

Gmelin Handbuch der Anorganischen Chemie

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U Uranium

Supplement Volume C 9

Compounds with Chlorine, Bromine, Iodine

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Compounds with Chlorine, Bromine, Iodine

With 50 Illustrations

by **Cornelius Keller**

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Preface

Between 1960 and 1970 the non-aqueous reprocessing of spent nuclear fuel was considered as an alternative to the well-known PUREX process. Uranium chlorides were involved in two respects:

the separation of uranium and plutonium by chlorination of the fuel oxides, the uranium and plutonium chlorides having different compositions and stabilities;

the separation of uranium, plutonium, and the fission products by extraction from molten chlorides.

As a result, the chemistry and physics of uranium chlorides were thoroughly investigated. However, the bromides and iodides have received much less attention since they have little technological significance. All the hexahalides, UX_6^+ , have special importance in the theory of metal-halide bonding because their octahedral symmetry permits comparison between theory and experiment.

The volume includes the references up to the end of 1977. Some more recent references are also included.

I want to thank Dr. David Brown/Harwell and the Gmelin Institute for their cooperation. Prof. Dr. Becke and Dr. Keim deserve special thanks. Their cooperation could not have been better.

Karlsruhe, June 1979

Cornelius Keller

Table of Contents

	Page
Compounds of Uranium with Chlorine, Bromine, Iodine	1
6 Compounds with Chlorine	1
Introduction	1
6.1 Binary Chlorides	3
6.1.1 Uranium Dichloride UCl_2	3
6.1.2 Uranium Trichloride UCl_3	3
Preparation	3
Physical Properties	4
Chemical Properties	7
6.1.3 Uranium Tetra Chloride UCl_4	13
Preparation	13
Existence and Properties of the UCl_4 Molecule	15
Physical Properties	15
Chemical Properties	21
Hydrates of UCl_4	29
6.1.4 Uranium Pentachloride UCl_5	29
Preparation	29
Physical Properties	30
Chemical Properties	33
6.1.5 Uranium Hexachloride UCl_6	34
Preparation	34
Physical Properties	35
Chemical Properties	37
6.2 Ternary and Polynary Chlorides or Chloro-Complexes	49
6.2.1 Ternary and Polynary Chlorides or Chloro-Complexes of Uranium(III)	49
Preparation	49
Physical Properties	50
Chemical Properties	51
6.2.2 Ternary and Polynary Chlorides or Chloro-Complexes of Uranium(IV)	51
Preparation	51
Physical Properties	53
Chemical Properties	59
6.2.3 Ternary and Polynary Chlorides or Chloro-Complexes of Uranium(V)	59
Preparation	59
Physical Properties	60
Chemical Properties	63
6.3 Oxide Chlorides	67
6.3.1 Uranium(III) Oxide Chloride UOCl	67
6.3.2 Uranium(IV) Oxide Dichloride UOCl_2	67
Preparation	67
Physical Properties	68
Chemical Properties	70
6.3.3 Uranium(V) Oxide Chlorides	70
Uranium(V) Oxide Trichloride UOCl_3	70
Uranium(V) Dioxide Monochloride UO_2Cl	71
6.3.4 Mixed Valence State Oxide Chloride $(\text{UO}_2)_2\text{Cl}_3$	71

