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U.S. DEPARTMENT OF COMMERCE, Philip M. Klutznick, *Secretary*
Luther H. Hodges, Jr., *Deputy Secretary*
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Vivian B. Parker

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The Thermochemical Properties of the Uranium-Halogen Containing Compounds

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Abstract

A detailed analysis and evaluation of the thermochemistry of 142 uranium-halogen containing compounds is presented, and a tabular summary of the thermochemical properties is given. The properties given, where data are available, are the enthalpy of formation, ΔHf°, Gibbs energy of formation, ΔGf°, entropy, S°, heat capacity, C_p°, and the enthalpy difference, $(H-H_0)$, all at temperature 298.15 K, and the enthalpy of formation at 0 K, ΔHf°_0. The values are consistent with the CODATA Key Values for Thermodynamics.

The analysis of the uranium-halogen containing compounds includes some vapor pressure equations and C_p equations. Some thermal functions which are not readily available in the accessible open literature are presented in the Appendix for compounds that required their use.

The tabular summary of ΔHf°, ΔGf°, etc. includes the values for those uranium compounds which were necessary for this evaluation.

Keywords: Data evaluation; enthalpy; entropy; Gibbs energy; heat capacity; thermochemical tables; uranium-halogen containing compounds.

I. General Description

1. Introduction

This report presents a detailed analysis and evaluation of the thermochemistry of 142 uranium-halogen containing compounds and a tabular summary of ΔHf°'s, ΔGf°'s, S°'s, Cp°'s, $(H-H_0)$'s at 298 K, $\Delta Hf°_0$'s for these compounds. It is part of an independent ongoing evaluation of the thermochemistry of the actinide compounds for inclusion in the NBS Technical Note 270 Series. The interest of the IAEA in sponsoring a series on the thermochemistry of the actinides by compound class, both at low and high temperatures, has led to our participation in this effort*.

Since this IAEA review uses the CODATA (1975) recommended values for the auxiliary key compounds, all compounds considered here have been evaluated on this basis and represent part of our contribution to the Halide Chapter of the IAEA sponsored series, "The Chemical Thermodynamics of Actinide Elements and Compounds".

The analysis of the uranium-halogen containing compounds includes some vapor pressure equations and C_p equations. Some thermal functions which are not readily available in the accessible open literature are presented in the Appendix for compounds that required their use.

The tabular summary of ΔHf°, ΔGf°, etc. includes the values for those uranium compounds which were necessary for this evaluation. The sources for these values are given in 4.1.

Users are invited to comment on the selections, correct errors and bring new measurements to our attention.

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* See Wagman et al. (1977). References are listed by author and year in the bibliography (Section IV).

2. Explanation of the Contents of the Text and Tables

The following material provides definitions and conventions used in the tables.

2.1 Conventions Regarding Pure Substances

The values of the thermodynamic properties of the pure substances given in these tables are for the substances in their standard states. These standard states are defined as follows:

For a pure solid or liquid, the standard state at any temperature is the substance in the condensed phase under a pressure of one atmosphere.

For a gas the standard state at any temperature is the hypothetical ideal gas at unit fugacity, in which state the enthalpy is that of the real gas at the same temperature and at zero pressure.

The phase of a substance is indicated in parentheses at the end of the chemical formula (see Table A).

The values of ΔHf° and ΔGf° given in the tables represent the change in the appropriate thermodynamic quantity when one mole of the substance in its standard state is formed, isothermally at the indicated temperature, from the elements, each in its appropriate standard reference state. The standard reference state at 298 K for each element except phosphorus has been chosen to be the standard state that is thermodynamically stable at 298 K and at one atmosphere pressure. For phosphorus the standard reference state is the crystalline white form; the more stable forms have not been well characterized thermochemically. The same reference states have been maintained for the elements at 0 K except for the liquid elements bromine and mercury for which the reference states have been chosen as the stable crystalline forms. The standard reference states for the elements are indicated in the tables by the fact that the values of ΔHf° and ΔGf° are exactly zero.

The values of S° represent the virtual or "thermal" entropy of the substance in the standard state at 298.15 K, omitting contributions from nuclear spins and isotopic mixing. Where data have been available only for a particular isotope, they have been corrected when possible to the normal isotopic composition.

2.2 Convention Regarding Solutions for the Tabulated Values

For all dissolved substances the composition of the solvent is indicated in parentheses following the chemical formula. Except in special cases, discussed below, the number of moles of the solvent associated with one mole of solute is stated explicitly. See Table A for the conventions used.

In some cases the concentration of the solute can not be specified. These are indicated as "AU" (aqueous, unspecified) for water solutions and by "U" for non-aqueous and mixed media. In all these cases the solution may be assumed to be "dilute".

The standard state for a non-dissociated solute in aqueous solution is taken as the hypothetical ideal solution of unit molality, which has been designated as "std. state, m = 1". For strong electrolytes in aqueous solution the conventional standard state is the ideal solution of unit activity (unit mean molality). The designation "A" is used for strong electrolytes in the standard state and "AO" for undissociated species in water solution. In non-aqueous media two standard states are commonly used. For the mole fraction scale, "std. state, $x_2 = 1$", x is added to the formula of the solvent. For the molal scale, "std. state, m = 1", either s or M is appended to the formula.

