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Review Article

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Knudsen effusion mass spectrometry studies on metal halides performed in 1990-2014

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Abstract Investigations on metal halide systems carried out by Knudsen effusion mass spectrometry in the period 1990-2014 are reviewed in the present paper.163 original papers were published focused on metal halides showing still considerable activity in this area. The fundamentals of the Knudsen effusion mass spectrometry method and thermodynamic background of the investigation are briefly reported. Data to the system studied, temperature ranges, Knudsen cell materials, vapor species identified in the equilibrium vapors and the thermodynamic properties obtained in the study are presented. The important issues of metal halide vaporization studies are briefly discussed and commented.

The studies of the vaporization of metal halogens by Knudsen effusion mass spectrometry aimed firstly atthe determination of gaseous complexes species in the vapor and determination of its thermodynamic data like sublimation enthalpy etc. and secondly at the determination of negative ions formation and various ion-molecule equilibria reactions of metal halide systems. Many of the studied materials have a crucial role for modern technologies, for example metal halide lamps, hot corrosion caused by halide salts, phosphorus recovery technologies or gas assisted separation of lanthanides. The investigation of such systems gives information on mechanisms of vaporization, volatility of the systems under various conditions (temperature, pressure etc.), reactivity, thermal stability, resistance etc. that could be further applied for various calculations and to predict the behavior of various components under various technological aspects.

Keywords metal halides, Knudsen Effusion Mass Spectrometry (KEMS), HTMS, thermochemistry, high temperature, vaporization

1. Introduction

Knudsen effusion mass spectrometry (KEMS), also called high temperature mass spectrometry (HTMS), is the most powerful method to analyse vapour species in equilibrium with the condensed phases. This method enables the identification of the major, minor and even traces of gaseous species and the determination of their partial pressures offering the highest potential for equilibrium vaporisation studies. Once the partial pressures are determined, one can obtain the vaporisation patterns, thermodynamic data like chemical potential, enthalpy ΔH or entropy ΔS of the ongoing chemical reactions. This method enables also the investigation of the new gaseous species, for example complexes species that arise only in the vapour phase through various gas reactions. Nowadays, in spite of rather rare applications of the method, it is still a powerful tool for thermodynamic investigations of equilibria between gas and condensed phases in various inorganic materials. At present, twenty six research groups work worldwide with this unique technique, showing still a large activity in this area [1].

Knudsen effusion mass spectrometry as a combination of Knudsen effusion cell with mass spectrometer was applied for the first time in 1948 by Ionov [2] by the determination of the vaporisation of alkali metal halides. It was realised that the equilibrium vapour over the alkali halides MX(c) consists of the monomer MX(g) and dimer $(MX)_2$ molecules. Before those investigations it was often assumed in the high temperature chemistry that the molecules in the gas phase should be simple and small, related to the chemical stoichiometry of the studied

compound (monomers). The identification of dimer molecules $(MX)_2$ brought about some entirely new aspects to the usual concepts of chemical bonding and valence because in many cases complex molecules are the predominant species. Therefore, the subject of gas chemistry at high temperatures has grown to become a branch as distinct and varied as solution chemistry [3].

The present paper is complement of the former review [1] and summarises the research activities of the metal halide system carried out by Knudsen effusion mass spectrometry in the period 1990-2014. 164 original papers, conferences papers and book chapters were published by twenty six research groups. Comparing with the former reviews[1], the investigations of metal halides constitute of 45% of all investigations of inorganic materials carried out by Knudsen effusion mass spectrometry since 1990.

The leading research groups in the metal halide vaporisation as well as by Knudsen effusion mass spectrometry are research groups from Russia where 7 groups are still active in this unique area. Several review papers regarding metal halide vaporisation were published in recent years by Boghosian and Papatheodoru [4] in 1996 and Miller [5] in 1992. The former reviews on halogens system were made by Hilpert [6] in 1989, Sidorov and Korobov [7] in 1981 or Hastie [8] in 1971. This review will be the continuation of the Miller review [5] from 1992. The most important motivation of the investigations of metal halides is their application for metal halide lamps. The former review considering high temperature metal halide vapours in metal halide lamps was made by Hilpert [9] in 1989 and Miller [10] in 1997 summarising metal halides system measured for those purposes. The investigation of vaporisation of metal halides for metal halides lamps are also part of the Miller [5] review from 1992.

2. Thermodynamics of the gaseous species and of condensed phase

An understanding of the vaporization process requires knowledge of both the condensed and the gaseous phases. The first step is the characterization of the vapor phase and the identification of the gaseous species. There are several possibilities to carry out such investigations; the most common are the static, boiling point, transpiration, Knudsen effusion and Langmuir free-evaporation methods. From those investigation methods Knudsen effusion and the Langmuir free-evaporation methods are the most versatile since the experimentsare carried out in the vacuum and the material is transported away from the investigated sample [11]. This paper focuses on the results of investigation of metal halide systems by means of Knudsen effusion mass spectrometry. The principles of the Knudsen effusion mass spectrometry and the identification of the gaseous species by this method were described in the former review [1].

The identification of the gas species allows the determination of other related thermodynamic data such as various equilibria, mechanism of vaporization or molecular structures of the gaseous species. Those data could be explored with great facility since the existing of the various gaseous species is known.

Knowledge of the partial pressures of the gas phase components in the system at the temperature T allows the determination of equilibrium constants K_p^o of the equilibria reactions, according to the equation (1).

$$\mathrm{K}_p^o = \Pi\left(\frac{p(i)}{\mathrm{p}^o}\right)^{\nu_i} \tag{1}$$

where ν_i is the stoichiometric coefficient of the reaction, and p^o denotes the standard pressure (10^5 Pa). The values of equilibrium constants, K_p^o,enable further the calculation of Gibbs energy functions for the respective processes according to the equation (2)

$$\Delta_r \mathrm{G}^o(\mathrm{T}) = \Delta_r \mathrm{H}^o(\mathrm{T}) - \mathrm{T}\Delta_r \mathrm{S}^o(\mathrm{T}) = -\mathrm{RT}\ln \mathrm{K}_p^o(\mathrm{T}) \tag{2}$$

The enthalpy changes can be determined from the experimental values of K_p^o in two independent ways according to second and third law methods of thermodynamics. The second law enthalpy of reaction consists of the equilibrium constant during measurement in a certain temperature range and could be evaluated according to equation (3)

$$\ln \mathrm{K}_p^o(T) = \frac{A}{T} + B \tag{3}$$

from which the value of enthalpy (4) and entropy (5) of the reaction can be determined as follows

$$A = \frac{-\Delta_r H^o(T_m)}{\mathrm{R}} \quad (4)$$

$$B = \frac{\Delta_r S^o(T_m)}{\mathrm{R}} \quad (5)$$

T_m is the average temperature of the experiment. These equations are true in the experiment temperature range, where one can assume invariance of enthalpy and entropy changes. Otherwise dependence is no more of a linear character and enthalpy of reaction is related to tangent to a line describing dependence of $\ln \mathrm{K_p^o}(T)$ versus inverse of temperature in the $1/T_m$ point. The value of reaction enthalpy in the mean temperature of the measurement can be converted into enthalpy at the standard temperature T_{st}, $\Delta H(T_{st})$ assuming knowledge of the Cp(T) or $[H(T) - H(T_{st})]$ functions in the T_m-T_{st} range, for all reactants taking part in the reaction. The functions of many compounds are tabulated in the thermodynamic tables. The standard temperature T_{st} is usually equal to 298 K.