	Page
6.3.5 Uranium(VI) Oxide Chlorides	72
Uranium(VI) Oxide Tetrachloride UOCl_4 (?)	72
Uranium(VI) Dioxide Dichloride UO_2Cl_2	72
Preparation	72
Physical Properties	73
Chemical Properties	76
$\text{U}_2\text{O}_5\text{Cl}_2$ (?)	79
6.3.6 Uranyl(VI) Chloride Hydrates and Hydroxide Chlorides	79
Summary	79
Hydrates $\text{UO}_2\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ and $\text{UO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$	79
Preparation	79
Physical Properties	80
Chemical Properties	82
Hydroxide Chlorides of Uranium(VI)	83
Preparation	83
Structure	84
Thermodynamic Properties	84
Spectra	84
Chemical Properties	85
6.4 Ternary and Polynary Oxide Chlorides or Oxochloro-Complexes	90
6.4.1 Uranium(IV) Oxochloro-Complex Cs_2UOCl_4	90
6.4.2 Uranium(V) Oxochloro-Complexes	90
Preparation	90
Physical Properties	90
Chemical Properties	92
6.4.3 Uranium(VI) Oxochloro-Complexes	92
Preparation	92
Physical Properties	94
Chemical Properties	101
6.5 Uranium Perchlorates	105
6.5.1 Uranium(IV) Perchlorates	105
6.5.2 Uranium(VI) Perchlorate and Hydrate $\text{UO}_2(\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$	105
6.6 Uranium(VI) Perchlorato-Complexes	108
6.7 N-Containing Uranium Chlorides	108
6.8 Chloride Fluorides	109
6.8.1 Binary Halides	109
Preparation and Properties	109
6.8.2 Chloride Fluoride Hydrides	111
6.9 Ternary Chloride Fluorides or Chlorofluoro-Complexes	111
7 Compounds with Bromine	113
Introduction	113
7.1 Binary Bromides	113
7.1.1 Uranium Tribromide UBr_3	113
Preparation	113
Physical Properties	116
Chemical Properties	118

	Page
7.1.2 Uranium Tetrabromide UBr_4	120
Preparation	120
The Molecule UBr_4	121
Physical Properties	122
Chemical Properties	125
7.1.3 Uranium Pentabromide UBr_5	127
Preparation	127
Physical Properties	127
Chemical Properties	129
7.2 Ternary and Polynary Bromides or Bromo-Complexes	132
7.2.1 Ternary and Polynary Bromides or Bromo-Complexes of Uranium(III)	132
7.2.2 Ternary and Polynary Bromides or Bromo-Complexes of Uranium(IV)	133
Preparation	133
Physical Properties	134
Chemical Properties	138
7.2.3 Ternary and Polynary Bromides or Bromo-Complexes of Uranium(V)	139
Preparation	139
Physical Properties	139
Chemical Properties	140
7.3 Oxide Bromides	142
7.3.1 Uranium(III) Oxide Bromide UOBr	142
7.3.2 Uranium(IV) Oxide Dibromide UOBr_2	142
Preparation	142
Properties	142
7.3.3 Uranium(V) Oxide Bromides	143
Uranium(V) Oxide Tribromide UOBr_3	143
Uranium(V) Dioxide Monobromide UO_2Br	144
7.3.4 Uranium(VI) Oxide Bromides	145
Uranyl(VI) Bromide UO_2Br_2	145
Uranyl(VI) Hydroxide Bromide $\text{UO}_2(\text{OH})\text{Br}$	146
Uranyl(VI) Bromide Hydrates	146
7.4 Ternary and Polynary Oxide Bromides or Oxobromo-Complexes	149
7.4.1 Complexes Containing Uranium(V)	149
7.4.2 Complexes Containing Uranium(VI)	151
Preparation	151
Physical Properties	151
Chemical Properties	155
7.5 Uranium Nitride Bromides	157
7.6 Mixed Halides Containing Bromine, Chlorine, and Fluorine	158
Summary	158
7.6.1 Trivalent Compounds UBrCl_2 , UBr_2Cl	158
7.6.2 Tetravalent Compounds	159
7.6.3 Mixed Halide Hydrides Containing Bromine	161
7.7 Polynary Mixed Halides or Mixed Halogeno-Complexes	161
7.7.1 Tetravalent Bromochloro-Complexes	161
7.7.2 Hexavalent Bromochloro-Complexes	162

	Page
8 Compounds with Iodine	164
Introduction	164
8.1 Binary Iodides	164
General	164
8.1.1 Uranium Tri-iodide UI_3	164
Preparation	164
Physical Properties	167
Chemical Properties	168
8.1.2 Uranium Tetraiodide UI_4	170
Preparation	170
Physical Properties	171
Chemical Properties	173
8.2 Ternary and Polynary Iodides or Iodo-Complexes	176
Uranium (IV) Iodo-Complexes M_2UI_6	177
8.3 Oxide Iodides	178
8.3.1 Uranium (III) Oxide Iodide UOI (?)	178
8.3.2 Uranium (IV) Oxide Di-iodide UOI_2	178
8.3.3 Uranium (VI) Dioxide Di-iodide UO_2I_2 (?)	178
8.4 Ternary and Polynary Oxide Iodides or Oxiiodo-Complexes	179
Complexes of Uranium (VI)	179
8.5 Iodates and Periodates	180
8.5.1 Compounds Containing Uranium (IV)	180
8.5.2 Compounds Containing Uranium (VI)	180
8.6 Iodato- and Periodato-Complexes of Uranium (VI)	181
8.7 Uranium Nitride Iodide UNI	181
8.8 Mixed Halides Containing Iodine and Another Halogen	182
8.8.1 Trivalent Compounds	182
8.8.2 Tetravalent Compounds	183
Preparation	183
Properties	183
8.8.3 Halide Hydrides	184
8.9 Mixed Halogeno-Complexes	184
Compounds Containing Uranium (IV)	184
Compounds Containing Uranium (V)	184
Compounds Containing Uranium (VI)	185
9 Compounds with Astatine	185
Table of Conversion Factors	186

