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**LITERATURE INFORMATION
APPLICABLE TO THE REACTION
OF URANIUM OXIDES WITH
CHLORINE TO PREPARE
URANIUM TETRACHLORIDE**

P. A. Haas

February 1992

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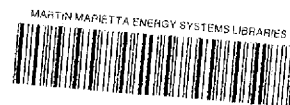
Chemical Technology Division

LITERATURE INFORMATION APPLICABLE TO THE REACTION OF
URANIUM OXIDES WITH CHLORINE TO PREPARE URANIUM TETRACHLORIDE

Paul A. Haas

Date Published: February 1992

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ABSTRACT

The reactions of uranium oxides and chlorine to prepare anhydrous uranium tetrachloride (UCl_4) are important to more economical preparation of uranium metal. The most practical reactions require carbon or carbon monoxide (CO) to give CO or carbon dioxide (CO_2) as waste gases. The chemistry of U-O-Cl compounds is very complex with valences of 3, 4, 5, and 6 and with stable oxychlorides. Literature was reviewed to collect thermochemical data, phase equilibrium information, and results of experimental studies. Calculations using thermodynamic data can identify the probable reactions, but the results are uncertain. All the U-O-Cl compounds have large free energies of formation and the calculations give uncertain small differences of large numbers. The phase diagram for UCl_4 - UO_2 shows a reaction to form uranium oxychloride (UOCl_2) that has a good solubility in molten UCl_4 . This appears more favorable to good rates of reaction than reaction of solids and gases. There is limited information on U-O-Cl salt properties. Information on the preparation of titanium, zirconium, silicon, and thorium tetrachlorides (TiCl_4 , ZrCl_4 , SiCl_4 , ThCl_4) by reaction of oxides with chlorine (Cl_2) and carbon has application to the preparation of UCl_4 .

1. INTRODUCTION

An anhydrous UCl_4 salt has the properties to be an important intermediate chemical for processing and applications of uranium compounds. This was recognized during the World War II program to prepare nuclear weapons; preparation of UCl_4 was studied at that time. These studies showed that uranium tetrafluoride (UF_4) was much easier to prepare and handle than UCl_4 . Also, the uranium fluorides were better than chlorides for gaseous diffusion separation of isotopes and for batch, bomb reductions to uranium metal. Therefore, most of the uranium that has been mined, concentrated, and purified to give uranium ore concentrates (uranium oxides) has been converted to UF_4 .

The use of uranium chlorides in place of uranium fluorides would have important economic advantages. The hydrogen fluoride (HF) and fluorine (F₂) required to prepare the uranium fluorides are expensive chemicals. Processes that use fluorine compounds end up with toxic and troublesome wastes, such as magnesium and calcium fluoride (MgF₂ and CaF₂) and isotopically depleted uranium hexafluoride (UF₆). If uranium chlorides were used, the recycle or reuse of the chlorides is more practical.

The proposed installation of a new industry for enrichment of uranium isotopes could benefit from the economic advantages of using uranium chlorides. The feed to an Atomic Vapor Laser Isotope Separation (AVLIS) process will be uranium metal.¹ The principal production of uranium metal for nuclear fuel cycles has previously been by batch metallothermic reductions of UF₄ using magnesium or calcium metal. For a large enrichment plant ($\geq 10^4$ ton U/year), the costs of the HF feed, the calcium (Ca) or magnesium (Mg) feed, and the disposal of MgF₂ or CaF₂ waste are major parts of the total uranium enrichment costs. Some alternate processes for preparation of uranium metal from UCl₄ allow recycle of Cl₂ from electrolytic cells. The application of these processes requires the reaction of uranium oxides with Cl₂ to prepare UCl₄.

The purpose and scope of this review is to collect, organize, and discuss the literature information useful to the reactions of uranium oxides and chlorine to prepare anhydrous UCl₄. The review is selective in that only one set of consistent and useful results is presented without reference to less useful or inconsistent information. An excellent comprehensive and critical review of the chemistry of uranium was prepared as an account of work and information from the U. S. Manhattan Project.² Such a review for the preparation of UCl₄ will not be repeated here. Well-organized and more complete presentations of thermochemical data for uranium compounds were published by Rand and Kubaschewski in 1963,³ Fuger et al in 1983,⁴ and Barin in 1989.⁵ An assessment of thermochemical data for the system uranium-oxygen-chlorine by Cordfunke and Kubaschewski⁶ illustrates the scatter of individual values, the limits of accuracies, and the dependence on estimated values. Selected values will be listed and discussed in the following sections without detailed reference to these limitations.

2. LITERATURE INFORMATION

The processes of interest for the preparation of the anhydrous UCl_4 are to react the uranium oxide feeds with chlorine (an oxidizing agent) and carbon or carbon monoxide (reducing agents). Oxidation and reduction reactions will take place and all possible uranium oxides, uranium chlorides, and uranium oxychlorides must be considered. Physical properties for these compounds are tabulated (Table 1). A consistent set of thermodynamic data for these uranium compounds is needed to allow calculations to identify the probable reactions. The data for C, CO, and CO_2 as reactants or products and for H_2O and HCl as impurities are included for convenience. Phase diagrams are important as they present useful equilibrium results. Finally, results are reviewed for the reported experimental studies of the reactions of uranium oxides, chlorine, and a reducing agent.

The principal component of a molten salt for a chlorination will probably be UCl_4 . Other physical information reported for UCl_4 includes:⁷

Heat of fusion at 863 K: 44.8 kJ/mol

Free energy of vaporization at 863 K: 218 kJ/mol

Entropy of vaporization at 1062 K: 133 J/mol K

Densities of molten UCl_4 are:

Temperature (°C)	Density (g/cm ³)
590	3.57
600	3.55
650	3.45
700	3.36
750	3.26

The properties, preparation, and chemistry of the uranium chlorides and oxychlorides are comprehensively reviewed by Brown.⁷

2.1 THERMOCHEMICAL DATA

The application for the thermodynamic data is to make calculations at the chlorination reactor conditions. The most useful values are the free energies of formation at 700 to 1100 K. A temperature of 700 K (427°C) is about the lowest temperature of interest for both practical rates of reaction and the use of molten chloride salts. The 1100 K

Table 1. Physical properties of U-O-Cl compounds

Compound	Molecular weight	Density at 298 K, (g/cm ³)	Melting point (K)	Boiling point (K)	Color at 298 K
U	238.03	19.05	1405	4091	Silver gray
UCl ₃	344.39	5.44	1114	1930	Olive-green
UOCl	289.48				Dark red
UCl ₄	379.84	4.87	863	1065	Dark green
UOCl ₂	324.94				Green
UO ₂	270.03	10.96	3110		Brown-black
(UO) ₂ Cl ₅	685.33				
U ₄ O ₉	1096.12	10.9	decom. ^a		Black
UCl ₅	415.30	3.8	~ 600	decom.	Red-brown
UOCl ₃	360.39				Brown
UO ₂ Cl	305.48		decom.		Brown-violet
U ₃ O ₈	842.09	8.30	decom.		Greenish-black
(UO ₂) ₂ Cl ₃	646.42				Black-brown
UCl ₆	450.75	3.5	452	decom.	Black or dark green
UOCl ₄	395.85				
UO ₂ Cl ₂	340.93	5.34	851	decom.	Yellow
UO ₃	286.03	7.29	decom.		Orange-yellow

^adecom. = decomposes without phase change.

(823°C) is above the boiling point of UCl_4 and is near the highest practical temperature. The enthalpies and entropies of formation at reference conditions are available for nearly all the uranium chlorides and oxychlorides, but the high-temperature data is much less complete. The enthalpies and free energies in recent (since 1975) assessments and collections of data are mostly 20 to 30 kJ/mol smaller (less negative) than those listed before 1970. It is probably inconsistent and misleading to use early and recent data together in one calculation.

A recommended set of data for calculations is tabulated (Table 2). This data is from the more recent publications.^{4,5,8-10} Data published for uranium chlorides and oxychlorides before 1975 is not consistent with this more recent data. The significance of and conclusions from the thermochemical data are discussed in Sect. 3.1.

Krahe listed vapor pressure equations as shown in Table 3.¹¹ Calculated values from these equations are shown in Fig. 1. The decomposition of UCl_5 (or UCl_6) into Cl_2 and UCl_4 must be considered; the UCl_5 or UCl_6 are stable only when excess Cl_2 is present.