Another way to calculate the reaction enthalpy from experimental K_p^o data is the third law method. It is important to know $GEF^o(T)$ for each compound taking part in the reaction, that is defined by equations (6-7).

$$GEF°(T) = \frac{G°(T) - H°(T)}{T} \quad (6)$$

$$GEF°(T) = \frac{H°(T) - H°(T_{st})}{T} - [S°(T) - S°(T_{st})] - S°(T_{st}) \quad (7)$$

The $GEF^o(T)$ function of a compound can be calculated from its Cp(T) in the T-T_{st} range and its entropy at the standard temperatures. The $GEF^o(T)$ functions are tabulated for many compounds at different temperatures. For gaseous species it can be computed from known or estimated molecular parameters by the method of statistical thermodynamics [12].

Other thermodynamic values which can be determined by Knudsen effusion mass spectrometry are the thermodynamic activities of the component. The thermodynamic activity a(*i*), of component *i*, at the temperature T, in the condensed phase of the investigated system can be obtained from the partial pressure of the pure component, $p^o(i)$, and its partial pressures over the mixture, p(*i*), determined at this temperature, eq (8).

$$a(i) = \frac{p(i)}{p^o(i)} = \frac{k \cdot I(i) \cdot \sigma(i)}{k' \cdot I(i)^o \cdot \sigma(i)} \quad (8)$$

Providing thermodynamic activity of one component of the binary system, the activities of the second component can be calculated by the Gibbs-Duhem method. At constant temperature and pressure, the Gibbs-Duhem equation can be written as follows, e.g. (9).

$$\sum_i x_i d \ln a(i) = 0 \quad (9)$$

where: $x_i$is the mole fraction of component i and *a*(*i*) the activity of the component i.

The summation extends over all components. Adding d ln a(*j*) to each side of the equation (9) and rearranging, one can obtain eq (10) for activities calculation [13]

$$d \ln a(j) = -\frac{x_i}{x_j} \cdot d \ln a(i) \quad (10)$$

Since the thermodynamic activities are obtained the other thermodynamic data like partial and integral mixing functions or thermodynamic functions of formation of condensed phases can be calculated.

This paper is a brief report on the experimental data obtained by KEMS for metal halides in the period 1990-2014. Basic information on the investigations of pure metal halides and their system are summarised and presented in Table 1. Sample compositions, temperature range, material of the Knudsen cells, gas species identified in the vapour and also thermodynamic quantities reported in particular paper are given in Table 1.Solid compounds present in the given concentration range are underlined if the thermodynamic functions of formation were determined.Most of the investigation of metal halide systems presented in this paper were undertaken in order to determine the thermodynamics properties of condense phases such as equilibria of the gas species, mix properties, Gibbs energies of formation etc. Many of the articles deal with negative/positive ion formations and their equilibria.

There are 163 original papers published via various groups in the period 1990-2014 investigating the vaporisation of pure metal halides and their various systems. Table 1 presents the investigation of metal halides made by Knudsen effusion mass spectrometry in the period 1990-2014. It is divided for sections that present the investigations grouped according to the investigation of the proper metal halide groups: iodides, chlorides, fluorides, bromides and their binary MX_n-MX_m and multicomponent MX_n-MY_m systems, where *M*- metal and *X*, *Y* are halogens. Over a half of the presented papers were concentrated on pure metal halides vaporisation with focus on fragmentation, vaporisation processes, obtaining thermodynamic data – enthalpies of sublimation, vaporisation or negative ion reactions, ion molecule equilibria etc. The most extensive studies of various equilibria and negative ion reactions (ion-molecule, ion-ion reactions) were undertaken by groups from Russia, especially from Kudin group [14-17]. Various pure metal halides were investigated, for example KCl, $NdCl_3$, CeI_3 and their complex gaseous species described and various equilibria and enthalpy of their formation evaluated.

3. Studies on pure metal halides

The most investigated groups in vaporisation studies of pure metal halides are metal chlorides. Thermodynamic and vaporisation of metal chlorides have a crucial role for various processes where 30 papers were published regarding pure metal chlorides vaporisation and 23 papers about various metal chlorides binary systems. Lanthanum chlorides were the most part of interest in various investigations, especially Kudin group [18-19] and Kapala *et al*. [20-21] were active in this area. The vaporization of various lanthanides chlorides were investigated, such as $CeCl_3$, $PrCl_3$, $NdCl_3$ and their enthalpy of sublimation determined. The lanthanide chlorides vaporize as $LnCl_n$,$(LnCl_n)_2$ and $(LnCl_n)_3$ that was presented, for example by Pogrebnoi*et al.* [22] by investigation of the vaporisation of $CeCl_3$ and $SmCl_3$ from the Mo cell. Other investigation made by Khasanshin, I.V., et al. [23] also indicated $SmCl_3$ in the vapour. Molecules like Ln_4Cl_{12} (where *Ln*= Dy, Ho, Tm, Lu) and Tm_5Cl_{15} in the vapour over condensed phase were found by Kudin [19] during investigation of lanthanide chlorides. Big area of interest was also the occurring of negative ions and their ionic molecular reactions.

The second mostly investigated groups of halogens are metal fluorides. There are 19 papers published about vaporization of pure metal fluorides. Similar as for chlorides, also for fluorides the occurrence of negative/positive ions was a part of interest. The vaporization of CoF_3 and the enthalpy of its sublimation was the common topic of Popovic*et al*. and Rau *et al.*[24-25] works. Rau *et al.* , Leskiv*et al.* [26] investigated the vaporization of CoF_3 that vaporize as CoF_3, Co_2F_6, F, F_2, that is in agreement with previous works [24-25, 27]. The ionization efficiency curves of CoF_3 were determined by Rau *et al.* [28]. In period 1990-2014 high temperature vaporization of CoF_3 was the most of extensive investigated among all investigations of fluorides.