Compounds of Uranium with Chlorine, Bromine, Iodine

David Brown

Chemistry Division, Atomic Energy Research Establishment, Harwell, England

6 Compounds with Chlorine

Introduction

The known uranium chlorides, oxide chlorides, and mixed halides containing chlorine are listed in Table 6/1 together with examples of chloro- and oxochloro complexes. The pre-1936 studies on uranium trichloride, tetrachloride, pentachloride, uranyl chloride, and related complexes are discussed in the Main Volume "Uran" p. 124/37, 192, 203, 215, 224/34. Only the important aspects of this early work will be dealt with in this Chapter.

*Compounds
with
Chlorine
Introduction*

Table 6/1

Uranium Chlorides, Oxide Chlorides, and Examples of Related Complexes^{1), 2)}.

Valence state	Chlorides	Oxide chlorides	Chloro-complexes	Oxochloro-complexes	Mixed halides containing chlorine
II	UCl ₂ ³⁾				
III	UCl ₃	UOCl	MUCl ₄ · 5 H ₂ O (M = K, Rb, NH ₄) M ₂ UCl ₅ (M = K, Rb, Cs, NH ₄) M ₃ UCl ₆ (M = K, Rb)	—	UBrCl ₂ , UBr ₂ Cl, UCl ₂ I, UClI ₂
IV	UCl ₄	UOCl ₂	M ₂ UCl ₆ (e.g. M = Li-Cs, N(C ₂ H ₅) ₄ , As(C ₆ H ₅) ₄ , P(CH ₃) ₃ H, P(C ₂ H ₅) ₄ , etc.) MUCl ₆ (e.g. M = Ca, Ba, Sr)	Cs ₂ UOCl ₄	UCl ₃ F, UCIF ₃ , UCl ₂ F ₂ , UBrCl ₃ , UBr ₂ Cl ₂ , UBr ₃ Cl, UCl ₃ I, UCl ₂ I ₂ , UCI ₃ , UBrCl ₂ I, UBr ₂ ClI
V	UCl ₅	UO ₂ Cl UOCl ₃	MUCl ₆ (e.g. M = Li-Cs, N(C ₂ H ₅) ₄ , As(C ₆ H ₅) ₄ , etc.) etc.) M ₃ UCl ₈ (M = N(CH ₃) ₄)	M ₂ UOCl ₅ (M = N(C ₂ H ₅) ₄ , As(C ₆ H ₅) ₄ , etc.)	—
V/VI	—	(UO ₂) ₂ Cl ₃	—	—	—

Table 6/1 (Continuation)

Valence state	Chlorides	Oxide chlorides	Chloro-complexes	Oxochloro-complexes	Mixed halides containing chlorine
VI	UCl ₆	UO ₂ Cl ₂ UO ₂ (OH)Cl	—	M ₂ UO ₂ Cl ₄ · 2 H ₂ O (e.g. M = Li-Rb) M ₂ UO ₂ Cl ₄ (M = numerous univalent cations) M(UO ₂) ₂ Cl ₅ (M = Na-Cs, NH ₄) K ₂ (UO ₂) _x Cl _{2x+2} (x = 2, 3, 4) MUO ₂ Cl ₄ · 2 H ₂ O (M = divalent cation) M ₂ (UO ₂ Cl ₄) ₃ · 2 H ₂ O (M = Al, Cr, Fe) M ₂ U ₂ O ₅ Cl ₄ · x H ₂ O (M = Na-Cs) M ₂ U ₂ O ₅ Cl ₄ (M = Na-Cs) M ₂ [(UO ₂) ₄ O ₂ (OH) ₂ Cl ₄ (H ₂ O) ₆] (M = K, Rb, NH ₄) KNa ₂ (UO ₂) ₂ Cl ₇	—