2.2 PHASE DIAGRAMS

Phase diagrams present equilibrium information in several different ways. With only two components, a composition versus temperature type of phase diagram can show a complete representation of the solid, liquid, and gaseous phases present. The diagram for $\text{UO}_2\text{-UCl}_4$ gives information important to understanding the chlorination behavior. Most of the other two-component phase diagrams for uranium oxides, oxychlorides, and chlorides are not available in published literature. For three components, a triangular diagram can show one variable (usually the liquidus temperature) vs all compositions. A third type of phase diagram can be calculated from the thermodynamic data. The calculations give the equilibrium concentration or solid phases present vs two of the concentrations as variables.

Table 2. Thermochemical data

Compound	$-\Delta_f H^\circ$ at 298 K (kJ/mol U)	S at 298 K (J/mol·K)	Free energy of formation ($-\Delta_f G^\circ$) (kJ/mol)		
			700 K	900 K	1100 K
UCl ₃	862.1	159.0	712.2	670.9	629.7
UOCl	947.3	102.9	836.8	807.2	795(E)
UCl ₄	1018.8	197.23	814.6	762.3	720(E)
UOCl ₂	1069.4	138.32	904.9	863(E)	na ^b
UO ₂	1084.9	77.03	963.5	930.8	897.7
(UO) ₂ Cl ₅	2197.4	326.4	na	na	na
U ₄ O ₉	4510.8	335.93	3972.9	3827.2	3680.1
UCl ₅	1041.4	246.9	816.3	763(E)	na
UOCl ₃	1140.1	169.9	946.8	888.3	835(E)
UO ₂ Cl	1169.4	112.5	na	na	na
U ₃ O ₈	3574.8	282.59	3114.0	2994.3	2874.5
(UO ₂) ₂ Cl ₃	2404.5	276.1	na	na	na
UCl ₆	1068.2	285.8	812(E)	760(E)	na
UOCl ₄	na	na	na	na	na
UO ₂ Cl ₂	1145.8	150.6	1017.7	960(E)	900(E)
UO ₃	1223.8	96.11	1043.0	992.9	942.3
CO	110.53	197.65	173.52	191.42	209.08
CO ₂	393.52	213.80	395.40	395.75	396.00
COCl ₂	220.08	283.80	187.05	177.84	168.66
CCl ₄	95.98	309.81	-1.74	-28.34	-54.56
HCl	92.31	186.90	98.75	100.15	101.43
H ₂ O(g)	241.83	188.83	208.81	198.08	187.03

^a(E) indicates estimated values.

^bThe term "na" indicates that values are not available in any of the known references.

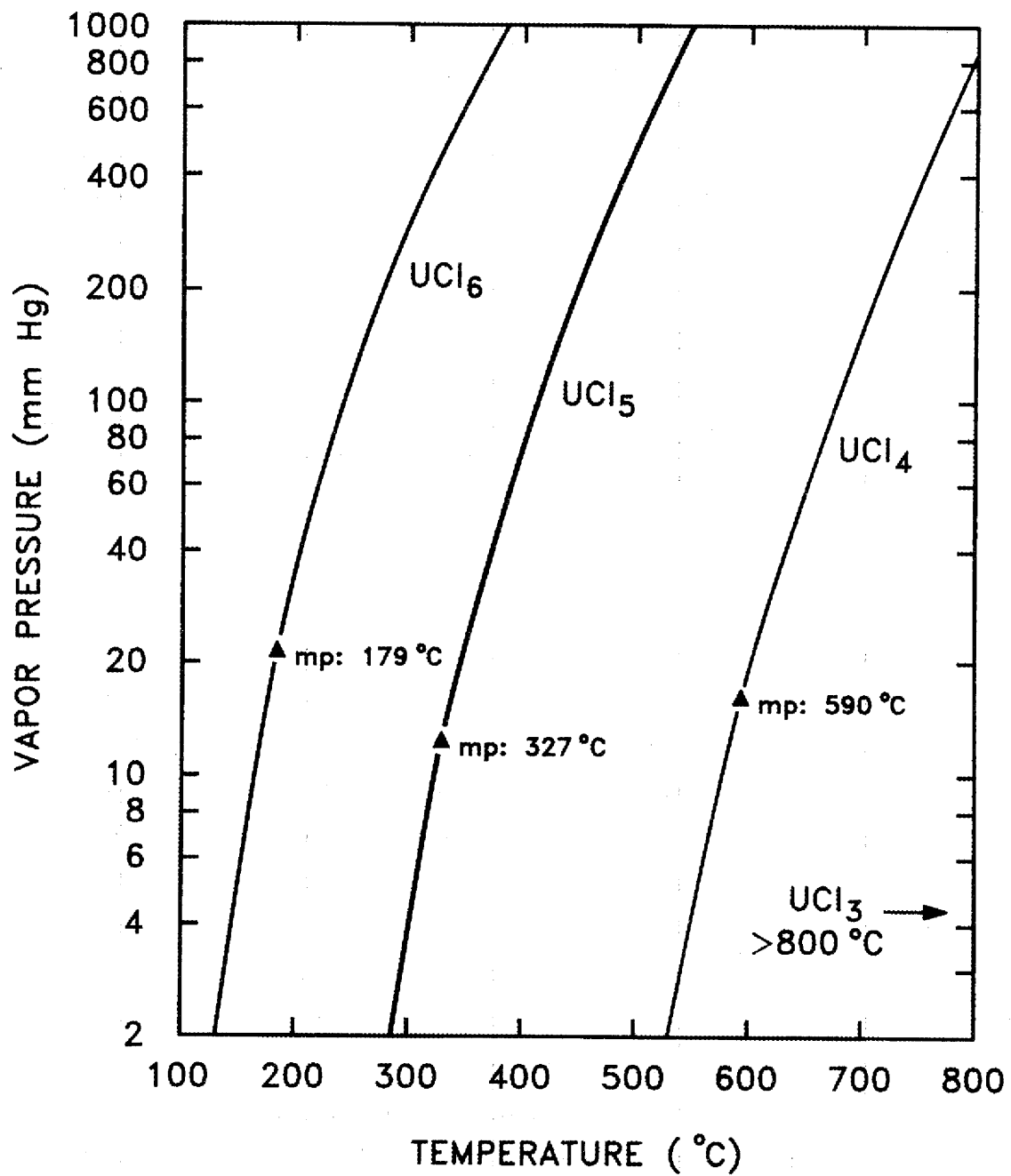


Fig. 1. Vapor pressures of uranium chlorides.

Table 3. Vapor pressure equations^a

Compound	A	B	C	Temperature (K)
UCl ₃ (s)	19.224	15,760	3.02	298 - 1110
UCl ₃ (l)	24.044	14,340	5.03	1110 - 1950
UCl ₄ (s)	20.329	11,350	3.02	298 - 863
UCl ₄ (l)	26.079	9,950	5.53	863 - 1062
UCl ₅ (s)	21.810	7,450	4.03	298 - 600
UCl ₅ (l)	26.027	6,210	6.29	600 - 800
UCl ₆ (s)	22.317	4,765	5.03	298 - 453
UCl ₆ (l)	26.120	4,060	7.04	453 - 650

$$^a \log P_{\text{atm}} = A - B/T - C \log T.$$

The phase relationships between tetravalent uranium oxide and chloride are shown in Fig. 2.¹² The phase diagram shows that there are three stable compounds over the entire range of composition—UCl₄, UOCl₂, and UO₂. There is a eutectic reaction between UCl₄ and the intermediate compound, UOCl₂. The melting point of pure UCl₄ is 590°C. A minimum melting point of 545°C occurs at the eutectic composition of UCl₄ + 6.9 mol % UO₂. A maximum solubility of about 13 mol % UO₂ in molten UCl₄ is reported at 810°C. At temperatures from 810 to 855°C, UCl₄ vapor is in equilibrium with solid UOCl₂. UOCl₂ decomposes at 855°C. At higher temperatures, vapor and solid UO₂ are in equilibrium. This phase diagram suggests practical limitations on the useful chlorination conditions and will be discussed further in this respect (Sect. 3.2).

A phase diagram with the Cl/U atom ratio as the concentration variable shows the melting points of the uranium chlorides and their eutectics (Fig. 3).¹¹ This diagram is a series of binary diagrams for U-UCl₃-UCl₄-UCl₅-UCl₆ as no more than two of these compounds can be present in equilibrium.