The value of ΔHf° for a solute in its standard state is equal to the apparent molal enthalpy of formation of the substance in the infinitely dilute real solution, since the enthalpy of dilution of an ideal solution is zero. At this dilution the partial molal enthalpy is equal to the apparent molal quantity. At concentrations other than the standard state, the value of ΔHf° represents the apparent enthalpy of the reaction of formation of the solution from the elements comprising the solute, each in its standard reference state, and the appropriate total number of moles of solvent. In this representation the value of ΔHf° for the solvent is not required. The experimental value for a heat of dilution is obtained directly as the difference between the two values of ΔHf° at the corresponding concentrations. At finite concentrations the partial molal enthalpy of formation differs from the apparent enthalpy.

The values of the thermodynamic properties tabulated for the individual ions in aqueous solution are based on the usual convention that the values of $\Delta Hf°$, $\Delta Gf°$, S° and $C_p°$ for H^+ (aq, std. state, m = 1) are zero. The properties of a neutral electrolyte in aqueous solution in the standard state are equal to the algebraic sum of these values for the appropriate kinds and numbers of individual ions assumed to constitute the molecule of the given electrolyte. For an ionic aqueous species e.g., HSO_4^-, the properties tabulated refer to that undissociated ion, i.e., they are not equal to the sum of those for its constituent ions. By adopting the above convention with respect to aqueous H^+, it follows that the thermodynamic relation $\Delta Gf° = \Delta Hf° - T(\Delta Sf° + n \cdot 0.5 S°(H_2))$ holds for individual ionic species, with n equal to the algebraic value of the charge. For neutral electrolytes the normal consistency relationship applies. See section 4.

2.3 Convention in the Text (Section II) for Reactions Involving Solutions

In the text reactions involving solutions are given as the authors presented them in the literature. The discussion accompanying the reactions gives the interpretation.

2.4 Chemical Formulae and Physical States for the Tabulated Values (Section III

These tables were reproduced from computer printout in which only capital (upper case) letters are available. Normal one-line chemical formulae are used, with the following modifications:

- Subscripts (counts of atoms): UCL'4 = UCl_4
- The apostrophe ' appears after each letter in a chemical symbol that would normally be written in lower case: UCL'BR'3 = $UClBr_3$

- The centered dot, used in hydrates and minerals, is shown as a colon: UF4:2.5H2O = $UF_4 \cdot 2.5H_2O$
- The physical state of the substance is appended to the chemical formula in parentheses: UCL'4(C) = UCl_4, crystalline

Conventions with respect to physical state are given in Table A.

2.5 Definition of Symbols for Thermochemical Properties for the Tabulated Values (Section III)

The headings used in the tabulated Thermochemical Values have the following meanings:

DH298 = $\Delta Hf°$, standard enthalpy of formation at 298.15 K;

DG298 = $\Delta Gf°$, standard Gibbs energy of formation at 298.15 K;

The others are self explanatory. All H and G relationships are in kcal/mol; all S and $C_p°$ relationships are in cal/mol·K.

All values refer to one mole of substance for the formula given.

3. Unit of Energy and Fundamental Constants

All of the energy values given in these tables are expressed in terms of the thermochemical calorie. This unit, defined as equal to 4.184 joules exactly, is used throughout the IAEA review series. Values reported in other units have been converted to calories by means of the conversion factors for molecular energy given in Table B.

Values in this report are consistent with the CODATA fundamental constants (1973).

The formula weights in the tables have been calculated from the molecular formula using the 1969 Table of Atomic Weights as given by IUPAC (1970).

4. Internal Consistency of the Tables

The processes given in the text have been obtained from the original articles, using consistent values for all subsidiary and auxiliary quantities. The original data were corrected where possible for differences in energy units, molecular weights, temperature scales, etc. Thus we have sought to maintain a uniform scale of energies for all processes in the text and tables. In addition the final tabulated values of the properties of a substance satisfy all the known physical and thermodynamic relationships among these properties. The quantities $\Delta Hf°$, $\Delta Gf°$, and $S°$ at 298.15 K satisfy the relation:

$$\Delta Gf° = \Delta Hf° - T\Delta Sf°$$

to the precision given. The special case of solutions is discussed in section 2.2. Furthermore the calculated value of any thermodynamic quantity for a reaction is independent of the path chosen for the evaluation.

4.1 The Use of Auxiliary Data

As indicated this evaluation uses as its basis the CODATA (1975) recommended values for the auxiliary key compounds. Parker et al. (1976) have incorporated these values into an extensive consistent set of CODATA compatible values for auxiliary values needed in this evaluation. Unless otherwise stated all values for the non-uranium containing auxiliary compounds are taken from the latter report or are consistent with it. Values for the thermal functions as a function of temperature for the auxiliary data are from JANAF (1971).