¹⁾ Chlorofluoro-complexes, bromochloro-complexes, and chloroiodo-complexes are listed in Tables 6/43 (p. 112), 7/1 (p. 114), and 8/1 (p. 165), respectively.—²⁾ Uranyl(VI)bromochloro- and chloroiodo-complexes are listed in Tables 7/1 and 8/1, respectively.—³⁾ Only known in a low-temperature matrice.

The extensive investigations undertaken during the Manhattan Project in the early 1940's led to a rapid expansion of knowledge on the preparation and properties of uranium chlorides. The original reports associated with that Project are not all now readily available and references [1 to 9] are recommended for authoritative accounts of various aspects of the investigations. Later reviews dealing with the preparation and properties of uranium chlorine compounds are available in references [10 to 22].

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6.1 Binary Chlorides

*Binary
Chlorides*

Four stable binary chlorides are known: UCl_3 , UCl_4 , UCl_5 , and UCl_6 . In addition the dichloride, UCl_2 , has recently been isolated in low-temperature matrices.

6.1.1 Uranium Dichloride UCl_2

*Uranium
Dichloride
 UCl_2*

Although it has been suggested that UCl_2 is formed by disproportionation of UCl_3 at high temperature or by hydrogen reduction of the trihalide, the evidence for its formation under such conditions is far from conclusive [1 to 3] and it is unlikely that this compound has ever been obtained as a stable phase at room temperature. According to Brewer et al. [4] the thermodynamic constants indicate that it is unlikely that any appreciable concentration can exist in the gas phase.

More recently [5] it has been identified at low temperature in solid matrices of nitrogen as the product of reactions such as:



and



The IR active symmetric (ν_1) and antisymmetric (ν_3) vibrations were recorded at 311 and 295 cm^{-1} , respectively, and from their relative intensities the bond angle in the dichloride was estimated to be 100° ; the estimated U-Cl bond length is $2.55 \pm 0.1 \text{ \AA}$ [5].

The calculated heat of formation of solid UCl_2 is -160 kcal/mole [6].

6.1.2 Uranium Trichloride UCl_3

*Uranium
Trichloride
 UCl_3*

6.1.2.1 Preparation

Preparation

Uranium trichloride was first prepared by Peligot [7] who reduced the tetrachloride with hydrogen at elevated temperature. This reaction has since been studied by a number of researchers [8 to 18]; whilst it proceeds at a satisfactory rate in the range 550 to 575°C at atmospheric pressure the rate is four times as fast at seven atmospheres [11, 14, 16, 18]. It is recommended that the temperature should be maintained below 575°C in the initial stages to prevent formation of liquid tetrachloride which becomes covered by a layer of solid UCl_3 . An attractive, alternative reductant is zinc since the by-product, ZnCl_2 , sublimes from the reaction zone as it forms; the reaction proceeds readily between 500 and 600°C [19 to 25]. The uranium-uranium tetrachloride reaction has also been employed [26]. Although reduction of the tetrachloride with gaseous ammonia [27, 28] or hydrogen iodide [26] has been reported these are less attractive routes to UCl_3 . Similarly the interaction of UCl_4 and UN at high temperature is of little importance [29].

The most satisfactory large-scale preparations of uranium trichloride involve the action of gaseous hydrogen chloride on the finely divided metal or the hydride at 250 to 300°C [3, 8, 30 to 39, 230]. Johnson et al. [30, 31] prepared kilogram amounts by this method, utilising the apparatus described for the tribromide preparation (see p. 115 and Fig. 7-1).

Molten PbCl_2 in KCl apparently oxidises metallic uranium to yield the trichloride [40] but this is not suitable for preparation of the simple salt; in addition, recent studies have shown that PbCl_2 will oxidise the trichloride [41] when present in an excess.

Non-aqueous solutions of the trichloride may be prepared by reduction of UCl_4 by reagents such as LiAlH_4 [42], sodium hydride [43] and sodium naphthalide [44], whilst reduction to U^{III} in aqueous media is readily achieved by, for example, electrolysis [45] or addition of metallic zinc [46].