4. Binary and multicomponent systems

Apart from pure metal halides binary and multicomponent MX_n-NX_mMX_n-MY_m systems were investigated. In such binary/multicomponent systems apart from gaseous species MX_n, NX_m and homo-complexes $(MX)_i$ in addition also hetero-complexes MNX_{n+m}, M_2NX_{2n+m}, $(MNX_{n+m})_2$ etc. gaseous species were determined. Those species, because of their high thermodynamic stability and partial pressure have a crucial role in the chemical transport through the gas phase.

As in the case of pure metal halide studies, also for binary and multicomponent systems the most investigated group were chlorides. 23 original papers were published considering various metal chloride systems and their vaporisation. The authors were interested in activities of the components like in Lisek*et al*. [29-31] or Butman *et al*. [32] and also with enthalpy of sublimation. Many of the presented papers focus on negative ion reactions and their equilibria, for example [33-36]. The mass spectrometry of negative ion reactions enables determination of electron affinity and unique thermodynamic data of various ions and species. Halides of lanthanides LnX_m and their negative ion reactions were of the interest of various researches of metal halogens in the period 1990-2014. As example one can considered the work of Kudin*et al.* [18] and the investigation of $LnCl_3$ where (*Ln* = La, Lu) where the thermal stability of $LaCl_4^-$ and $LuCl_4^-$ were determined.

5. Technology aspects

5.1. Chemical metallurgy using gas phase transport

Knowledge on thermochemical properties of gaseous complexes is crucial for some specific technologies based on metal halide vapours. Adachi, Murase and co-workers [37-40] demonstrated that a vapour transport process mediated by vapour complexation with highly volatile chloride like alkali metal chloride or Al_2Cl_6 can be used

for separation of lanthanides and actinides based on differences in the volatility of the involved metal halides. The method appears to have potential for treating and separating nuclear fuel materials. The Authors performed chemical vapour transport experiments in several binary and ternary systems (like Pr-Er, Pr – Sm, Pr-Nd, Pr-Gd-Er) using transportation of gaseous complexes $LnACl_4$ or $LnAl_nCl_{3+3n}$, *Ln* = Lanthanides, *A* = alkali metal. This technique is based on the difference in the temperature dependences of the formation-decomposition equilibria for the vapour complexes and is suitable for the separation of rare earth on the industrial scale. Installation demonstrated in [37-40] consisted of two electric furnaces, one of them playing a role of the source of volatile component (Al_2Cl_6, *A*Cl) and the second comprised several divided heaters so to produce various heating zones and temperature gradients. Metal halide complexes were formed in the gaseous phase above the container with the raw material (lanthanide chloride or oxide mixture) and carried along the furnace by the carrier gas stream (N_2, Cl_2). Heavier rare earth chlorides were concentrated in deposits in lower temperature zones while lighter ones were selectively deposited in different zones of higher temperatures.

The method was also used for recovering of lanthanides from different lanthanide containing scrap like high performance permanent magnets, phosphors for lamps or colour displays and hydrogen storage alloys for anode materials of secondary batteries.

Gaseous metal halide complex formation plays also important role in some other high temperature industry processes. There are some observations published in the literature indicating formation of gaseous metal halides in cement production process [41]. In spite of low content of these compounds in the cement plant, their contribution to corrosion and metal transport processes going on in the installation is quite large.The example of the applications of metal chlorides is phosphorus recovery where the sewage sludge ashes are treated thermochemicaly with gaseous Cl-donor coming from, for example, $CaCl_2$ or $MgCl_2$ [42]. One of the methods of production of silicon begins with silicon tetrafluoride that is a by-product of the production of superphosphate fertilizer from phosphate rock [43]. Further example is the manufacturing of titanium dioxide, where purer oreis firstly reduced with carbon and then oxidised again with chlorine. Also during obtainingof aluminium alloys in channel induction of melt for its better quality the selective chlorination of meal takes place [44].

5.2. Metal halide discharge lamps (MHD)

Formation of thermodynamically stable and volatile complexes at high temperatures is characteristic for the metal halide systems. The concept of high intensity discharge lamps (MHD) with high luminous efficacy and a good colour rendering index based on admixture of lanthanide iodide admixture was recognized a few decades ago resulting in large interest in vaporization characteristics of these compounds. Due to the still too low vapour pressure of the pure lanthanide iodides (most volatile halides) at the temperature limited by ceramic arc tube, additional components (metal halides) are added to the MHD metal halide charge. Goal of these components is to transport considerably more lanthanide atoms in the form of various gas complexes into the high voltage arc [6]. All molecular species formed in the arc tube dissociate in the high temperature discharge area resulting in formation of free *Ln* atoms and their excitation and/or ionization. The species recombine and relax in colder area emitting light composed on the characteristic spectra of *Ln* atoms present in the halide charge. Luminous efficacy of MHD lamp depends on the concentration of lanthanide atoms present in the gaseous phase in form of different gas species. By mixing different metals (mainly lanthanides) in the MHD halide charge one can get the light of different colour and intensity.

The stability of the 1,1-heterocomplexes *ALnXn* (g), mostly contributing to the *Ln* atoms concentration in gaseous phase is therefore of key interest for modelling the MHD lamp. The respective papers are quoted in Table 1 and gaseous species identified in the equilibrium vapours. The iodide systems of NaI quasi binary systems and MI_n have importance for the practical use, therefore the NaI-MI_n were the most investigated systems from iodides (8 papers pro 12 published). For bromides the mostly investigated system was NaBr-MBr_n (4 papers pro 6 published). The systems such as NaI+ErI_3[45] NaI+DyI_3[46]NaI(s)+ScI_3[47], NaI-TmI_3[48], NaI-CeI_3[49] and their thermodynamic activities or/and enthalpy of sublimation, fragmentation, vaporization were determined. Also bromide systems NaBr-KBr [50], NaBr-$DyBr_3$ [51-52] and their vaporization, excess molar free Gibbs energy or enthalpy of sublimation were determined. The great number of studies of various system for metal halides lamps and their vaporization together with thermodynamic data such as equilibrium constants, partial pressures, enthalpy and entropy changes etc.one could find in Miller work [10] or former review from Miller [5] and Hilpert [9].The book written by Miller [10] contains apart from system for metal halide laps the

researches regarding NaBr, CsBr, DyF_3, $DyBr_3$, $SnCl_2$, $SnBr_2$,$DyBr_3$, DyI_3 and systems *AX – MY* (*A,M*-metals, *X,Y* – halogens), $SnBr_2$-SnI_2, *AX*-MX_n SnI_2-ScI_3 , Na-Sn-Br-I, *AX-LnX* at various temperatures and in various compositions.