The tables in Section III also include values for those key non-halogen containing uranium compounds that were necessary for the present evaluation. These values also maintain consistency with other IAEA chapters. In addition, the values listed for the oxides are in agreement with the independent evaluations of Parker (1975, 1976a), CODATA (1978), Rand et al. (Part XI: The Actinide Oxides) and Glushko (1978).

These compounds and the sources for their values are listed below.

U(cs) and U(g)

The tabulated values are from Oetting et al. (1976).

U^{3+}(aq, std. state), U^{4+}(aq, std. state) and UO_2^{2+}(aq, std. state)

The tabulated values are from Fuger and Oetting (1976).

UO_2(c)

S°, C_p° and $H-H_0$ are obtained from the C_p measurements of Westrum and Huntzicker (1971); ΔHf° is from the combustion measurements of Huber and Holley (1969).

$UO_3(c,\gamma)$

The S°, C_p° and $H-H_0$ are from the C_p measurements of Westrum (1966). The ΔHf° is obtained from the solution calorimetry of Fitzgibbons et al. (1967) on the uranium oxides and the decomposition measurements on $UO_3(c,\gamma)$ of Cordfunke and Aling (1965).

U_3O_8(c)

The S°, C_p° and $H-H_0$ are obtained from Westrum and Grønvold (1959) and Girdhar and Westrum (1968), the ΔHf° from the combustion measurements of Huber and Holley (1969).

4.2 Uncertainties

Each selected value in the tabular summary, Section III, contains the final assigned uncertainty, i.e. the estimate by the evaluator of the accuracy of the selected value. In some cases these uncertainties are calculated from (1) the uncertainties assigned to the individual reactions (usually given as 2σ) and the auxiliary data and (2) how well the calculated values for a property (obtained from the various reaction paths) agree within their assigned uncertainties.

Where possible or warranted the various uncertainties and the uncertainty on the selected value are also given in the individual evaluation (Section II).

In many cases, however, the final uncertainty is based on (2) and/or the evaluator's judgment, since a strictly mathematical calculation is not warranted (i.e. (1) is not applicable since no measure of precision is available, and a quantitative estimate of the uncertainty on the individual processes can not be made. In these cases no uncertainties are given in the individual evaluations (Section II)).

In both approaches, however, the final uncertainty is partly subjective.

The uncertainties for the C_p°'s and $(H-H_0)$'s appear in square brackets and are arbitrarily assigned as "10 in the last place".

4.3 Relationship to Other Tables of Thermodynamic Properties

The chemical thermodynamic properties in the present tables of halogen containing compounds may be combined with those published by

CODATA (1975, 1978) and Parker et al. (1976) in order to calculate the change in a property for a process. However, we recommend against these values being combined with those in any other tabulation or with a property reported in an original research paper. In particular, we warn against indiscriminate combination with the NBS Technical Note 270 Series. Values consistent with auxiliary data in the NBS Technical Note 270 Series are available and will be included in that series.

There are several reasons for avoiding the combination of thermochemical data from more than one table. The most important is that different large-scale tables use different thermochemical properties of formation for substances that are ubiquitous in thermochemical measurements. Outstanding examples are in the common inorganic acids and their ions. Another reason is that the groups preparing different tables may have relied on different measurements as the basis for selecting property values.

It is difficult to predict a priori how a change in one selected formation property would affect values assigned to other substances because of the way these are linked by complex networks. In general, it may be expected that the advantage of internal consistency of a table will be lost if values from several sources are combined and the experimental measurements may be reproduced poorly.

No general, simple algorithm can be suggested for overcoming this problem. If it becomes necessary to extend a table of data to substances other than those tabulated, the user is advised to consult the group that prepared the table about the procedure that is contemplated.

5. Arrangement of the Tables

The compounds in the tables are entered according to the Standard Order of Arrangement, (see Figure 1), by the principle of latest position. In this scheme, a compound is listed under the element occurring latest in the list; water of hydration is neglected. Within a given element-table will be found all of the compounds of that element with elements occurring earlier in the order; the arrangement within a table follows the same ordering.

However, for the alkali metal halogen-containing compounds the arrangement is by compound class, i.e., UF_6, UO_2F_2, UCl_4, and UBr_4, in combination with the alkali metals.

TABLE A: Physical State Conventions for Section III

The following conventions are used to designate the physical state of a substance. These apply to the tables in Section III. This information appears in a parenthetical expression appended to the molecular formula. Some of the explanations imply a thermochemical value, particularly those for solutions. These normally are used in describing enthalpy measurements.