Although there is evidence for the formation of higher chlorides on sublimation above $\approx 840^\circ\text{C}$ in vacuo, attributed to disproportionation of the trichloride [2, 3, 30, 35, 47], Tarasova and Rachev [48], who have shown that 50 to 70% yields of pure UCl_3 may be achieved by use of Mo or Ta evaporation vessels at $900 \pm 20^\circ\text{C}$, suggest that the problem is interaction of UCl_3 with quartz and/or air rather than disproportionation. Removal of volatile impurities, e.g. UCl_4 [49], is easily done by heating the trichloride at $\approx 750^\circ\text{C}$ in vacuo following which further purification is achieved by converting it to UCl_3I in iodine at 500°C . This mixed halide is appreciably more volatile than the trichloride and on cooling decomposes to yield pure UCl_3 and free iodine [9, 50]. A suitable apparatus for this reaction is shown in Fig. 7-1, p. 115; the first condensation furnace is maintained at 400°C and the second at 300°C . The trichloride iodide decomposes to deposit the trichloride mainly in the 400°C region of the apparatus [9].

Physical Properties

6.1.2.2 Physical Properties

Structural Data

UCl_3 crystallises with hexagonal symmetry in space group $\text{P6}_3/\text{m}$ (Nr. 176)- C_{6h}^2 ; $Z=2$; there is excellent agreement between the various unit cell dimensions determined by X-ray powder crystallography [21, 38, 51], for which the most recent values are $a = 7.440 \pm 0.001$, $c = 4.321 \pm 0.001$ Å [21]. Slightly larger values, 7.469 ± 0.004 and 4.334 ± 0.002 Å, respectively, were obtained during a neutron diffraction study [22, 52], which confirmed the earlier structure proposed by Zachariasen [51] on the basis of X-ray powder data. The nine-co-ordinate, symmetrically tricapped trigonal prismatic configuration is illustrated in Fig. 6-1; the U-Cl bond distances are 2.938 (3) Å to the three capping chlorine atoms and 2.931 (2) Å to the six atoms at the vertices of the trigonal prism. Chains of polyhedra joined on the prism basal faces lie parallel to [001] along the $\bar{c}$ axes and are linked symmetrically to three other chains [22, 52].

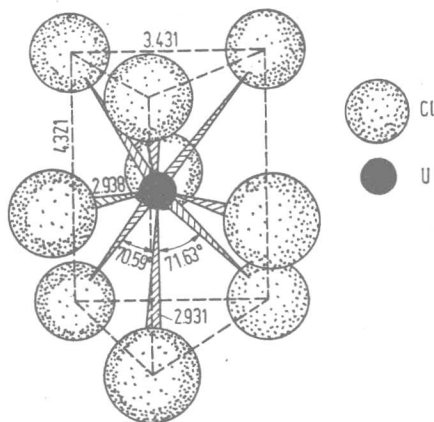


Fig. 6-1

The nine-coordinate symmetrically tricapped trigonal prismatic configuration of chlorine atoms around the uranium atom in UCl_3 (distances in Å) [22].

Mechanical, Thermal, and Thermodynamic Properties

With two molecules per unit cell the calculated density of UCl_3 is 5.52 g/cm^3 ; experimental densities obtained by pycnometric measurements are 5.35 g/cm^3 [12, 30], 5.44 g/cm^3 [56], and 5.02 g/cm^3 [57]. The determinations of the density of molten UCl_3 are not in agreement. Thus,

According to [58, 59] $D = 6.3747 - 1.5222 \times 10^{-3}T$ ($T = 1138$ to 1296 K) whilst [60] reports $D = 11.482 - 7.943 \times 10^{-3}t$ ($t = 946$ to 1031°C). The surface tension is reported to be given by $\sigma \text{ (in mJ/cm}^2\text{)} = 224.7 - 95.7 \times 10^{-3}T$ ($T = 1138$ to 1296 K) and the molar volume at 1123 K is $82 \text{ cm}^3/\text{mole}$ [58]. According to [60] the value is $71.8 \text{ cm}^3/\text{mole}$ at 1115 K.