Metal halide complexes possessing mostly ionic or polarized bonds between metal and halide atoms undergo strong fragmentation in the mass spectrometer ion source. It is why the interpretation of mass spectra (assignment of ion intensities to the neutral precursors) is often difficult and needs special methods and experiments (like recording of ionization efficiency curves or isothermal evaporation of complex sample with simultaneous recording of mass spectrum). Therefore accuracy of thermodynamic functions derived from KEMS studies for such a complex systems is in many cases low, especially for secondary processes involving components of low concentration. Example of this complexity is a system Na-Sn-Br-I system studied as potential MHD lamp charge by Miller et al [53].

Some papers on the topic were also published to better understanding of corrosion and chemical interaction between the halide charge and ceramic arc tube machined from transparent polycrystalline alumina. Gaseous species like $NaAlI_4$, $NaAlBr_4$, AlOI, AlOBr were identified as result of such degradation processes in MHD lamps by Markus et al [54]. The corrosion of arc tube was also confirmed by $DyAlO_3$(s) and $Dy_4Al_2O_9$(s) phases identified by XRD and SEM/EDX after the vaporization experiment [55].

6. Summary and conclusions

This paper summarises the investigations of metal halides and their systems carried out by Knudsen effusion mass spectrometry in the period 1990-2014. The thermodynamic fundamentals of determination of the gaseous species and of condensed phase are briefly described. Basic information such as sample compositions, temperature range, material of the Knudsen cells, gas species identified and also thermodynamic quantities in the pure metal halides investigation and their system are summarised and presented in Table 1. Most of the vaporisation studies by Knudsen effusion mass spectrometry of metal halide systems were undertaken in order to determine the thermodynamic properties of condensed phases that is equilibria of the gas species, activities, Gibbs energies of formation etc. Many of the studies aimed also in the investigation of negative/positive ion formations and their equilibria. Some of the studied materials are of practical importance for high technology applications like in the case of metal halide lamps. The obtained thermodynamic data give information about vaporisation behaviour under various conditions, thermal stability, reactivity etc. that could be used for other technologies where high temperatures occur.

Table 1. Mass spectrometric investigations for the determination of thermodynamic properties ofmetal halides and their vaporization.Solid compounds present in the given concentration range are underlined if the thermodynamic functions of formation were determined.

Sample	Effusion cell	Temperature range	Gaseous species	Solid phases	References
Pure metal iodides					
InI_3(s)	Pt	350-450	InI_3, In_2I_6	InI_3(s)	[56]
TmI_3(s) TmI_2(s)	W, Mo, C	<900	TmI_3, TmI_2, Tm_2I_6, TmI	$\underline{TmI_3}$	[57]
$(AgI)_{0.5}$-$(AgPO_3)_{0.5}$	Ta	773-923	I, I_2, PO, AgI, O_2	$\underline{(AgI)_{0.5}\text{-}(AgPO_3)_{0.5}}$	[58]
CeI_3	Mo	<1000	CeI_3, Ce_2I_6	$\underline{CeI_3}$	[59]
TiI_2, TiI_3	C	499-713	TiI_2, TiI_3, TiI_4, I		[60]
RbI, AgI		702-1011	RbI, AgI, $RbAg_4I_5$	Ion molecule eq.	[61]
LiI	graphite	583-726	LiI, Li_2I_2, Li_3I_3, Li_4I	$\underline{LiI}$	[62]

CsI single crystals	Mo, stainless steel holder	600-890	CsI, Cs_2I_2	CsI, free surface measurements	[63]
SmI_3	Mo	900-1270	SmI_3, SmI_2, Sm_2I_4		[64]
CdI_2	silica	534-613	CdI_2, Cd_2I_4	CdI_2	[65]
BeI_2	Kh18N10T	537-570	BeI_2, Be_2I_4	BeI_2	[66]
MI_2 M=Cr, Fe, Mn, Co		653-952	MI_2, M_2I_4		[67]
PrI_3	Mo	842-1048	PrI_3, Pr_2I_6/negative ions	PrI_3	[68]
TmI_3		820-990	TmI_3, $(TmI_3)_2$	TmI_3	[69]
PrI_3	Mo	856-1048	PrI_3, Pr_2I_6	PrI_3	[70]
YbI_2			Ion apperances		[71]
Pure metal chlorides					
$CeCl_3$ $SmCl_3$	Mo	959-1227	$CeCl_3$, $SmCl_3$, Ce_2Cl_6, Sm_2Cl_6, Sm_3Cl_9	$CeCl_3$ $SmCl_3$	[22]
KCl(s)	Mo	930-1040, 840-1040	KCl, K_2Cl_2	KCl, K_2Cl_2	[72]
$SmCl_2$	Mo	1037-1303	$SmCl_2$, $SmCl_3$	$SmCl_2$	[23]
$NdCl_2$	Mo	800-1100	$NdCl_2$, $NdCl_3$	Negative ions	[73]
$SnCl_2$(s)	Mo	382-504	$SnCl_2$, Sn_2Cl_4	$SnCl_2$	[74]
$BeCl_2$	Stainless steel	547	BeCl, Be_2Cl_4		[75]
$LuCl_3$	Mo	885-1100	$(LuCl_3)_n$, Cl-$(LuCl_3)_n$, n= 1-6	$LuCl_3$, ion molecule equilibria	[76]
KCl single crystal	Ceramic, stainless steel	710-1020	KCl, K_2Cl_2	Surface charge, surface structuire	[77]
$LnCl_3$ (Ln=La, Ce, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu)	Mo	840-1300	$LnCl_3$, Ln_2Cl_6, Ln_3Cl_9 (without Ln, Yb), Ln_4Cl_{12}(for Dy, Ho, Tm, Lu), Tm_5Cl_{15}		[19]
$LnCl_3$ Ln=Ce, Pr, Nd, Dy	silica	869-1176	$LnCl_3$, Ln_2Cl_6	$LnCl_3$	[21]
$LnCl_3$ Ln= Ce, Pr, Nd, Dy	silica	800-1100	$LnCl_3$, Ln_2Cl_6	$LnCl_3$	[20]
CsCl	Mo	832-917	Ions	Ionic composition	[35]

