_p values than the same species in crystalline phase. Similar to the other groups, ΔS^o increases for gas phase compounds over the crystalline phase. The only compounds of note include $Cu^{I}Cl$ (g) which features positive DH_f° (+91.2) and DG_f° (20.5 kJ/mol) values and the barely negative values for $Nb^{III}Cl_3$ (s) DH_f° (-0.6) and DG_f° (-44.5 kJ/mol). See **Table 15**.

Overall, this shows that the same treatment methods suggested for **FP** chlorides could be applicable to **CP** chlorides as well. Unlike the **FP TM**s, several of the **CorP TM**s form dimers within the gas phase and the thermodynamic values for the dimers are surprisingly well-documented. For all these species, formation of the dimer is significantly more exothermic than the corresponding monomer within the gas phase, suggesting that the dimer would be the predominant species as they volatilize.

Table 15. Enthalpy of formation (ΔH_f^o, kJ/mol), standard entropy (ΔS^o, J/molK), free energy of formation (ΔG_f^o, kJ/mol), and heat capacity (C_p, J/molK) thermodynamic data for aluminum and transition metal (**TM**) corrosion product chlorides.

Compound	ΔH_f^o	ΔS^o	ΔG_f^o	C_p	Ref
Crystalline Phase					
$AlCl_3$	–704.2	109.3	–628.8	91.1	30
$AlCl_3$	–705.4	109.3	–737.9	91.1	34
$TiCl_2$	–513.8	87.4	–464.4	87.4	30

$TiCl_2$	–515.5	87.4	–541.5	69.8	[34]
$TiCl_3$	–720.9	139.7	–653.5	97.2	[30]
$TiCl_3$	–721.7	139.7	–763.4	97.1	[34]
VCl_3	–580.7	131.0	–511.2	93.2	[30]
VCl_3	–581.2	131.0	–620.2	93.2	[34]
$CrCl_2$	–395.4	115.3	–429.8	69.3	[34]
$CrCl_3$	–556.5	123.0	–486.1	91.8	[30]
$MnCl_2$	–481.3	118.2	–440.5	72.9	[30]
$MnCl_2$	–481.3	118.2	–516.5	73.0	[34]
$FeCl_2$	–341.8	118.0	–302.3	76.7	[30]
$FeCl_2$	–341.6	117.9	–376.8	76.5	[34]
$FeCl_3$	–399.5	142.3	–334.0	96.7	[30]
$FeCl_3$	–399.3	147.8	–443.3	96.9	[34]
$CoCl_2$	–312.5	109.2	–269.8	78.5	[30, 34]
$NiCl_2$	–305.3	97.7	–259.0	71.7	[30]
$NiCl_2$	–305.3	98.0	–334.6	71.7	[34]
$CuCl$	–137.2	86.2	–119.9	48.5	[30]
$CuCl$	–136.8	87.4	–162.9	53.3	[34]
$CuCl_2$	–220.1	108.1	–175.7	71.9	[30]
$CuCl_2$	–218.0	108.0	–250.2	71.7	[34]
$NbCl_3$	–0.6	147.3	–44.5	97.4	[34]
$NbCl_4$	–694.5	184.1	–749.4	119.8	[34]
$NbCl_5$	–797.5	210.5	–683.2	148.1	[30]
$NbCl_5$	–797.3	214.1	–861.2	147.9	[34]
$TaCl_3$	–550.5	154.8	–596.6	93.1	[34]
$TaCl_4$	–707.5	192.5	–764.9	119.8	[34]
$TaCl_5$	–859.0	221.7	–925.1	147.9	[30, 34]
WCl_2	–260.3	130.5	–299.2	77.8	[34]
WCl_4	–443.1	198.3	–502.2	129.7	[34]
WCl_5	–513.0	217.6	–577.9	155.6	[34]
WCl_6	–602.5				[30]
WCl_6	–593.7	238.5	–664.8	175.4	[34]

Liquid Phase

$TiCl_4$	–804.2	252.3	–737.2	145.2	[30]