Recent determinations of the melting point of UCl_3 , which have fallen in the range 1107 to 1144 K [e.g. 41, 61 to 63], are close to those reported earlier [2, 4, 30, 64, 65] and to the value 1100 K recommended by Rand and Kubaschewski in 1963 [66].

Although Altman [2] reported the vapour pressure of the trichloride and the data were subsequently fitted [67] to the empirical equation,

$$\lg p \text{ (p in Torr)} = -12000/T + 10.00 \text{ (from } 873 \text{ to } 1273 \text{ K)}$$

is not clear exactly what the process involved was. Thus, UCl_4 and UCl_5 were observed as intermediates when the trichloride was heated [2] and the "disproportionation pressures" of UCl_3 (to form $\text{UCl}_4(\text{g}) + \text{U}(\text{s})$) reported by Shchukarev [47] and also by Hardy-Grena [35] give the following relationships, respectively:

$$\lg p \text{ (p in Torr)} = -11149/T + 8.90 \text{ (from } 590 \text{ to } 790^\circ\text{C)}$$

$$\lg p \text{ (p in Torr)} = -11552/T + 8.97 \text{ (above } 790^\circ\text{C)}$$

The agreement between these three sets of data indicates that the same process was probably being studied. However, it is not clear whether it was volatilisation of UCl_3 or disproportionation to metallic uranium. Since metallic uranium has not been observed and Tarasova and Rachev [48] have obtained reasonable yields of UCl_3 on sublimation from tantalum evaporators at $\approx 900^\circ\text{C}$. In addition, Rand and Kubaschewski [66] have drawn attention to the discrepancy of 10 kcal/mole between the experimental energies of dissociation [47] and those calculated from known heats and entropies; they suggest that the uranium tetrachloride may arise by interaction of oxygen with the trichloride. Until further data are available the thermodynamic functions calculated on the basis of Altman's data [4, 66 to 69] should be treated with caution.

Information published prior to 1962 on the heat capacity, entropy, heat and free energy of formation of the trichloride [4, 71 to 78] and on the following equilibrium [72, 79, 80]:



has been assessed by Rand and Kubaschewski [66]. The following values were recommended:

$$\text{UCl}_3(\text{s}): \Delta H_f, 298 = -213.5 \pm 2.0 \text{ kcal/mole}; S_{298} = 38.0 \pm 0.2 \text{ cal} \cdot \text{mole}^{-1} \cdot \text{K}^{-1};$$

$$C_{p, 298} = 24.4 \text{ cal} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}; C_p = 20.8 + 7.75 \times 10^{-3}T + 1.05 \times 10^{-5}T^2 \text{ cal} \cdot \text{mole}^{-1} \cdot \text{K}^{-1} \text{ (from } 298 \text{ to } 900 \text{ K)}$$



Moskvin [55] has recently estimated the entropy of solid UCl_3 as $36.7 \text{ cal} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$.

The estimated values for the latent heat and entropy of fusion, the entropy of evaporation and boiling point are, respectively, 11.1 kcal/mole , $10.0 \text{ cal} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$, $23.9 \text{ cal} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$ at 1930 K [66]. Calculated values for the lattice energy (in kcal/mole) are 1014 [53], 1049 [54], 1071 [56].

The early (pre-1963) thermodynamic data obtained for UCl_3 dissolved in LiCl-KCl [81 to 87], $\text{Cl}_2\text{-LiCl-KCl}$ [88], or NaCl-KCl [89] melts by EMF measurements on cells such as, for example, $\text{U}(\text{s}) \mid \text{UCl}_3 \text{ in melt} \parallel \text{AgCl in melt} \mid \text{Ag}(\text{s})$

have been assessed by Rand and Kubaschewski [66] who provide recommended relationships for the standard free energy of the reaction:



These are:

$$\Delta G \text{ (in cal/mole)} = 12600 + 4.575 \lg (N_{\text{UCl}_3}/N_{\text{AgCl}}^3) - 15.9T \text{ (LiCl-KCl melts, } 650 \text{ to } 850 \text{ K)}$$

$$\Delta G \text{ (in cal/mole)} = 7600 + 4.575 \lg (N_{\text{UCl}_3}/N_{\text{AgCl}}^3) - 11.1T \text{ (NaCl-KCl melts } 900 \text{ to } 1100 \text{ K)}$$

Literature to 6.1 see p. 38/49