			equilibria	of vapor, ionic-molecular reactions	
$YbCl_2$, $YbCl_3$	Mo	1000-1300	$YbCl_2$, $YbCl_3$ + negative ions	$YbCl_2$, $YbCl_3$	[36]
CsCl: test experiment for KC assembly development	Mo		CsCl	CsCl	[78]
$LnCl_3$ Ln=La, Lu		962-1386	The enthalpy stability of $LaCl_4^-$, $LuCl_4^-$		[18]
$LnCl_3$ (Ln=La, Lu)	Calculated data		$Ln_2Cl_7^-$ ions		[79]
$NdCl_2$	Mo	800-1100	Positive and negative ions	Ion-molecule, ion-ion reactions	[80]
$PdCl_2$	Quarz	779-1713	Pd_2Cl_4, Cl_2	$PdCl_2$	[81]
$EuCl_2$	Mo	1154-1267	$EuCl_2$, Eu_2Cl_4	$EuCl_2$	[82]
RbCl	Mo	741-1008	RbCl, $(RbCl)_n$ n=2-4	RbCl	[83]
$HoCl_3$	Mo	887-1096	$HoCl_3$, Ho_2Cl_6, Ho_3Cl_9, Ho_4Cl_{12}	$HoCl_3$	[84]
$LaCl_3$	Mo	937-1144	$LaCl_3$, La_2Cl_6	$LaCl_3$	[85]
$NdCl_3$	Mo	872-1147	$NdCl_3$, Nd_2Cl_6	$NdCl_3$	[86]
KCl	Mo, Cu	760 - 1020	Negative ionreactions		[15]
$EuCl_2$	Mo	1180-1500	Negative ionreactions		[16]
$CuCl_2$	Mo, Cu	500-890	Ion reactions		[17]
$DyCl_3$	Mo	850-1057	$DyCl_3$, Dy_2Cl_6 + negative ions	$DyCl_3$	[87]
$LaCl_3$	Mo	937-1144	$LaCl_3$, La_2Cl_6 + negative ions	$LaCl_3$	[88]
$LnCl_3$ Ln=Ce, Sm	Mo	958-1227	$LnCl_3$, $(LnCl_3)_2$, Sm_3Cl_9 + negative ions	$LnCl_3$	[89]
$PtCl_2$(s) $PtCl_4$(s)	quarz	743-923	Pt_6Cl_{12} Pt_3Cl_3, $PtCl_3$, $PtCl_2$, Cl_2	$PtCl_2PtCl_4$	[90]
Pure metal fluorides					
MF_n M=V, U, Rn, Pt, Tb	Pt, Ni	900-1200	F(g)		[91]

ErF_3(s), TmF_3(s)	C, W	1266-1635	ErF_3, TmF_3	$\underline{ErF_3}$, $\underline{TmF_3}$	[92]
NpO_2F_2	Pt	820-985	NpF_4	$\underline{NpO_2F_2}$	[93]
DyF_3	Pt, Ta, Mo	1280-1440	DyF_3, Dy_2F_6	$\underline{DyF_3}$	[94]
CoF_3	Pt	750, 1022, 1103	CoF_3, CoF_4, F_2, F,	CoF_4^- negative ion $\underline{CoF_3}$	[24]
CoF_3(s)-TbF_4(s) to obtain CoF_4(g) TbF_3(s)	Ni	640-690	CoF_4, CoF_3	Ionization eff. curves	[28]
CoF_3	Ni	723 Isothermalvaporization	F, CoF_3, Co_2F_6	$\underline{CoF_3}$	[27]
MnF_3	Ni	884-1015	MnF_3, Mn_2F_6		[95]
NpF_4(s)	Pt	820-980	NpF_4	$\underline{NpF_4}$	[96]
FeF_3, FeF_3+pieces F	Pt, Ni	980-1222	FeF_3, FeF_2, F		[97]
Ln-F system *Ln*= Sc, Y, La	Two stage Mo	1201-1479	*Ln*F, *Ln*F_2	$\underline{LnF_3}$	[98]
LiF single crystal	Mo	1070-1235	LiF, Li_2F_2 + positive ions	Thermal emission of positive ions	[99]
CoF_3, K_2NiF_6, TbF_4, CeF_4	Ni	580-900	F, F_2, CoF_3, CoF_4, Co_2F_6, CeF_4	$\underline{CoF_3}$,$\underline{CeF_4}$	[25]
BaF_2	Mo	1050-1400	BaF_2/ positive, negative ions		[100]
Thick KF layer on metal substrate (Mo ribbon)	-	670-990	Ions (K^+, F^-, K_2F^+) emitted from the samples		[101]
CoF_3	Pt, Ni/NiF_2	694-778	CoF_3, Co_2F_6, F, F_2		[26]
DyF_3	Pt, Ta, Mo	1280-1441	DyF_3	$\underline{DyF_3}$	[102]
$KPbF_6$		652-736	$KPbF_6$	$\underline{KPbF_6}$	[103]
MF_n *M*=Al, Sc, Ti, V, Cr, Mn, Fe, Zn, Al, U			Negative ionreactions		[104]
Pure metal bromides					
$EuBr_2$(s)	C	1049-1301	$EuBr_2$	$\underline{EuBr_2}$	[105]
$CrBr_3$(s)	Si	773-923	$CrBr_4$, $BrBr_2$, CrBr		[106]
KBr single crystal	Ceramic holder	600-920	Only ions	Ionic sublimation Surface charge Vacancy formation energies	[107]
CsBr(s)	Mo	612-895	CsBr,		[108]