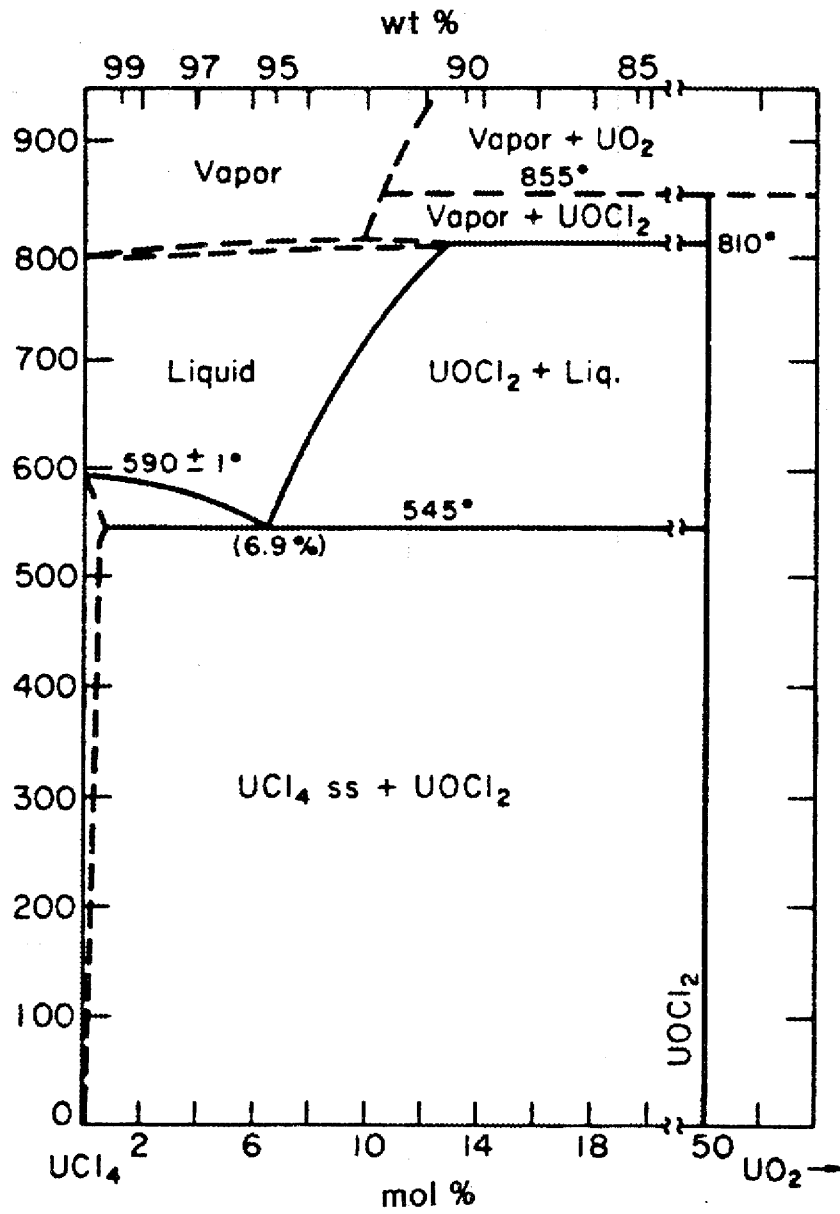


Fig. 2. Phase diagram for UCl_4 - UO_2 .¹²

For reasons discussed in Sect. 3.2, a ternary mixture of $\text{UCl}_4\text{-MgCl}_2\text{-NaCl}$ might be the preferred melt for reaction of UO_2 , Cl_2 , and C. While this ternary diagram has not been determined, the three binary diagrams ($\text{UCl}_4\text{-MgCl}_2$, $\text{UCl}_4\text{-NaCl}$, $\text{MgCl}_2\text{-NaCl}$) have been published.¹³ These binary diagrams give the liquidus temperatures for the three sides of a ternary $\text{MgCl}_2\text{-NaCl-UCl}_4$ phase diagram. The three binary diagrams are simple, and simple liquidus curves for the ternary are very probable. Estimated curves were drawn (Fig. 4) with shapes similar to those for other published ternary diagrams. These curves are derived from the binary data and should be considered interpolations between them instead of extrapolations.

An important use of thermochemical data is to calculate the equilibrium compositions at specified temperatures. Uranium has five major valences (0, 3, 4, 5, 6) and also has some stable compounds of apparent intermediate valences (4.5, 5.33, 5.5). Only two of the major valences can be in equilibrium at a specified condition. Uranium and chlorine give a series of compounds (U , UCl_3 , UCl_4 , UCl_5 , UCl_6). Each composition from $\text{Cl/U}=0$ to $\text{Cl/U}=6$ will have an equilibrium overpressure of Cl_2 gas. These equilibrium concentrations can be calculated from thermodynamic data. They can be conveniently represented by equations with temperature as a variable and do not require phase diagrams. The melting points and eutectics were shown in Fig. 3.

Thermochemical data can also be used to calculate equilibrium compositions for the U-O-Cl system. Because of the multiple valences of uranium and the formation of oxychlorides, over twenty U-O-Cl compounds are possible. At least seventeen of these compounds have been reported experimentally.⁶ The results can be presented as diagrams showing the composition of the solid phase with a specified temperature as a constant and two gas activities (Cl_2 and O_2 or CO) as the variables. A result of interest for the chlorination of UO_2 to UCl_4 is reported by Krahe (Fig. 5).¹¹ Chlorine pressures near 1 atm give a melt that consists of UCl_4 and UCl_5 . UCl_4 is the stable composition for a wide range of both Cl_2 and CO (or O_2) concentrations. Krahe's result looks very good with respect to utilization of Cl_2 and the formation of UCl_4 as the product. Cordfunke discusses the U-O-Cl phase calculations and the limitations from the precision of the data.⁶ He shows that small differences in the data can cause phases to appear or disappear from the calculated results. He estimates a need for 0.25% precision for enthalpies and 1% for entropies. The data for uranium oxychlorides is probably not this good. The poor

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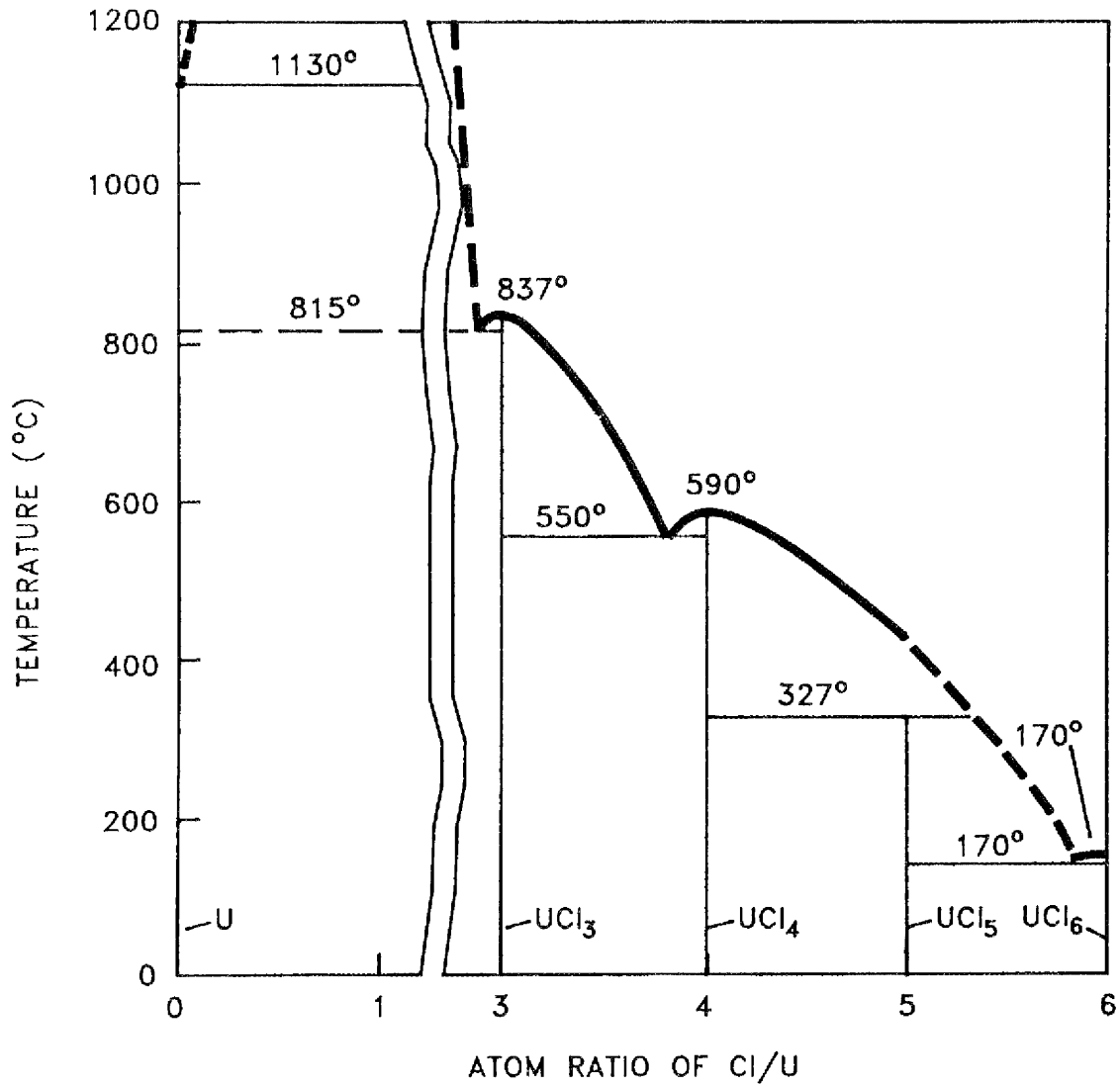