Basic Symbols	Explanation
(G)	Gaseous, e.g., HCL'(G) for $HC\ell(g)$
(GS)	Gaseous reference standard state for an element, e.g., O2(GS) for $O_2(g)$
(C)	Crystalline, e.g., NH4CL'(C) for $NH_4C\ell(c)$
(CS)	Crystalline reference standard state for an element, e.g., RB'(CS) for Rb(c)
(L)	Liquid, e.g., H2O(L) for $H_2O(\ell)$
(LS)	Liquid reference standard state fo an element, e.g., BR'2(LS) for $Br_2(\ell)$
(AM)	Amorphous
(GL)	Glassy
(A)	Hypothetical standard state of the ideal aqueous solution at unit activity. For a neutral electrolyte the value of a property is equal to the algebraic sum of the values for the ions assumed to constitute the molecule of the electrolyte, e.g. HCL'(A) = H+(A) + CL'-(A). For an ionic species this notation is commonly used to refer to the undissociated ion as written. e.g., HSO4-(A)

Symbol	Explanation
(AO)	Hypothetical standard state of the ideal aqueous solution at unit activity of the undissociated (non-ionized) species, e.g., HF(AO), HF2-(AO). May also be used whenever the designation (A) could be ambiguous. Note that the descriptions HSO4-(A) and HSO4-(AO) are equivalent, but that HF(A) and HF(AO) are not.
(AU)	Aqueous solution of undefined, but usually dilute, concentration, e.g., XE'O3(AU).

The symbols used above occasionally are modified by numbers to distinguish two substances in the same state that have the same molecular weight, as for isomers: (AU2), (C3). They are also used in combination with descriptive material, e.g. (C:HE'), (C:AL') etc. to mean "crystalline, hexagonal , "crystalline, alpha form", etc.

Special notations for substances in solutions

The notations for the "state" of a substance in solution may combine a definition of the system, e.g. HCℓ in 220 moles of water, and a specification of the thermochemical property associated with it. Usually the thermochemical property is the apparent integral enthalpy or free energy of formation or an absolute entropy, i.e. the formation properties of the solvent are not included. If a partial molal property is tabulated the notation D: ("D" for "differential") occurs as the first term in the state bracket. The notations given below illustrate the differences for integral and differential (partial molal) properties, and extrapolated values. Examples are given for aqueous, mixed, and non-aqueous solvents.

Symbol	Explanation
HCL'(200H2O)	An aqueous solution of specified composition, e.g. one mole of $HC\ell$ in 200 moles H_2O. The value of ΔHf represents the apparent integral enthalpy of formation.
HCL'(D:200H2O) and H2O(D:HCL'+200H2O)	These represent the partial molal (enthalpy of formation of the substance in a solution of specified concentration, e.g. the partial molal enthalpy of formation of $HC\ell$ and H_2O respectively, in a solution consisting of 1 mole $HC\ell$ and 200 moles H_2O.
UCL'4(HCL'O4+50H2O)	This describes a solute dissolved in a mixed solvent, e.g. one mole of $UC\ell_4$ in a mixture of 1 mole of $HC\ell O_4$ and 50 moles H_2O. The value of ΔHf represents the apparent integral enthalpy of formation of the substance, $UC\ell_4$, in the medium.
UCL'4(HCL'O4+ 50H2O:AU)	This represents a solute at an unspecified but usually dilute concentration in a solvent mixture of fixed composition.

TABLE B

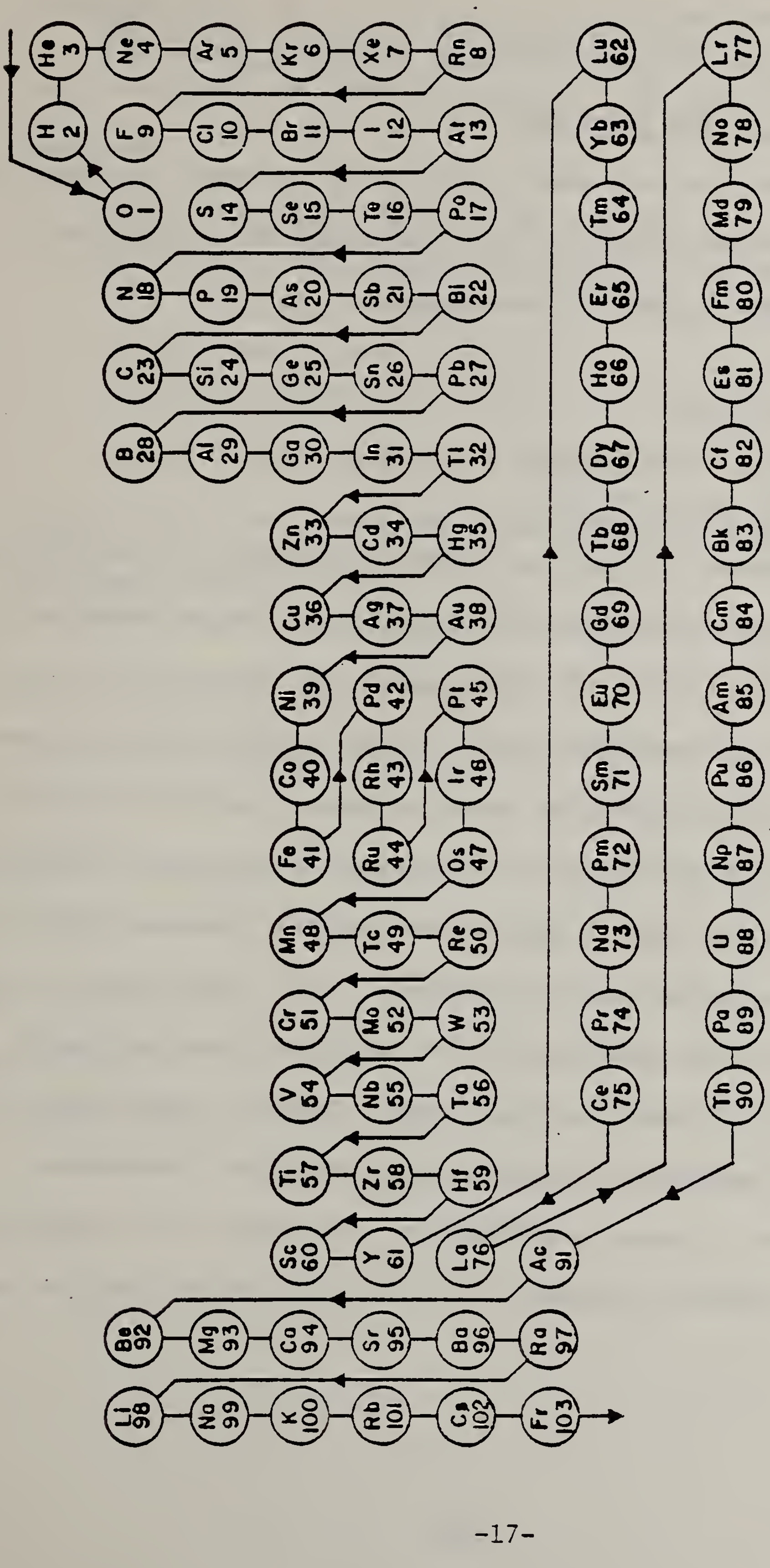
CONVERSION FACTORS FOR UNITS OF MOLECULAR ENERGY