			$(CsBr)_2$, $(CsBr)_3$, $(CsBr)_4$		
KBr single crystals	Ceramic holder	724-918	KBr, K_2Br_2	Kinetic of vaporization	[109]
$DyBr_3$(s)	Mo	803-1053	$DyBr_3$, $(DyBr_3)_2$	$DyBr_3$	[110]
$DyBr_3$(s)	Mo	803-1053	$DyBr_3$, $(DyBr_3)_2$	$DyBr_3$	[111]
Thick KBr layer on metal substrate (Mo ribbon)		700-1000	Thermionic current K^+		[112]
$PrBr_3$	Mo	804-957	ions		[113]
$LaBr_3$	Mo	848-1046	$LaBr_3$, La_2Br_6	$LaBr_3$	[114]
$LuBr_3$	Mo	791-953	$LuBr_3$, Lu_2Br_6, Lu_3Br_9, Lu_4Br_{12}	$LuBr_3$ /negative ions	[115]
$ErBr_3$		815-979	$ErBr_3$, Er_2Br_6	$ErBr_3$/ negative ions	[116]
$LaBr_4$		1007-1157	$LaBr^-$ ion reaction		[117]
LnBr_3 *Ln*= La, Ce, Er, Ho, Lu		850-1150	Electronic work function of congruently sublimic ion crystals		[118]
$GdBr_3$ $TbBr_3$		878-1044 860-1067	$GdBr_3$, Gd_2Br_6, $TbBr_3$, Tb_2Br_6, Tb_3Br_9	$GdBr_3$ $TbBr_3$ / ion reactions	[119]
CeBr, PrBr	Mo	789-994 804-957	$CeBr_3$, Ce_2Br_6, $PrBr_3$, Pr_2Br_6	$CeBr_3$, Ce_2Br_6, $PrBr_3$	[120]
$EuBr_2$	graphite	1049-1261	$EuBr_2$, Eu_2Br_4	$EuBr_2$	[121]
$CeBr_3$ $CeBr_3$singlecrystal	Mo	851-994	$CeBr_3$, Ce_2Br_6	$CeBr_3$	[122]
LnBr_3 *Ln*=La, Ce, Pr, Nd, Gd, Tb, Ho, Er, Tm	Mo	770-1040	$LnBr_3$, $(LnBr_3)_2$	$LnBr_3$	[123]
$LnBr_3$ Ln=Sm, Yb	C		$SmBr_2$, $EuBr_2$, $YbBr_2$, $SmBr_3$, $YbBr_3$	Atomisationenergies,$SmBr_3$, $EuBr_3$, $SmBr_3$, YBr_3	[124]
LnBr_3 (*Ln*=Sm, Yb) *Ln*Br_2 (*Ln*=Sm, Yb, Eu)	Mo, C	850-1300	$YbBr_3$, $YbBr_2$, ,Y_2Br_4, Yb_2Br_5,		[125]

			Yb_2Br_6, YbBr, Yb, $SmBr_3$, $SmBr_2$, Sm_2Br_4,Sm_2Br_5, Sm_2Br_6, $EuBr_2$, Eu, EuBr, Eu_2Br_4, Br, Br_2		
$YbBr_2$, $YbBr_3$	Mo, C	850-1150	Br_2, Br, Yb, YbBr, $YbBr_2$, $YbBr_3$, Yb_2Br_4, Yb_2Br_5,Yb_2Br_6, negative ions		[126]
Various pure metal halides					
LiF, NaCl, KCl, KBr, CsI	Ceramic crystal holder	656-1070	MX, M_2X_2 (M-atom, X-halogen), Li_3F_3	Kineticofthevaporization	[127], [128]
BaF_2, BaI	Mo	Ionization cross section measurement			[129]
DyX_3, X=Cl, Br, I	Mo	1208-1587	Structural parameters and vibrational frequencies		[130]
UCl_4, UBr_4, ThI_4	C	578-730	Torsion effusion	UCl_4, UBr_4, ThI_4	[131]
NaCl, NaBr, NaI, KCl, KBr, KI, RbCl, RbI			Calculatedworkfunctions		[132]
MX (*M*= Na, K, Rb, Cs) (*X*=F, Cl, Br, I)			Work function determination, desorption enthalpies of ions		[133]
Iodides System					
NaI+ErI_3(s)	Ni	898-1016	$NaErI_4$, $Na_2Er_2I_8$	NaI/ErI	[45]
NaI+DyI_3 (l; s+l)		980-1020	NaI, $(NaI)_2$, DyI_3, $NaDyI_4$, Na_2DyI_5	Activities at 1000K	[46]
NaI(s)+ScI_3(s)	C	700-900	NaI, ScI_3, $NaScI_4$, Na_2ScI_5	NaI,ScI_3	[47]
NaI-CeI_3		728-923	NaI, $(NaI)_2$, CeI_3, $NaCeI_4$, Na_2CeI_5		[49]
BaO(s)+I(g) Sc+BaI(s)/CaI_2(s)	Mo/ tandem Mo cell	1458-1777	Ba, Sc, Ca, I, BaI, ScI, CaI		[134]

$NaI-TbI_3$	Ni	765-885	$NaTbI_4$, NaJ, TbI_3, (Na_2TbI_5, $Na_2Tb_2I_8$)		[135]
$GeI_4(g)+Ge(s)$	Steinless steel + Ni chamber	400-780	Research the best conditions for GeI_2 as the main species		[136]
$NaI-PrI_3$	Mo	623-1025	NaI, PrI_3, $NaPrI_4$, $(NaI)_2$, $(PrI_3)_2$, Na_5PrI_5		[137]
$NaI-PrI_3$	Mo	~769-1000	NaI, Na_2I_2, PrI_3, Pr_2I_6, $NaPrI_4$	Activities at 900 K	[138]
$CsI-DyI_3$	Mo	680-960	CsI, $(CsI)_2$, DyI_3, $(DyI_3)_2$, $CsDyI_4$, Cs_2DI_5	Cs_3DyI_6, $Cs_3Dy_2I_9$	[139]
Ln-*Ln*I_3 (*Ln*=La, Ce)	Mo	860-1300	*Ln*I_2, *Ln*I_3, Ln_2I_6, negative ions		[140]
NaI-TlI-InI	W	1000-1600	$NaTlI_2(g)$, $NaInI_2$, $TlInI_2(g)$		[141]
Chlorides systems					
$FeCl_3(s)$ $1FeCl_3$-GIC(s) $2FeCl_3$-GIC (s)	quarz	428-452	Fe_2Cl_6, Cl_2, $FeCl_3$, HCl		[142]
Ti + AgCl	Double chamber effusion cell C with Ti lid	1494-1612	Ti, TiCl, $TiCl_2$, $TiCl_3$, Ag, AgCl		[143]
AgCl(l) Cu-Ni + AgCl Cu, Ag, $+Cl_2$	graphite	800-950 1220-1420	AgCl, Ag_3Cl_3 CuCl		[144]
$ThCl_4(s)$ Th+CaCl	C, Pt, two stage Mo	680-760 1952-2193	$ThCl_4$ $ThCl_2$, CaCl, $ThCl_3$, ThCl, Ca	$ThCl_4$	[145]
NaCl-AgCl		850 (mean temp)	NaCl, Na_2Cl_2, AgCl, Ag_2Cl_2, Ag_3Cl_3, $NaAgCl_2$, Na_2AgCl_3,	NaCl-AgCl(exess molar Gibbs energy, miscibility gaps)	[146]