Fig. 3. Phase diagrams for the compounds of uranium and chlorine.⁷

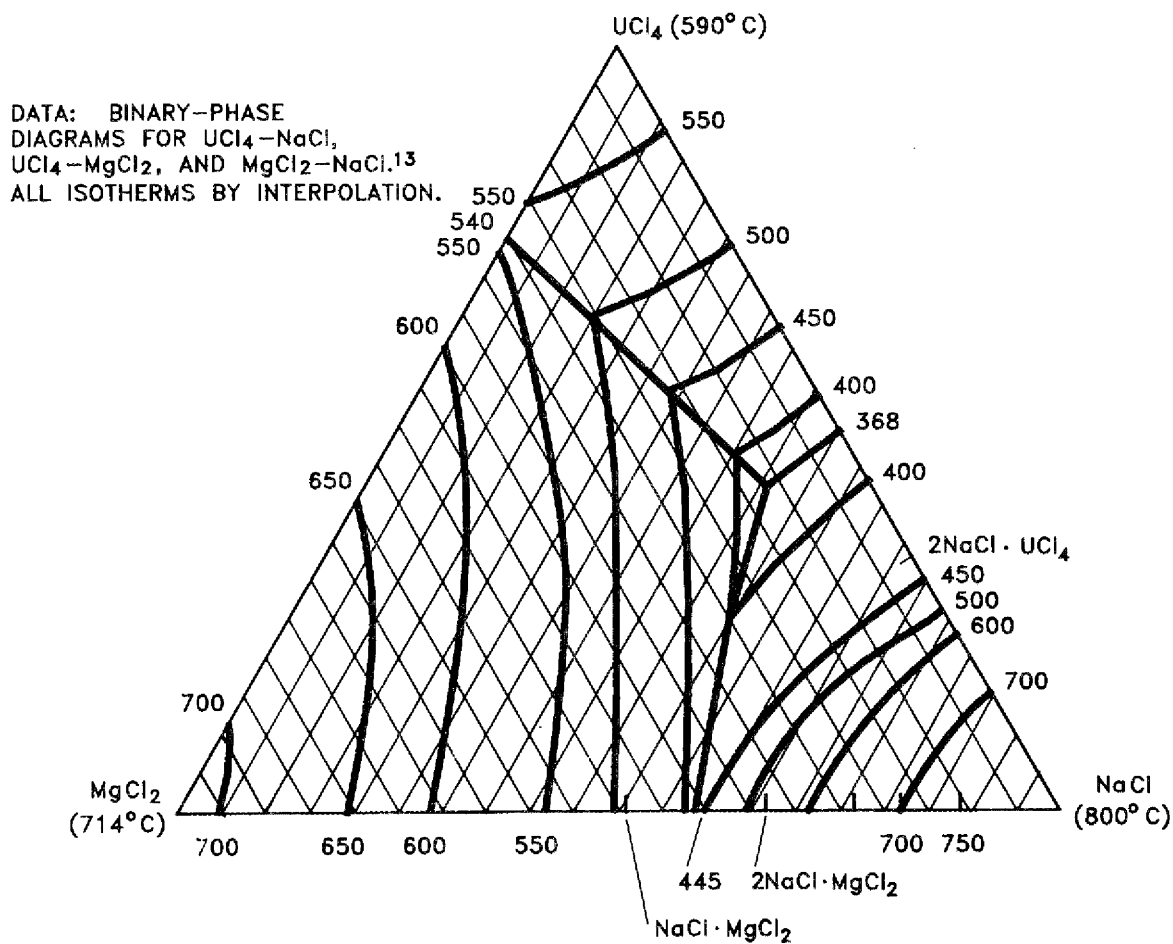
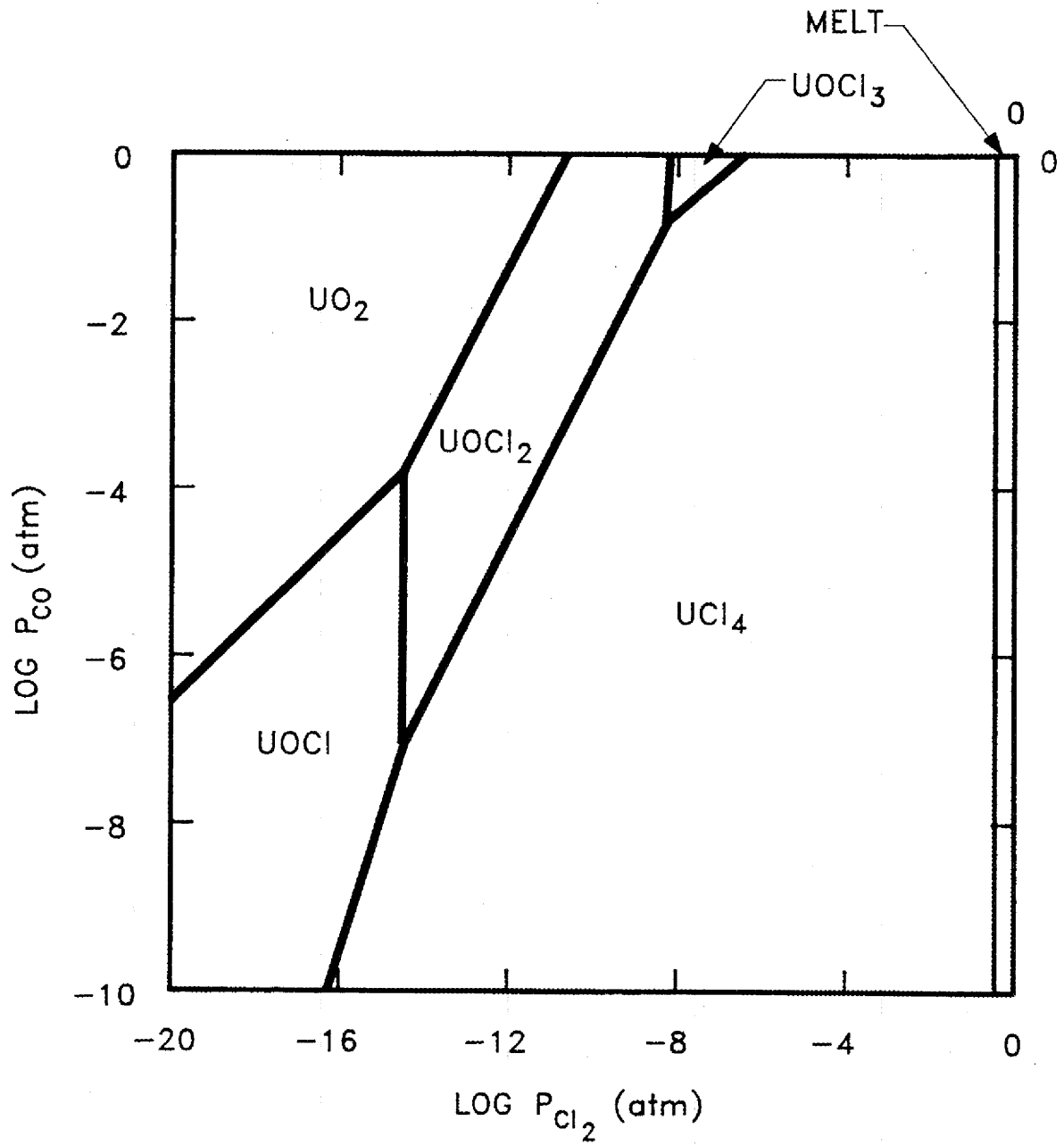


Fig. 4. Liquidus temperatures ($^{\circ}\text{C}$) for $\text{UCl}_4\text{-MgCl}_2\text{-NaCl}$.