	J/mol	cal/mol	cm^3 atm/mol	kWH/mol	Btu/lb-mol	cm^{-1}/molecule	eV/molecule
1 J/mol =	1	2.390057 x10^{-1}	9.86923	2.77778 x10^{-7}	0.429923	8.35935 x10^{-2}	1.036435 x10^{-5}
1 cal/mol =	4.184	1	41.2928	1.162222 x10^{-6}	1.798796	3.49755 x10^{-1}	4.33644 x10^{-5}
1 cm^3 atm/mol =	0.1013251	2.42173 x10^{-2}	1	2.81458 x10^{-8}	4.35619 x10^{-2}	8.47011 x10^{-3}	1.050166 x10^{-6}
1 kWh/mol =	3,600,000	860,421	3.55292 x10^{7}	1	1,547,721	300,937	37.3117
1 Btu/lb-mol =	2.32600	5.55927 x10^{-1}	22.9558	6.46111 x10^{-7}	1	1.944384 x10^{-1}	2.41075 x10^{-5}
1 cm^{-1}/molecule =	11.96266	2.85914	118.0622	3.32296 x10^{-6}	5.14302	1	1.239852 x10^{-4}
1 eV/molecule =	96484.56	23060.4	952,230	2.68013 x10^{-2}	41480.9	8065.479	1

The underlined numbers represent the fundamental values used in deriving this table. The remaining factors were obtained by applying the relationships:

$$n_{ij} = n_{ik} \cdot n_{kj} \qquad n_{ii} = n_{ik} \cdot n_{ki} = 1$$

STANDARD ORDER OF ARRANGEMENT



Standard Order of Arrangement of the Elements and Compounds
based on the
Periodic Classification of the Elements

Figure 1

II. The Evaluation and Analysis of the Thermochemistry of the Uranium-Halogen Containing Compounds

1. The Evaluation Procedure

Although the compounds evaluated are arranged systematically, it is recommended that the user first read the evaluations for the key compounds in the following order:

1. $UCl_4(c)$
2. $UO_2Cl_2(c)$
3. $UF_6(c)$ and $UO_2F_2(c)$
4. $UF_3(c)$ and $UF_4(c)$

This arrangement follows the stepwise procedure of evaluating the thermochemical properties by the sequential method described by Garvin et al. (1976). In this method, the values for the key compounds are determined first, so that a framework or network of values is developed for those compounds that are essential for the determination of the properties of many other compounds.

Initially, this procedure involves the compounds whose properties can be determined independently, i.e., they involve no other compounds of the same element (in this case, uranium) and/or they depend only on known auxiliary data. Ideally, there should be definitive measurement paths between these key compounds as indications of mutual confirmation. Thereafter, the properties of other compounds dependent on these first selections are chosen.