			$NaAg_2Cl_3$		
LnCl_3-KCl (*Ln*=Nd and/or Er)	Mo	1018-1273	KCl, K_2Cl_2, $NdCl_3$, K*Ln*Cl_4,	$\underline{KNdCl_4}$	[147]
CsCl-*Ln*Cl (*Ln*=Ce, Nd)	Si, Ta	850-1050	CsCl, Cs_2Cl_2, $LnCl_3$, $LnCl_6$, $CsLnCl_4$	$\underline{Cs_3LnCl_6}$	[148]
RbCl, $GdCl_3$ RbCl-$GdCl_3$	Ir	666-982	RbCl, Rb_2Cl_2, $GdCl_3$, $RbGdCl_4$	Activities, $\underline{RbCdCl_6}$	[29]
NaCl-$NdCl_3$	Silica	833-1116	NaCl, $NdCl_3$, $NaNdCl_4$		[149]
CsCl-$CeCl_3$	silica	749-1098	CaCl, Cs_2Cl_2, $CeCl_3$, Ce_2Cl_6, $CsCeCl_4$	Activities, $\underline{CsCeCl_6}$, $\underline{CsCe_2Cl_7}$	[30]
CsCl-$NdCl_3$	Silica, Ta	736-1077	CsCl, Cs_2Cl_2, $NdCl_3$, Nd_2Cl_6, $CsNdCl_4$	Activities, $\underline{Cs_3NdCl_6}$, $\underline{CsNd_2Cl_7}$	[31]
Cs_3CeCl_6, (Cs_3CeCl_6+liquid) region	Mo	1007	No assignment of the ion to the neutral precursor	Activities $\underline{Cs_3CeCl_6}$	[32]
CrOCl/ Cr_2O_3 + Cl_2(g)	Corundum lined C	900-1350	$CrOCl_2$, $CrCl_3$, Cl_2, O_2		[150]
$TiCl_3$-$TiCl_2$ $TiCl_{2.13}$	In reference	533-1090	$TiCl_4$, $TiCl_3$, $TiCl_2$		[151]
NaCl-$CeCl_3$	Silica	919-1046	NaCl, Na_2Cl_2, $CeCl_3$, $NaCeCl_4$		[152]
ACl-$LnCl_3$ (A=Na,Cs; Ln=Pt, Nd)	Silica, Ta	750-1120	ACl, A_2Cl_2, $LnCl_3$, Ln_2Cl_6, $ALnCl_4$		[153]
$FeCl_2$+AlOCl, $FeCl_2$+AlOCl+AlF_3 +KCl	Pt	998-1039	$FeCl_2$, $AlCl_3$, $AlFCl_2$, AlF_2Cl, $AlFCl_3$ + negative ions	Electron affinity $\underline{FeCl_3}$	[34]
$CrCl_3$, $CrCl_3$-Cr	Two section Pt cell	720-860	$CrCl_4$, $CrCl_3$, $CrCl_2$, Cr_2Cl_4	$\underline{CrCl_3}$, $\underline{CrCl_4}$	[154]
$YbCl_3$-$LuCl_3$ $YbCl_3$-$DyCl_3$	Mo	940-1070	*Ln*Cl_3, Ln_2Cl_6 (*Ln*=Yb,Lu,Dy)	$\underline{YbCl_3}$	[155]

			$DyYbCl_6$, $DyLuCl_6$, $YbLuCl_6$		
$ErCl_3$, $ErCl_3$-$DyCl_3$	Mo	969-1097	$ErCl_3$, Er_2Cl_6, Er_3Cl_9, $ErDyCl_6$, $DyCl_3$	$\underline{ErCl_3}$, $\underline{Er_2Cl_6}$, $\underline{Er_3Cl_9}$, /negative ions	[156]
CsCl(s)+$PuCl_3$(s)	Pt	600-850	CsCl	$\underline{CsPuCl_6CsPu_2Cl_7}$	[157]
$CaCsCl_3$	Pt	772-885	CaCl, $(CaCl)_2$	$\underline{CaCsCl_3}$	[158]
$RuCl_3$, $RhCl_3$	quarz	591-724 500-683	Cl_2	MCl_3 + M M= Ru, Rh	[159]
Fluorides system					
Pt-MnF_3 + F_2 Pt-TbF_4	Pt	650-750 800-1200 1080-1230	PtF_4, PtF_2, MnF_4, MnF_3	MnF_3-F, MnF_4, MnF_3 bond energies	[160]
VF_3, FeF_3, AlF_3 + TiF_3, $BaTiF_6$	Ni, Pt	770-1100	TiF_4/ TiF_5^-/ ion molecule equilibria		[161]
CrF_2-ScF_3 CrF_3-UF_4 CrF_3-Cr-ScF_3 CrF_2 CrF_3-VF_3 Cr-CrF_3 CrF_3-FeF_3	Ni, Pt	918-1350	Focused on CrF_4, CrF_3, CrF_2, CrF, FeF_3 /negative ions equilibria		[162]
BF_3+AlF_3/$LiBO_2$	Ni	1002-1131	Negative ion reaction BF_4^-, BF_3(g)		[163]
UC(s), UF_4-Ag +UF_6(g), Ag-Cu + SF_6(g)	C	1091-2405	UF_5, AgF, UF, UF_2		[164]
Zr-ZrF_4 Hf-HfF_4		1147-3040	ZrF_4, ZrF_3, ZrF_2, ZrF, Zr, HfF_4, HfF_3, HfF_2, HfF, Hf	Equilibria reactions	[165]
Cr/CoF_3 +TbF_4	Ni	<920	CoF_3, CoF_4, CrF_4, CrF_5, CrF_6, F_2	$\underline{CoF_4}$	[166]
AlF doped KF + BF_3/PF5		1002	PF_5, BF_3	Negative ions, gas inlet in KC	[33]
NaF-Na_3AlF_6	Ni	974-1090	$NaAlF_4$, NaF, Na_2F^+, AlF_4^- negative ions	Absolute partial pressure of ions in the volume KC	[167]
CeF_4(s)+FeF_3(s)	Prefluorinated Ni	600-1300	FeF_4		[168]
CoF_3-TbF_4	Ni	620-720	CoF_4		[169]