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Fig. 5. Diagram for log P_{CO} vs log P_{Cl₂} at 400°C.¹¹

information on the composition or chemical purity of the samples that were used is an important source of error. Cordfunke gives three phase diagrams for O_2 and Cl_2 pressures as the concentration variables to illustrate the effects of small differences in data.⁶ Krake gives over twenty calculated results with gas concentrations, temperature, and the activity of carbon or CO as variables.¹¹

2.3 EXPERIMENTAL RESULTS FOR REACTIONS OF CHLORINE WITH URANIUM OXIDES

A search of technical literature did not reveal any significant reports for the preparation of pure UCl_4 from reaction of uranium oxides with Cl_2 and C or CO. There is extensive literature on the production of UCl_4 by reaction of carbon tetrachloride (CCl_4) with uranium oxides.^{2,14} One such process was used at Oak Ridge for producing calutron feed for isotope separations. The CCl_4 cannot be produced by a simple reaction of C with Cl_2 . Therefore, the reactions of CCl_4 with uranium oxides do not provide efficient overall reactions of Cl_2 to prepare UCl_4 .

There are many literature descriptions concerning the reactions of chlorine with uranium oxides. Some of these were intended to produce uranium chlorides with some results for carbon as a reactant and CO_2 or CO as products. Experiments using chlorine gas feed to graphite distributors immersed in molten salts showed good rates of reaction of Cl_2 . These graphite distributors provide a carbon source of relatively low-surface area and reactivity, and the rates of formation of CO and CO_2 are much better than might be expected. Canning demonstrated nearly complete utilization of Cl_2 for up to 90% chlorination of uranium oxides in NaCl-MgCl₂ at 700 and 800°C.¹⁵ Analyses indicate 80 to 85% UCl_4 and 15 to 20% UCl_5 at the end of chlorination. Gibson claims a similar result with all the uranium soluble in the NaCl-KCl melt at the end of chlorination.¹⁶ Gens studied the volatilization of uranium chlorides from nuclear fuels and appeared to find the formation of some non-volatile UO_2Cl_2 .¹⁷ Lyon reported rapid reactions of uranium oxides in molten NaCl-KCl at 850°C with Cl_2 to give UO_2Cl_2 .¹⁸

The reactions of uranium oxides with CCl_4 have been more carefully studied than the reaction with Cl_2 and C or CO. Since the free energy of formation of CCl_4 is positive above 415°C, the use of CCl_4 above this temperature is somewhat thermodynamically

equivalent to use of C and Cl_2 . Budayev provides good thermodynamic analyses and experimental results of reactions with CCl_4 .¹⁴ Reaction products at 200 and 300°C were UO_2 and UCl_4 . Reaction products at 400 to 700°C included UO_2 , UCl_4 , UOCl_3 , UOCl_2 , and $\text{U}_2\text{O}_3\text{Cl}_3$. The experimental results showed stepwise reaction with many intermediate products, including CO, COCl_2 , Cl_2 , and all the uranium oxychlorides.

Gens reported that the U_3O_8 treated with $\text{CCl}_4\text{-Cl}_2$ is first converted to UO_2Cl_2 and is then further reacted to give UCl_4 , UCl_5 , and UCl_6 .¹⁹ Jangg found high conversions to volatile UCl_4 and UCl_5 at 700 to 900°C using CCl_4 while Cl_2 gave mostly UO_2Cl_2 .²⁰

Katz and Kabonowitch published an excellent review of the literature on the chemistry of uranium up through 1946.² The overall results for preparation of uranium chlorides indicate the following conclusions:

1. There were no complete and practical conversions of UO_2 to pure UCl_4 by reactions with chlorine and C or CO.
2. UO_2 was clearly the preferred uranium oxide feed. Uranyl compounds were much less reactive. Higher oxides, such as U_3O_8 and UO_3 , gave larger amounts of UCl_5 as compared to the UCl_5 yield from UO_2 at similar conditions.
3. The conversion of UO_2 to UOCl_2 appears to liberate more energy than the conversion of UOCl_2 to UCl_4 . Therefore, an incomplete conversion is likely to leave large amounts of UOCl_2 instead of unreacted UO_2 and UCl_4 .
4. The first reported preparation of UCl_4 was by the reaction of a $\text{UO}_2\text{-C}$ mixture with Cl_2 gas. The major disadvantages were the major yield of UCl_5 , the high reaction temperature, and the phosgene in the waste gas.
5. The reaction of UO_2 with CCl_4 proceeds at lower temperature and gives less UCl_5 and phosgene than UO_2 with C and Cl_2 . Common conditions were 350 to 450°C in CCl_4 vapor or 150 to 250°C in liquid CCl_4 under pressure.
6. Phosgene (COCl_2) was an effective reagent at temperatures of 450°C or higher.
7. The higher chlorides (UCl_5 , UCl_6) are formed when the higher oxides (U_3O_8 , UO_3) are converted to chlorides and are also formed by reaction of UCl_4 with Cl_2 .

3. DISCUSSIONS AND CONCLUSIONS

The application of literature information to plan a development program for UCl_4 preparation is given here. The use of thermodynamic data is the logical first step, but has important limitations. The experimental results reported in the literature show reactions of chlorine and uranium oxides with little information on what reactions are occurring. The chemistry and preparation of TiCl_4 , ZrCl_4 , ThCl_4 , and SiCl_4 have important similarities to those of UCl_4 . Therefore, references for preparation of these compounds are reviewed as sources of information applicable to UCl_4 .

3.1 THERMOCHEMICAL CONSIDERATIONS

Uranium dioxide is one of the most stable metal oxides and has a larger free energy of formation than UCl_4 . This means that many of the reactions that might convert UO_2 to UCl_4 are thermodynamically unfavorable. The displacement of the oxygen in UO_2 by reaction with Cl_2 is not practical. While the rate of reaction of UCl_4 with air is low at room temperature, the thermodynamic equilibrium is a high ratio of Cl_2/O_2 in the gas. At 225°C or higher, UCl_4 reacts with air to release Cl_2 .

The practical conversion of UO_2 to UCl_4 by a chemical reaction requires a reducing agent which yields an oxide product that is more stable than the chloride (i.e., it does not react with UCl_4). Carbon and carbon monoxide meet this criteria. Both have large free energies of formation while CCl_4 has a zero value at about 415°C and decomposes thermally at higher temperatures. Hydrogen oxide and hydrogen chloride are about equally stable, and the oxide (water) reacts with uranium chlorides to form HCl and UOCl_2 or UO_2 . The equilibrium pressure of H_2O over UO_2 in HCl gas is very small, and conversion to UCl_4 by countercurrent treatment of UO_2 with HCl (as used to prepare UF_4 using HF) is completely impractical. For the same reasons, UCl_4 prepared in aqueous solutions cannot be dehydrated to anhydrous UCl_4 . Thermal or other treatments give removal of HCl leaving UO_2 or UOCl_2 as the product.

Thermodynamic calculations are a logical first step to identifying the probable chemical reactions for conversion of UO_2 to UCl_4 . The use of thermochemical data does not identify the probable reactions with any certainty or degree of confidence. There are

several major causes of uncertainty. Uranium chemistry is complex with stable valences of 3, 4, 5, and 6, and with stable oxychlorides. UO_2Cl_2 and UOCl_2 are well known compounds and others are possible. All of the possible products must be considered. The uranium chlorides are more volatile with increasing valence, but UCl_5 and UCl_6 are less stable with increasing temperature and decreasing Cl_2 partial pressure. All of the uranium compounds have large heats of formation, and calculating the free energy of these reactions usually results in a small difference from two large numbers. Small percentage uncertainties for the large numbers give large uncertainties for the differences.

The relationships between the U-O-Cl compounds can be illustrated by a matrix listing. Data are available for heats and entropies of formation at 298 K for nearly all of these compounds (Tables 2 and 4). The free energies of formation at 900 K would allow more realistic and useful calculations. However, because the free energy of formation data at high temperatures is much less complete, this matrix listing contains less certain or estimated values (Table 5).

Table 4. Heats of formation for U-O-Cl compounds at 298 K

Valence	- (Heats of formation), kJ/mol U			
	All Cl	One O	Two O	>Two O
0	U^a	U	U	U
3	UCl_3 862.1	UOCl 947.3		
4	UCl_4 1018.8	UOCl_2 1069.4	UO_2 1084.9	
4.5		$(\text{UO})_2\text{Cl}_5$ 1098.7		U_4O_9 1127.7
5	UCl_5 1041.4	UOCl_3 1140.1	UO_2Cl 1169.4	
5.33 or 5.5			$(\text{UO}_2)_2\text{Cl}_3$ 1202.3	U_3O_8 1191.6
6	UCl_6 1068.2	UOCl_4 ~ 1140	UO_2Cl_2 1145.8	UO_3 1223.8

^a $\Delta_f H^\circ = 0$.