VCl_4	–569.4	255.0	–503.7		[30]
VCl_4	–570.1	258.6	–647.2	156.9	[34]
			Gas Phase		
$AlCl_3$	–584.6	314.5	–678.4	71.0	[34]
$(AlCl_3)_2$	–1295.7	475.0	–1437.4	158.3	[34]
$TiCl_2$	–237.2	278.3	–320.2	57.7	[34]
$TiCl_3$	–539.3	316.8	–633.8	72.5	[34]
$(TiCl_3)_2$	–1247.5	482.1	–1391.2	169.7	[34]
$TiCl_4$	–763.2	353.2	–726.3	95.4	[30]
$TiCl_4$	–763.2	354.8	–868.9	95.5	[34]
VCl_4	–525.5	362.4	–492.0	96.2	[30]
VCl_4	–525.5	366.5	–634.8	93.2	[34]
$CrCl_2$	–136.2	307.9	–228.1	57.7	[34]
$CrCl_3$	–325.2	317.6	–419.9	76.0	[34]
$MnCl_2$	–264.1	295.4	–352.2	57.1	[34]
$FeCl_2$	–140.9	299.3	–230.1	57.6	[34]
$(FeCl_2)_2$	–431.4	464.5	–569.9	125.9	[34]
$FeCl_3$	–254.0	344.2	–356.6	77.70	[34]
$(FeCl_3)_2$	–660.5	537.1	–820.6	173.7	[34]
$CoCl_2$	–93.7	298.5	–182.7	59.6	[34]
$(CoCl_2)_2$	–349.7	450.4	–484.0	127.5	[34]
$NiCl_2$	–70.2	298.2	–159.1	60.6	[34]
$CuCl$	+91.2	237.2	+20.5	35.1	[34]
$(CuCl)_3$	–263.7	429.5	–391.8	124.3	[34]
$NbCl_5$	–703.7	400.6	–646.0	120.8	[30]
$NbCl_5$	–703.3	404.1	–823.8	119.0	[34]
$TaCl_3$	–322.2	346.0	–425.3	75.5	[34]
$TaCl_4$	–574.1	377.3	–686.6	99.0	[34]
$TaCl_5$	–764.8	413.0	–888.0	120.1	[34]
WCl_2	–12.6	309.4	–104.8	58.4	[34]
WCl_4	–335.8	379.3	–448.9	98.8	[34]
WCl_5	–412.5	405.5	–533.5	120.2	[34]
$(WCl_5)_2$	–869.1	711.4	–1081.1	263.3	[34]
WCl_6	–513.8				[30]

WCl_6	–493.6	419.3	–618.6	143.8	34

The enthalpic and entropic phase transition data for the **CorP** chlorides is more limited than the formation data, with only Fe and W having more than one oxidation state with documented values. $FeCl_x$ provides an interesting exception to the trends observed in the **FP** chlorides, where $Fe^{II}Cl_2$ and $Fe^{III}Cl_3$ have almost identical ΔH_{fus} values despite the change in oxidation state. The minimal energetic difference in $Fe^{II}Cl_2$ vs. $Fe^{III}Cl_3$ can also be observed in the thermodynamic data in **Table 15**, where there is a ~12–18% difference in DH_f°, DS°, and DG_f°. Similar to the **FP** data, the majority of the sublimation data was estimated using **Eq. 10** and may not be representative of experimental values. In general, ΔS_{fus} increases with oxidation state, paralleling the **TM FP** chlorides. The tungsten species W^VCl_5 and $W^{VI}Cl_6$ have surprisingly low values considering their high oxidation states, but without data on the other oxidation states, wider trends cannot be drawn and it again illustrates the need for more complete thermodynamic data on these fundamental compounds, see **Table 16**.

Table 16. Enthalpic (ΔH, kJ/molK) and entropic (ΔS, J/molK) heats of fusion (fus), vaporization (vap) and sublimation (sub) for aluminum and transition metal (**TM**), corrosion product chlorides.

Cmpd	ΔH_{fus}	ΔS_{fus}	ΔH_{vap}	ΔS_{vap}	ΔH_{sub}	ΔS_{sub}	Ref
$AlCl_3$		75.9					34
$TiCl_4$			35.8	87.5			34
VCl_4			37.1	86.8			34
$CrCl_2$	46.9	43.1	179.9	114.1	226.8[a]	157.2[a]	34
$MnCl_2$	37.7	40.8	147.4	97.7	185.1[a]	138.5[a]	34
$FeCl_2$	43.0	45.2					34
$FeCl_3$	43.1	74.7					34
$CoCl_2$	43.9	44.2					34
$NiCl_2$		59.4		119.9[a]	220.1	179.3	34
CuCl	6.9	9.7					34
$NbCl_5$	33.9	70.7	52.3	100.7	86.2[a]	171.4[a]	34
$TaCl_5$	35.1	71.7	53.2	105.1	88.3[a]	176.8[a]	34
WCl_5					20.6	39.1	34
WCl_6	6.7	12.1	59.8	97.6	66.5[a]	109.7[a]	34