MnF_3+TbF_4	Ni	650-900	MnF_4, F_2, F		[170]
TbT_4(s) CoF_3(s)-TbF_4(s)	Ni	600-720	F, F_2, CoF_4, CoF_3		[171]
KF-K_3AlF_6 (+CeF_3)	Ni	<900	Positive / negative ions		[172]
K_2NiF_6, K_3TbF_7, Cs_2MnF_6, K_2PtF_6	Ni	561-1013	F, F_2, KF, K_2F_2, TbF_4, CsF, Cs_2F_2, K_2PtF_6, K_3TbF_4		[173]
Bromides system					
NaBr-KBr	Quarz glass	750-850	NaBr, KBr, Na_2Br_2, K_2Br_2, $NaKBr_2$	NaBr-KBr (excess molar free Gibbs energy)	[50]
NaBr-$DyBr_3$	Mo	763-1009	NaBr, $(NaBr)_2$, $DyBr_3$, $(DyBr_3)_2$, $NaDrBr_4$, Na_2DyBr_5		[51]
NaBr-$DyBr_3$	Mo	703-1025	NaBr, $(NaBr)_2$, $DyBr_3$, $(DyBr_3)_2$, $NaDyBr_4$, Na_2DyBr_5	3NaBr*$DyBr_3$	[52]
Eu-$EuBr_2$ Eu-Ba-$BaBr_2$ $EuBr_2$-$LaBr_3$		1073-1231	Eu, EuBr, $EuBr_2$, BaBr, $BaBr_2$		[174]
NaBr-$LnBr_3$ Ln=La, Lu	Mo, C	812-1184	NaBr, Na_2Br_2, Na_3Br_3, $NaLnBr_4$, $LnBr_3$, Ln_2Br_6, Na_2LnBr_5		[175]
$LaBr_3$-$LuBr_3$, $CeBr_3$-$LuBr_3$, $PrBr_3$-$LuBr_3$	Mo	942-1155	Negative ionreactions		[14]
Various systems					
NaI-TmI_3 NaBr-$TmBr_3$	PCA	744-1134	Na*X*, Na_2X_2, TmX_3, Tm_2X_6, $NaTmX_6$, AlX_3, $NaAlX_4$ (*X*-halogen)		[48]
NaCl-$SnCl_2$	Mo two	713-963	Na*X*, $(NaX)_2$,		[176]

$NaBr-SnBr_2$	comparment cell	653-893	SnX_2, $NaSnX_3$, (X=Cl, Br)		
UF_4+Cl_2,UF_5+ClF_3, UF_5+Cl_2, UCl_4+F_2,	Pt	<900	UF_3Cl, UF_2Cl_2, UF_4, UF_5, UF_6		[177]
NaBr-NaI	Mo	693-783	NaBr, NaI, Na_2Br, Na_2BrI, Na_2I_2	NaBr-NaI	[178]
MAg_4I_5 (M=K,Rb,Cs) CuCl, CuI, Li_4SiO_4, $Li_{0.2}VO_{2.6}$, $Li_4TiP_2O_9$, $RbCl-GdCl_3$	Mo	500-1400	Ag_3I_3, AgI, MI, M_2I_2, $MAgI_2$, M_2AgI_3, I_2, I, Cu_3Cl_3, Cu_4Cl_4, Cu_5Cl_5,Cu_3I_3, Li, $LiVO_3$, O_2, $MLi(VO_3)_2$, V_2O_4, V_4O_8, V_4O_{10}, $LiPO_3$, $LiPO_2$, PO, P_4, P_3, P_2, P, RbCl, Rb_2Cl_2, $GdCl_3$, Gd_2Cl_6, $RbGdCl_4$, Rb_2GdCl_6		[179]
$SnBr_2-SnI_2$	Mo	473-584	$Sn_2Br_xJ_{4-x}$ (x=0-4), Sn_2Br_4, Sn_2Br_3J, $Sn_2Br_2I_2$,Sn_2BrI_3, Sn_2I_4	Structure and bonding	[180]
$LuCl_3 – LuBr_3$	Mo withgraphiteinsert	913-1104	Ions: $LuCl_4^-$, $LuBr_4^-$, $Lu_2Br_7^-$		[181]
Na-Sn-Br-I	Mo	623-913	NaBr, NaI, $(NaBr)_2$, Na_2BrI, $(NaI)_2$, $SnBr_2$, SnBrI, SnI_2, $NaSnBr_3$, $NaSnBr_2I$, $NaSnBrI_2$, $NaSnI_3$		[53]
$NaX+TmX_3$ X=Br, I	PCA	1200-1600	NaX, Na_2X_2, AlX_3, TmX_3,		[182]

			$NaAlX_4$, $NaTmX_4$, Na_2TmX_5		
ThX_n n= 1-4 UX_m m=1-5*X*=F, Cl, Br, I			Bond dissociacione nergies	$\underline{UF_4}$, $\underline{ThF_4}$, $\underline{UCl_4}$, $\underline{ThCl_4}$, $\underline{UBr_4}$, $\underline{ThBr_4}$, $\underline{ThI}$	[183]
U-F, U-Cl, U-Br, Th-F, Th-Cl, Th-Br, UO_2F_2, NpF_4, NpO_2F_2, Ru-F	Report		UX, UX_2, UX_3, UX_4, UX_5, Th*X*, ThX_2, ThX_3, ThX_4, (*X*-halogen), UF_4, UOF_4, UO_2F_2, UF_5, NpF_4, RuF_4, RuF_3, RuF_2, RuF		[184]
Tc, Re, Ta, W (s) + F_2(g)+ClF_3(g)+O_2(g)	Pt	<1073	TcF_5, TcO_3F, $TcOF_4$, TcO_2F_3, TcO_3Cl, $TcOCl_3$, $TcO_2Cl_{x\ (x=2,3)}$, $TcOF_2Cl$, $TcOFCl_2$, ReF_6, ReO_3F,ReO_2F_3, $ReOF_4$, WF_6, WO_2F_2, WOF_4, WO_2Cl_2,WF_5Cl, TaF_5, $TaOF_3$, $TaOCl_3$, $TaF_xCl_{5-x(x=1,2,3,4)}$		[185]
Ba + *LnX* *Ln*=Sm, Eu, Yb *X*=Cl, Br, I	graphite	1106-1294	SmCl, EuCl, YbCl,SmBr, EuBr, YbBr, SmI, EuI, YbI		[186]
NaBr, CsBr, DyF_3, $DyBr_3$, $SnCl_2$, $SnBr_2$,$DyBr_3$, DyI_3 *AX* – *AY*, $SnBr_2$-SnI_2 *AX*-MX_n SnI_2-ScI_3 Na-Sn-Br-I, *AX*-	Book			$\underline{NaBr}$, $\underline{CsBr}$, $\underline{DyF_3}$, $\underline{DyBr_3}$,*AX* – *AY*, AX-MX_n	[10]

Ln*X*			

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