The halogen compounds listed above are only part of the uranium key network, which includes all of the following compounds:

1. $U(c)$, $U_3O_3(c)$, $UO_2(c)$, and $UO_3(c,\gamma)$
2. $UCl_4(c)$, $UO_2Cl_2(c)$, and $UO_2(NO_3)_2 \cdot 6H_2O(c)$
3. U^{4+}(aq, std. state) and UO_2^{2+}(aq, std. state)
4. $U(g)$, $UN(c)$, $US(c)$, and $UC(c)$
5. $UF_6(c)$ and $UO_2F_2(c)$, $UF_3(c)$ and $UF_4(c)$

The non-halogen compounds listed above in 1, 2, and 3, as well as U(g) from 4 are considered fixed auxiliary data for this evaluation (see Section I 4.1).

2. The Analysis of the Data

The purpose of thermochemical data evaluation is the selection of reliable values, i.e., ones that can be used with confidence. When properly documented, an evaluation not only presents the results but also explains how they were obtained. This explanation is analogous to the detailed experimental section of a thermochemical measurement paper. An explanation of our evaluation is provided here to assist the user and to reduce the need for reinvestigation in the future.

The evaluator usually works with some incomplete records. There are not enough data to solve all of the problems that arise. Therefore, it is necessary to "squeeze" the maximum amount of information out of the existing data. That will become apparent in the individual evaluations that follow.

Complete thermochemical cycles, where possible, are given. The same measurements are repeatedly considered from different points of view. The work of a research group on related systems is considered in order to assess the likely accuracy for the system of immediate interest and to modify or avoid suspect reactions and paths in determining the "best" values.

3. The Evaluations of the Uranium-Halogen Containing Compounds

3.100 U-X (X=F, Cl, Br, or I) with/without O

3.101 U-F Compounds

$UF_n(g)$ (n = 1,2,3)

Gurvich et al. (1977) have recently published the ideal gas thermodynamic functions for UF(g), $UF_2(g)$, and $UF_3(g)$ based on estimates for the molecular constants and frequencies. These estimates are:

Values for Molecular Constants of UF

Molecule	ω_e	$\omega_e x_e$	B_e	α	$D_0 \cdot 10^7$	Number of Electronic States
			cm^{-1}			
UF	580	1.72	0.230	0.0014	1.5	82 with statistical weight=2 and $T_e \leqq 51000$ cm^{-1}

Values for Molecular Constants of UF_2 and UF_3 in the Ground State

	UF_2	UF_3
Symmetry	C_{2v}	C_{3v}
σ	2	3
r(U-F), Å	2.00±0.05	2.00±0.05
<F-U-F, degrees	110^{+50}_{-20}	115^{+3}_{-5}
$I_A I_B I_C \cdot 10^{117}$, $g^3 \cdot cm^6$	2920±2000	13690±2300
ν_1, cm^{-1}	575±100	600±100
ν_2, cm^{-1}	140±50	100±50
ν_3, cm^{-1}	525±100	550(2)±100
ν_4, cm^{-1}	-	140(2)±50

Other details are to be found in Gurvich et al. (1977). The functions are retabulated in the Appendix. They are to be considered approximate.

Zmbov (1969) has made a mass spectrometric study of high temperature equilibria (1201-1313 K) of the following:

$$UF_4(g) + Ca(g) \rightarrow CaF(g) + UF_3(g) \qquad (1)$$

$$UF_4(g) + 2Ca(g) \rightarrow 2CaF(g) + UF_2(g) \qquad (2)$$

From his reported ΔH's at the mean temperature and his tabulated K's, the following are obtained at 298 K:

	$\Delta H°$ kcal/mol	
	2nd law	3rd law*
(1)	23.5±4.0	25.6
(2)	21.2±5.0	36.0

The 2nd law value for $\Delta H°_2$ appears unreasonable compared to the values for ΔH_1, so that ΔH_1 = 23.5±4.0 kcal/mol is accepted, resulting in $\Delta Hf°$ $UF_3(g)$ = -248±5 kcal/mol. $\Delta Hf°$ $UF_2(g)$, then, may be obtained from the 3rd law $\Delta H_3 = H_2 - H_1$:

$$UF_3(g) + Ca(g) \rightarrow UF_2(g) + CaF(g);\ \Delta H_3 = 10.4 \text{ kcal/mol} \qquad (3)$$

The resultant $\Delta Hf°$ $UF_2(g)$ = -129±7 kcal/mol.

From a comparison of the $\Delta H°$'s for:

$$UF_n(g) \rightarrow U(g) + nF(g)$$

a reasonable estimate for $\Delta H°$ when n = 1 is 148±5 kcal/mol resulting in $\Delta Hf°$ UF(g) = -2±5 kcal/mol.

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[*] Obtained using the thermal functions of $UF_4(g)$ without the addition of 8.2 cal/mol·K to S° $UF_4(g)$, since a similar contribution may be necessary on S° $UF_3(g)$ and S° $UF_2(g)$. Most of the contribution would cancel resulting in third law values close to those given.

UF_3(c), UF_4(c) and $UF_4 \cdot 2.5H_2O$(c)

The entropy of UF_3(c) at 298 K has been estimated as 30.0±1.0 cal/mol·K in comparison with $\Delta S\ [PuF_3(c)-PuF_4(c)]^*$ and S° UF_4(c). Krestov (1972) has estimated the Cp (298-1000 K) as:

$$Cp = 21.2 + .0073T \text{ cal/mol·K.}$$

Thermal functions have been generated from this equation and the estimated S°.