Table 5. Free energies of formation for U-O-Cl compounds at 900 K (627°C)

Valence	- (Free energy of formation), kJ/mol U			
	All Cl	One O	Two O	>Two O
0	U	U	U	U
3	UCl ₃ 670.9	UOCl 807.2		
4	UCl ₄ 762.3	UOCl ₂ 863	UO ₂ 930.8	
4.5		(UO) ₂ Cl ₅ 880 (Est.)		U ₄ O ₉ 956.8
5	UCl ₅ 763	UOCl ₃ 888.3	UO ₂ Cl 960 (Est.)	
5.33 or 5.5			(UO ₂) ₂ Cl ₃ 990 (Est.)	U ₃ O ₈ 998.1
6	UCl ₆ 760	UOCl ₄ 900 (Est.)	UO ₂ Cl ₂ 960	UO ₃ 992.9

The complexity of the uranium conversion chemistry is partly shown by a diagram giving the free energies of the simple oxidation and reduction reactions (Fig. 6). This diagram was simplified by omitting the compounds of U(4.5) and U(5.5) valences. It also does not show the reactions of two U-O-Cl compounds to give a third U-O-Cl compound. The reductions are shown for $\frac{1}{2}\text{C}$ to $\frac{1}{2}\text{CO}_2$. Similar conclusions would apply for C to CO or CO to CO₂ as the three free energies are 197.9, 191.4, and 204.3 kJ at 900 K. The three free energies are equal at 973 K (700°C), and the probable products from carbon are CO₂ below 700 K and CO at higher temperatures.

Some general conclusions from examinations of Tables 4 and 5 and Fig. 6 are:

- At a given valence state, the uranium oxchlorides are more stable than the chlorides.
- At a given valence state, the uranium oxides are more stable than the chlorides.

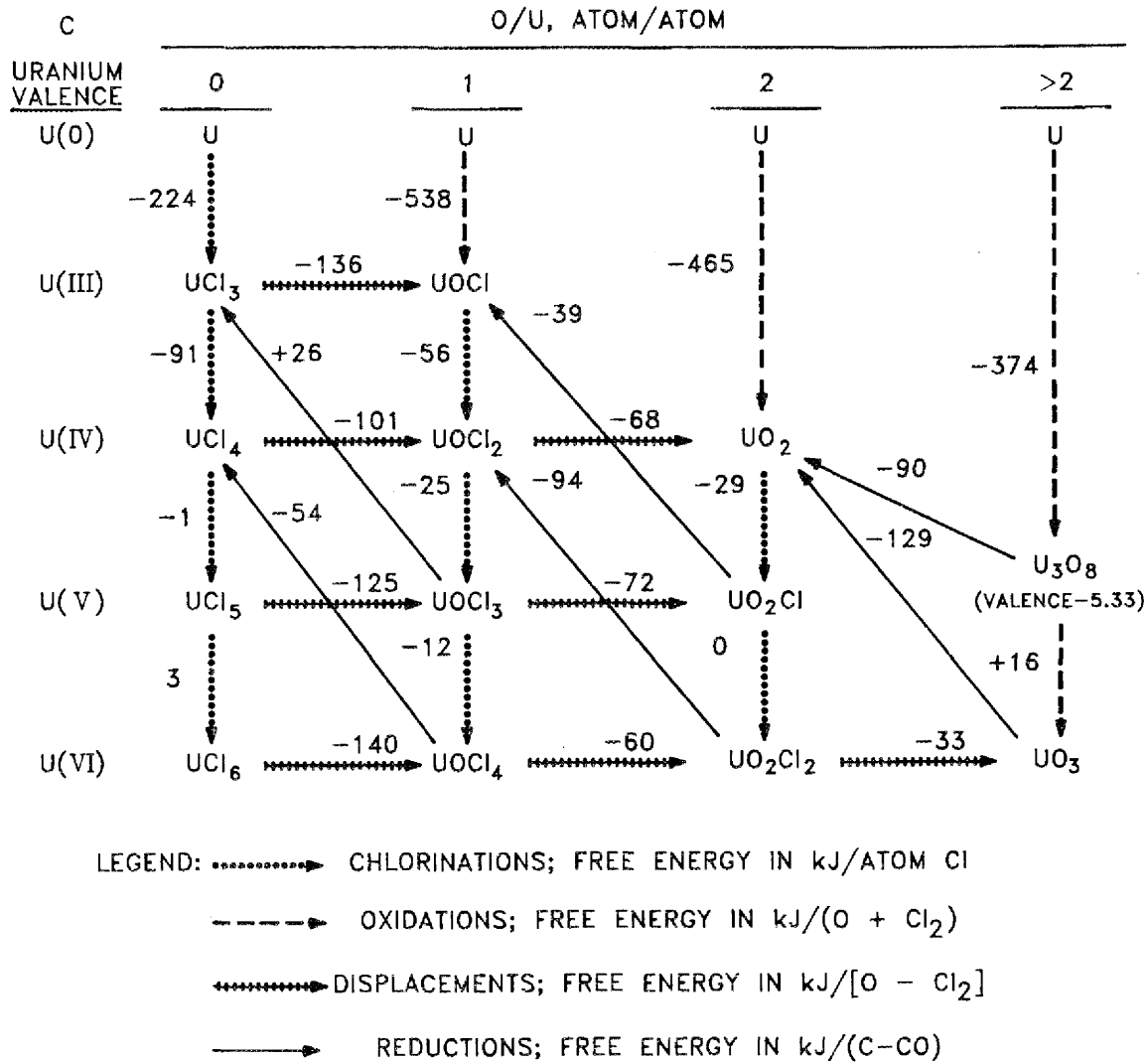


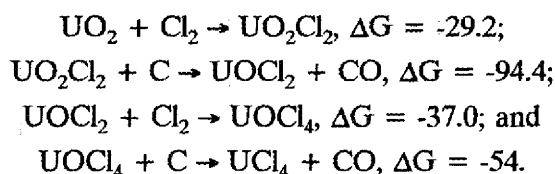
Fig. 6. Conversion reactions for U-O-Cl compounds and free energies at 900 K.

- All additions of chlorine to oxides or oxychlorides of lower valence [less than U(VI)] are favorable to yield oxychlorides of higher valence.
- The oxychlorides can be formed by both direct reaction of chlorine and by reaction of a uranium chloride with an oxide or oxychloride.

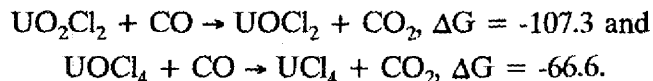
Since oxychlorides are the intermediate compounds for conversion of UO_2 to UCl_4 , their stability can be of critical importance to complete conversions. A conversion may appear favorable overall, but one of the steps for the intermediate may be much less favorable. For example, consider the following overall reaction:



At 900 K, $\Delta G = -214.3$ kJ, but individual steps show:



These numbers indicate that the reactions should take place, but older data indicate they could stop at UO_2Cl_2 or UOCl_4 . If using CO to give CO_2 as the product is considered, then the two reduction reactions change to:

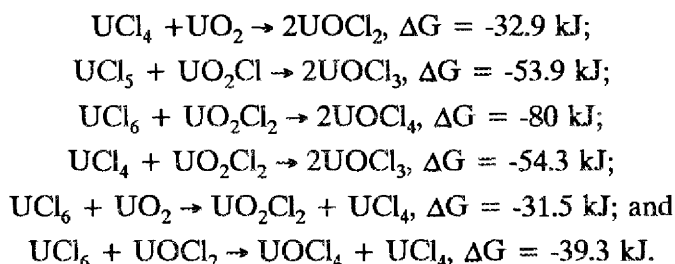


The uncertainties for $\Delta_r G^\circ$ values of UO_2Cl_2 and UOCl_4 may be larger than the above ΔG values, so it is difficult to be certain that the reactions are thermodynamically favorable. The more favorable calculation for CO as compared to C may also be misleading. The C would be present as a solid with a thermodynamic activity of 1, while CO would be mixed with other gases and would have a lower activity for 1 atm total pressure.