[a] Calculated values using **eq. 10**

6. Summary and Outlook

The data collected herein show several consistent trends that can assist in gap-filling, allowing researchers to perform well designed experiments. Across all elements the thermochemical properties, melting point (T_M), boiling point (T_B), and heat capacity (C_p) are by far the most well documented properties. Despite being a fundamental property of metal compounds, data for sublimation temperature (T_{sub}) and the triple point temperature (T_{TP}) are far less common. The dearth of sublimation and triple point data likely arise from temperature and pressure both playing an important role leading to difficulty in making the proper measurements. The $T_{M,}$ T_B, and C_p of compounds are heavily influenced by oxidation state, coordination number, and ionic size. In general, the T_M and T_B of compounds decrease as oxidation state increases. This typically includes a decrease in the coordination number and ionic size. Even in molten salt solution where all the ions may exist as a variety of $[M_xCl_y]^{n-}$ compounds, the melting point of compounds generally track with the charge (n) of the species, 0 < -1 < -2. Small changes in ionic radius allow subtle changes in T_M to be observed, *e.g.*, the **An**^{III}Cl$_3$ compounds where the largest ion, U^{III} (T_M = 835 °C) to the smallest ion, Cf^{III} (T_M = 545 °C). While large changes in ionic radius such as the **Ae**Cl$_2$ compounds that display large changes in T_M from Be (T_M = 415 °C) to Ba (T_M = 961 °C), here changes in solid state lattice may also affect the observed properties.

The vapor pressure data indicate that higher order chlorides volatilize more readily than lower order chlorides. This volatility trend is somewhat consistent with the trends noted above related to melting/boiling temperature, although, gaps in the data prevent trends for all groups from being made. Some compounds are reported as having unique gas phase properties related to stability and oligomerization. While the actinide compounds Pu^{IV}Cl$_4$ and Bk^{IV}Cl$_4$ appear to only be stable in the gas phase, other transition metal compounds such as Cu^{I}Cl, Ag^{I}Cl, Pd^{II}Cl$_2$, Ru^{III}Cl$_3$, and Mo^{II}Cl$_2$ have positive gas phase DH_f° and DG_f° values. The literature also suggests that both UCl$_x$ (x = 4, 5), **A**/**Ae**, and **TM** chlorides have complex gas-phase speciation with a non-negligible degree of oligomerization. Although, oligomerization has not been reported for many of the elements examined, this could be due to a lack of data. In general, the thermochemical data suggests that under reactor relevant conditions, 560 °C < T < 740 °C, main group (**MG**) compounds will readily volatilize, **TM**s with higher formal valences (^{3} +4), typically those from rows two and three, will readily volatilize, while compounds with lower formal valences will remain in the melt. The high T_M and T_B of the **An**s, **RE**s, **A**, and **Ae** metals mean that all of these elements will remain in the melt. The non-volatile **FP** and **CorP** will have to be removed by other means from the fuel for continuous running, recycling, or disposition. This emphasizes the importance of understanding structural changes during phase transitions within molten salt melts where the exact composition of the melt is often unknown.

The thermophysical data, that of the DX_f° (X = H, G), and DS°, as well as DX_E (X = H, G, S; x = fusion, vaporization, or sublimation) are far more sparse than thermochemical data, but approximate trends can still be drawn. The radioactive actinides are surprisingly well documented, compared to the non-radioactive **TM** and **RE** compounds. The confluence of several data sources does come with some contradictory values, which may require reexamination. In all likelihood, the more recent sources are the more reliable values, but without standardized procedures and conditions, it cannot be said for sure. $Pu^{IV}Cl_4$ appears to ignore observed thermochemical trends, reinforcing the importance of understanding it for volatilization-based separation methods. The **An**Cl_x and **TM**Cl_x compounds demonstrate that oxidation state significantly affects thermophysical properties. Compounds with higher formal oxidation states have more negative $DH_f°$ and $DG_f°$ values while DS° becomes more positive.

Safe, more efficient separation and waste disposal methods are only possible with a more complete understanding of the thermophysical and thermochemical properties of all relevant elements. The complicated nature of molten salt reactor waste streams require a finely tuned knowledge base of all of the possible components of the mixture. Especially considering many of the **FP**Cl_x compounds have very similar properties to one another and are difficult to separate from each other. Further and more comprehensive research that fills the gaps in the literature is a necessity for the advancement of molten salt reactors.

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