Burns et al. (1960) measured the low temperature heat capacities (1.3-20 K) of UF_4(c). These measurements are in agreement (in the overlapping range) with those of Osborne et al.'s (1955) measurements, 5-300 K. The smoothed functions tabulated by Burns et al. are accepted here.

Dworkin (1972) measured the heat content of UF_4(c,l) (298-1400 K). His smoothed tabulated functions extrapolated to 1600 K are accepted and are represented by :

$$H_T-H_{298} = -9650 + 29.53T + 1.15\times10^{-3}T^2 + 2.21\times10^5T^{-1} \text{ cal/mol: } (298\text{-}1309 \text{ K})$$

$$\Delta H_{fusion} = 11{,}230 \text{ cal/mol; } \Delta S_{fusion} = 8.6 \text{ cal/mol·K; } (1309 \text{ K})$$

$$H_T-H_{298} = -9420 + 39.57T \text{ cal/mol } (1309\text{-}1400 \text{ K})$$

The earlier results of King and Christensen (1961) are in fair agreement.

The measurements of Settle et al. (1963) and Hayman (1967) are in good agreement on the direct fluorination of U(c) to UF_6(c,g); this lent support to the $\Delta Hf°$'s of UF_3(c) and UF_4(c) obtained from

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[*] Osborne et al. (1974, 1975) reported S° = 30.14±0.10 and 35.18±0.10 cal/mol·K for PuF_3(c) and PuF_4(c), respectively.

the fluorinations of $UF_3(c)$ and $UF_4(c)$ to $UF_6(g)$ by Hayman (1967) resulting in $\Delta Hf°\ UF_3(c) \approx -357$ and $\Delta Hf°\ UF_4(c) \approx -454$ kcal/mol. The reappraisal made here of the $\Delta Hf°$'s of $UF_6(c)$ and (g) necessitate a complete reevaluation of the $\Delta Hf°$'s $UF_3(c)$ and $UF_4(c)$. A tabular summary is also given (Table 1).

A. The Measurements on the Enthalpy of Formation of $UF_3(c)$

1. Room Temperature Calorimetry

Khanaev and Khripin (1970) measured the following ΔH's (kcal/mol) at 323 K:

$$(UO_2Cl_2 + 3FeCl_2 + HCl + 3/4HBF_4 + 1/4H_2O)_{soln.\ I} \rightarrow UF_3(c) + (3FeCl_3 + 3/4H_3BO_3)solv.;\ \Delta H_1 = +34.43\pm.12 \tag{1}$$

$$UO_2Cl_2(c) + (3FeCl_3 + 3/4H_3BO_3)solv. \rightarrow (UO_2Cl_2 + 3FeCl_3 + 3/4H_3BO_3)_{soln.\ II};\ \Delta H_2 = -8.79\pm.03 \tag{2}$$

$$(3FeCl_2 + UO_2Cl_2 + HCl + 3/4HBF_4 + 1/4H_2O)_{soln.\ I} \rightarrow 3FeCl_2(c) + (UO_2Cl_2 + HCl + 3/4HBF_4 + 1/4H_2O)_{soln.\ IX};\ \Delta H_3 = 3x(2.642\pm.035) \tag{3}$$

$$(UO_2Cl_2 + HCl + 3/4HBF_4 + 1/4H_2O)_{soln.\ IX} + 3FeCl_3(c) \rightarrow (3FeCl_3 + UO_2Cl_2 + HCl + 3/4HBF_4 + 1/4H_2O)_{soln.\ V};\ \Delta H_4 = 3(-7.198\pm.05) \tag{4}$$

$$(UO_2Cl_2 + 3FeCl_3 + 9/4H_2O + HCl)_{soln.\ IV} \rightarrow 2H_2O_{soln.} + (UO_2Cl_2 + 3/4HBF_4 + 3FeCl_3 + 1/4H_2O + HCl)_{soln.\ V};\ \Delta H_5 = +2.124\pm.01 \tag{5}$$

Use was made of the following Khanaev (1968) measurements which they confirmed:

$$(UO_2Cl_2 + 3FeCl_3 + 3/4H_3BO_3)_{soln.\ II} + 3HF(1.33H_2O) \rightarrow (UO_2Cl_2 + 3FeCl_3 + 3/4HBF_4 + 9/4H_2O)_{soln.\ III} + 3.99H_2O(l)\quad \Delta H_6 = -15.18\pm.12 \tag{6}$$

$$(UO_2Cl_2 + 3FeCl_3 + 3/4HBF_4 + 9/4H_2O)_{soln.\ III} + HCl(3.91H_2O) \rightarrow (UO_2Cl_2 + 3FeCl_3 + 3/4HBF_4 + 9/4H_2O + HCl)_{soln.\ IV} + 3.91H_2O(l)\quad \Delta H_7 = +4.04\pm0.004 \tag{7}$$