Many of the reactions to change between the U-O-Cl compounds are shown in Fig. 6. Large values for the negatives of the free energies of reaction (kJ/equiv at 900 K) show reactions that are thermodynamically favored. Positive values in Fig. 6 indicate that the

reactions are not thermodynamically favorable. The data for the oxychlorides are uncertain, and values ranging from -20 to +20 kJ do not justify predictions. The formation of UCl_5 and UCl_6 appears to require excesses of Cl_2 and will not be complete. Otherwise, all additions of Cl_2 are favorable, and oxychlorides should add chlorine to give UO_2Cl_2 or UOCl_4 . The reductions of UO_3 or U_3O_8 to UO_2 are highly favorable. The reduction of UOCl_3 to give UCl_3 is unfavorable. Some of the other reactions give free energies of reaction that are too near zero to justify predictions. A practical preparation of UCl_4 probably requires that the chlorinations to U(VI) and the reductions of UO_2Cl_2 and UOCl_4 be possible since the intermediates would otherwise accumulate as stable products.

The equilibrium mixture among the uranium compounds for normal operation of a chlorination reactor will always be UCl_4 and uranium oxychlorides containing one oxygen. The feed of UO_2 will be limited to prevent excessive solids; therefore, O/U ratios will be much less than one. Because of the lower stability of the chlorides as compared to the oxychlorides, any uranium compounds containing two oxygens will react with a uranium chloride to form two oxychlorides with one oxygen in each. Any U(VI) or U(V) will be much more stable as oxychlorides than as UCl_6 or UCl_5 . Therefore, the amounts of UCl_5 and UCl_6 will be small unless the moles of U(VI) and U(V) exceed the moles of oxychlorides. Some of the reactions and their free energies at 900 K are:



The first five reactions indicate that the uranium chlorides will react to give oxychlorides. The first four show that an oxychloride containing two oxygens will react with uranium chlorides to give two oxychlorides. The last two show that UCl_6 will react with a U(IV) oxychloride to give UCl_4 and an U(VI) oxychloride.

3.2 SELECTION OF CHLORINATION CONDITIONS

One feed material must be the uranium oxides from ore refineries. Recycling considerations to eliminate large amounts of waste require the use of Cl_2 gas from electrolytic cells.

Thermochemical data show larger free energies of formation for uranium oxides than for chlorides of the same valence. Therefore, the overall reaction must include a reducing agent that has a much more stable oxide than chloride. Carbon or carbon monoxide are the most practical reducing agents that meet this requirement. Hydrogen (as H_2 or hydrocarbons) does not meet this requirement since H_2O will react with uranium chlorides to form HCl . Sulfur and phosphorus (and some of their compounds) can meet this thermochemical requirement, but they are expensive feeds and give troublesome waste oxides in comparison to carbon.

The overall reaction from the above considerations shows one or two solids (uranium oxides, C) and gaseous feed (Cl_2 , perhaps CO) and a gaseous product (CO_2 or CO). Even with stepwise reactions, the reactions between two phases with one of them a solid tend to be slow or incomplete. The phase diagram for UO_2 and UCl_4 (Fig. 2) shows several indications toward practical conditions for conversion of UO_2 into UCl_4 . The use of a liquid melt with reaction of UO_2 and UCl_4 to give $UOCl_2$ in solution appears favorable to high rates of reaction. Then the Cl_2 and carbon can react with the $UOCl_2$ or other oxychlorides in solution. The Cl_2 can also react with UCl_4 to give UCl_5 or UCl_6 as soluble chlorinating agents in the melt.

Both the temperature and the fraction of UO_2 in the charge must be limited to maintain the desirable liquid melt condition. All of the UO_2 reacts with UCl_4 to form $UOCl_2$ and any $UOCl_2$ above the solubility is present as solids. An equimolar mixture of UO_2 and UCl_4 gives all $UOCl_2$ solids without any melt. Since C will also be a solid, the preferred concentration to ensure a fluid melt will be less UO_2 than the solubility limit (from 6.9 mol % at $545^\circ C$ to about 13 mol % at $810^\circ C$). The preferred temperatures will be intermediate between the melting point and boiling point of UCl_4 (590 to $792^\circ C$). The vapor pressure of UCl_4 is also an important consideration.

The addition of a diluent salt to the melt would relax some of the composition and temperature limits indicated by the UCl_4 - UO_2 phase diagram. The diluent salt should be unreactive with the carbon, Cl_2 , UO_2 , and UCl_4 , should have a low volatility at 600 to $800^\circ C$, and should melt below $600^\circ C$. An equimolar mixture of $MgCl_2$ - $NaCl$ meets these requirements better than any single salt. Mixtures of $MgCl_2$ - $NaCl$ are commonly used for electrolytic production of Mg and Cl_2 and have good properties.

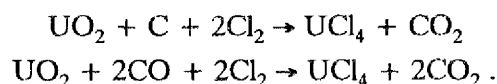
There are no published phase diagrams for UCl_4 - UO_2 - $MgCl_2$ - $NaCl$ or for any ternary mixtures of these components. However, reasonable liquidus temperatures and UO_2

solubilities can be estimated from four binary phase diagrams. Binary diagrams for $\text{MgCl}_2\text{-NaCl}$, $\text{MgCl}_2\text{-UCl}_4$, and NaCl-UCl_4 ¹³ can be used to give liquidus temperatures for the three sides of a ternary $\text{MgCl}_2\text{-NaCl-UCl}_4$ phase diagram. The three known binary diagrams are all simple and simple liquidus curves for the ternary are very probable. Estimated curves were drawn (Fig. 4) with shapes similar to those for other published ternary diagrams. The $\text{UCl}_4\text{-UO}_2$ binary phase diagram gives the data needed for a UO_2 solubility versus temperature in units of moles UO_2/UCl_4 (Fig. 7). Experimental data for fluoride salt mixtures show that the UO_2 solubilities are proportional to the UF_4 concentration; that is, moles $\text{UO}_2/\text{moles UF}_4$ is dependent on the temperature and the other salt compositions but independent of the UF_4 concentration. Figure 7 shows the data for the solubility of UO_2 in UF_4 also. The data for UCl_4 and UF_4 could be represented by a single curve. Considering the $\text{MgCl}_2\text{-NaCl-UCl}_4$ ternary together with the $\text{UO}_2\text{-UCl}_4$ binary, it is likely that replacement of part of the UCl_4 by UO_2 up to the solubility limits shown by Fig. 7 would have only small effects on the liquidus temperatures of Fig. 4. As an example of the results of these assumptions, a charge of 20 mol % MgCl_2 -20 mol % NaCl -60 mol % ($\text{UCl}_4 + \text{UO}_2$) would be expected to be all liquid above 500°C with UO_2 solubilities from 4 mol % at 500°C to 8 mol % at 800°C .

3.3 SALT PROPERTIES AND PROCESS CONTROL CONSIDERATIONS

The practical chlorination of uranium ore concentrates to UCl_4 on a large scale would require continuous processes with controlled inventories of the process materials. The literature data indicate that a molten salt reaction with feeds of UO_2 , Cl_2 , and C or CO might be most practical. The UCl_4 product must have low concentrations of unreacted carbon or oxygen. Large amounts of unreacted chlorine in the product gas are also very undesirable. Countercurrent flows with high conversion to UCl_4 in a melt (low oxychlorides, UCl_5 and UCl_6) would be extremely difficult to accomplish. A more practical concept is to remove UCl_4 as a vapor from a melt with compositions favorable to high utilizations of the Cl_2 feed. The chlorination reactor will have three reactant feed streams and two products leaving the reactor.

The most likely overall reaction will be one of:



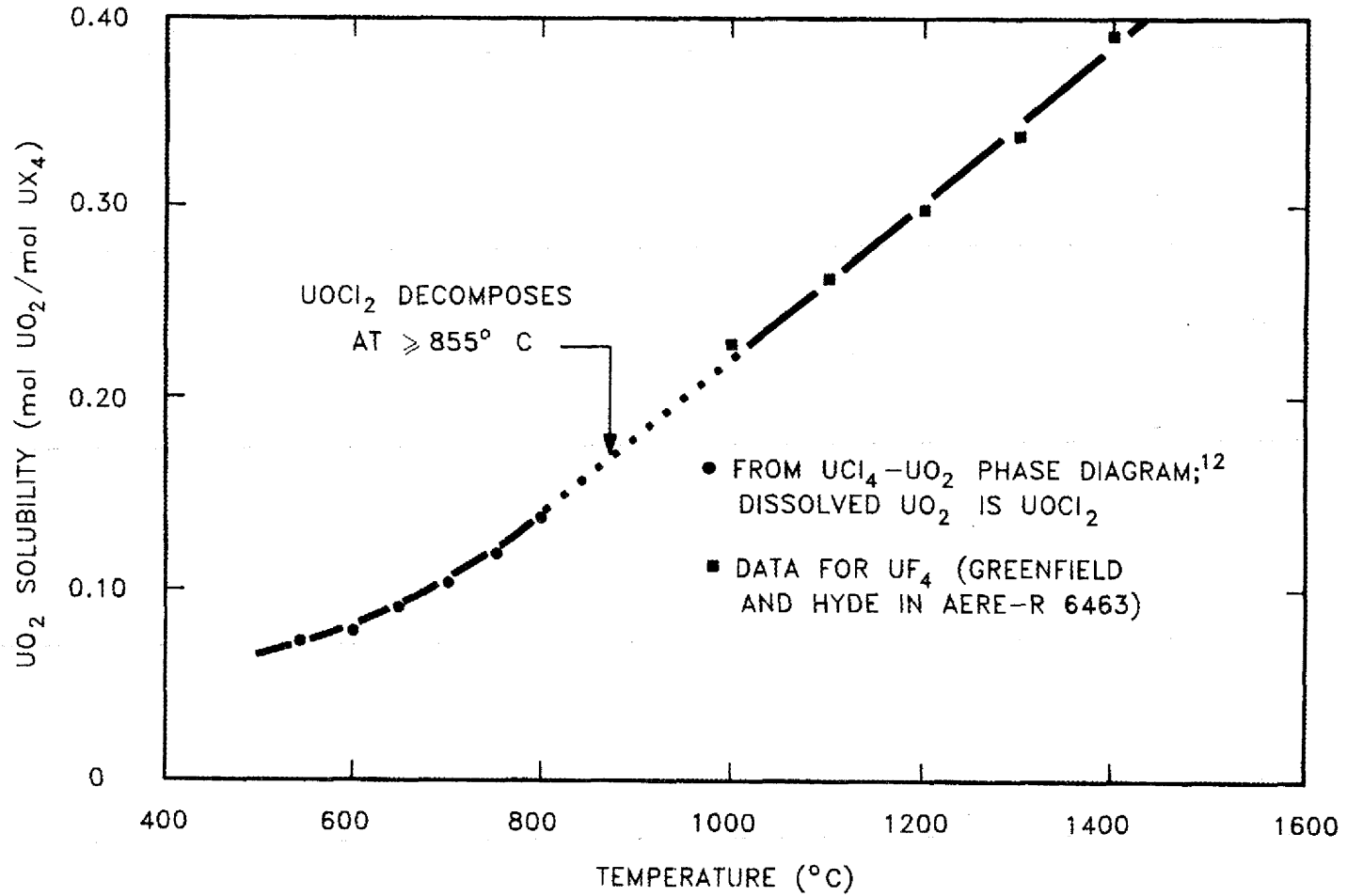


Fig. 7. Solubility of UO₂ in UCl₄ and UF₄.

Reactions with either CO or carbon and with other uranium oxides as feed will also have five primary flows of feeds and products. Small amounts of unreacted Cl_2 or of CO in addition to CO_2 and large amounts of a nonreactive diluent gas (N_2 or CO_2) do not change the need to control five process inventories or process flows.

All gases including the gaseous products, unreacted Cl_2 or CO, and nonreactive diluent gas leave by displacement without need for a control measurement. This leaves four other flows requiring control.

One flow can be set to establish the system capacity. This is most logically the Cl_2 feed rate. Since there is little or no chlorine inventory in the melt, a change in the chlorine feed rate can give an immediate change in the rate of Cl_2 reactions. It would normally be desirable to have a good inventory of UO_2 , C, or CO and the molten chloride salt to allow high utilizations of Cl_2 . Depleting one of these charge components to provide control of the reaction rate contributes to high, undesirable losses of unreacted Cl_2 .

The condensed phase in the chlorination reactor is likely to contain more UCl_4 than any other component. Therefore, it is logical to measure the condensed phase level or volume and use this measurement to control the UCl_4 exit rate. The gas leaving the charge should be at a vapor pressure equilibrium; that is, saturated with UCl_4 vapor. The UCl_4 vapor rate could be changed by changing the charge temperature (to increase the vapor pressure of UCl_4) or by changing a diluent gas rate. Liquid or solid UCl_4 could be recycled to the charge to control the net outflow of UCl_4 . Use of nonvolatile diluent salts such as CaCl_2 , MgCl_2 , or NaCl would reduce the vapor pressure of UCl_4 by reducing the UCl_4 concentration. The diluent salts could provide some automatic changes in the rate of UCl_4 vapor. When the UCl_4 is depleted, the lower concentration of UCl_4 would result in a lower rate of vaporization. Excess UCl_4 would result in a higher rate of UCl_4 vaporization. For pure UCl_4 , concentration in the melt and the vapor pressure do not change as the amount in the charge varies.

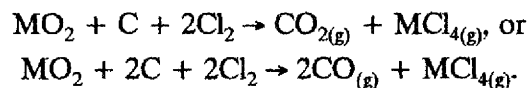
After the rates of gas exit flow, Cl_2 feed, and UCl_4 vapor are determined as described, the feed rates of UO_2 and C or CO remain to be controlled. While the rate of Cl_2 losses to the exit gas can depend on the charge inventories, measurement of Cl_2 losses is a poor control criteria. A high utilization of Cl_2 is desirable and conditions that allow increases in Cl_2 losses are undesirable. Also, increases in Cl_2 losses could result from deficiencies in either UO_2 , or C-CO and could also result from excessive UOCl_2 or C solids

with poor gas-charge contact. Since a high Cl_2 loss might have several causes, it would not be a dependable control measurement for one feed. The UO_2 and C feed rates should be controlled on a long-term basis by some direct measurement on the reactor charge—either measurements of salt properties or analyses of samples for C and oxygen. A review of the limited literature on uranium salt properties did not indicate any promising possibilities for use of measurements of the salt properties at 600 to 800°C.

Based on the lack of information for measurement and use of salt properties for control, the UO_2 and C feed rates will probably be set to agree with the Cl_2 feed rate with periodic adjustments from analyses of charge samples. Good inventories of UO_2 and C appear desirable both to ensure good utilization of Cl_2 and to make control from periodic samples more practical.

3.4 PREPARATION OF TiCl_4 , ZrCl_4 , SiCl_4 , AND ThCl_4 FROM OXIDES

The chemistry and preparation of these metal chlorides have important similarities to those of UCl_4 . For all of them, the tetrachlorides have been produced from oxides using Cl_2 and carbon as follows:



The ThCl_4 preparations were small scale. The other three conversions have been production processes and should provide practical information that applies to production of UCl_4 . For silicon, the free energy of reaction is positive, but the reactions can be completed by removal of the SiCl_4 gas.

This conversion of TiO_2 to TiCl_4 is used on a large scale (10^6 tons/year) to prepare titanium dioxide pigments. The TiCl_4 is a more volatile product (mp 248 K and bp 409 K) than UCl_4 , and can be handled as a liquid at room temperature. While the process concepts for preparation of TiCl_4 are old and well known, the details of plant design and operation are proprietary with little publication as technical literature. The descriptions published in the 1950s²¹ and 1980s²² are very similar.

One description of a plant operation is as follows: A mixture of 20 to 30 wt % calcined coke and 70 to 80 wt % TiO_2 ore is fluidized at 900 to 1000°C using Cl_2 gas. The reactor is lined with SiO_2 brick and some oxygen feed may be used to preheat the reactor or replace heat losses (the chlorination reactions are exothermic). The exit gases contain the TiCl_4 product as vapor, some excess Cl_2 , CO_2 , and CO (ratios near 2 mol/mol), and volatile chlorides of impurity metals such as Fe, Mn, Cr, and Al. The chlorides are separated using the differences in volatility and melting points to give a purified TiCl_4 liquid as the product. An alternate to the fluidized bed is to flow the chlorine up through a fixed bed of TiO_2 -carbon briquettes. Electrical resistance heating may be used to generate supplementary heat in the fixed bed. The use of SiO_2 brick linings without excessive attack is possible as a result of the low surface area of the brick as compared to the mixture of fine SiO_2 and carbon that is used for preparation of SiCl_4 .

A similar chlorination of ZrO_2 -C briquettes at 600-800°C was developed for preparation of ZrCl_4 .²³ Fixed beds of 66-cm diam were operated using ZrO_2 -C briquettes to produce 100 mol ZrCl_4 /h. The ZrCl_4 leaves the reactor as vapor and is collected as condensed solids.

ThCl_4 has been prepared using by reacting crushed ThO_2 -C compacts with Cl_2 in a KCl-NaCl melt at 900°C.²⁴ Careful operation was required to give complete conversions to ThCl_4 without residues of ThOCl_2 . The containers were silica (quartz).

4. ACKNOWLEDGEMENT

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