The summation, $\Delta H_1 + \Delta H_2 - \Delta H_3 - \Delta H_4 + \Delta H_5 + \Delta H_6 + \Delta H_7 = \Delta H_8 = +30.292 \pm 0.25$ corrected to 298 K using a $\Delta C_p = 30$ cal/mol·K results in:

$$UO_2Cl_2(c) + 3FeCl_2(c) + 3HF(aq) + HCl(aq) \rightarrow 2H_2O(l) + 3FeCl_3(c) + UF_3(c);\ \Delta H_8 = 29.54 \pm 0.32 \text{ kcal/mol} \quad (8)$$

The integral values for ΔHf $HCl(3.92H_2O)$ and ΔHf $HF(1.33H_2O)$ are appropriate here. The resultant ΔHf° $UF_3(c)$ is -354.9±0.8 kcal/mol.

Khanaev and Khripin also measured the ΔH_{soln} of $UCl_4(c)$ as part of their series of measurements. The reaction follows:

$$UCl_4(c) + (3FeCl_3 + 3/4H_3BO_3 + 2H_2O)_{solv.} \rightarrow (UO_2Cl_2 + 2FeCl_2 + FeCl_3 + 3/4H_3BO_3 + 4HCl)_{soln.\ VI};\ \Delta H_9 = -18.44 \pm .02 \quad (9)$$

The summation from a rearrangement of the reactions, $\Delta H_9 + \Delta H_6 + \Delta H_1 - 3x\Delta H_7 - 1/3\Delta H_3 - 1/3\Delta H_4 = \Delta H_{10} = -6.754 \pm 0.018$, corrected to 298 K with a $\Delta C_p = -48$ cal/mol·K is:

$$FeCl_2(c) + UCl_4(c) + 3HF(aq) \rightarrow FeCl_3(c) + UF_3(c) + 3HCl(aq);\ \Delta H_{10} = -5.564 \pm 0.20 \text{ kcal/mol} \quad (10)$$

so that ΔHf° $UF_3(c) = -354.67 \pm 0.8$ kcal/mol. The two paths are in good agreement.

As shown in the section on $UO_2Cl_2(c)$, the ΔHf° $UO_2Cl_2(c) = -297.0 \pm 0.5$ kcal/mol obtained from the above Khanaev and Khripin reactions (relating $UO_2Cl_2(c)$ to $UCl_4(c)$) is in excellent agreement with the selected value for $UO_2Cl_2(c)$, and this lends support to the above values for $UF_3(c)$.

It is important to note that the value for $\Delta Hf°\ UF_4(c) = -452.3 \pm 0.9$ kcal/mol derived from Khanaev (1968) [see section on $UF_4(c)$] and the above values for $UF_3(c)$ lead to:

$$UF_3(c) + 1/2F_2(g) \rightarrow UF_4(c);\ \Delta H_{11} = -452.3 + 354.8 = -97.50 \pm 0.8 \text{ kcal/mol} \quad (11)$$

Hayman (1967) has fluorinated $UF_3(c)$ as well as $UF_4(c)$ and U(c) to obtain $UF_6(g)$:

$$UF_3(c) + 3/2F_2(g) \rightarrow UF_6(g);\ \Delta H_{12} = -153.39 \pm 0.45 \quad (12)$$

$$U(c) + 3F_2(g) \rightarrow UF_6(g);\ \Delta H_{13} = -510.47 \pm 0.64 \quad (13)$$

$$UF_4(c) + F_2(g) \rightarrow UF_6(g);\ \Delta H_{14} = -56.82 \pm 0.17 \quad (14)$$

It appears that ΔH_{13} is in error as shown in the discussion on $UF_6(c)$ and $UF_6(g)$. If it is assumed that the error is systematic in all the measurements, then $\Delta Hf°\ UF_3(c) = \Delta H_{13} - \Delta H_{12} = -357.1$ kcal/mol. If only ΔH_{13} is in error, and ΔH_{12} and ΔH_{14} are reasonably correct, then using the selected $\Delta Hf°\ UF_6(g)$, $\Delta Hf°\ UF_3(c) = -513.25 + 153.39 = -359.86 \pm 0.6$ kcal/mol and $\Delta Hf°\ UF_4(c) = -513.25 + 56.82 = -456.4 \pm 0.5$ kcal/mol.

With either assumption one obtains $\Delta H_{11} = -96.6 \pm 0.5$ kcal/mol, as contrasted with -97.5 from the Khanaev measurements.

There are other possibilities in interpreting the Hayman results: the errors in ΔH_{12} and ΔH_{14} are proportional to the error in ΔH_{13}; the errors are random and the uncertainties on ΔH_{12}, ΔH_{13}, and ΔH_{14} are too small and the $\Delta Hf°$'s of $UF_3(c)$ and $UF_4(c)$ could be more positive.

2. High Temperature EMF Measurements Involving UF_3(c)

The values cited here depend on the estimated thermal functions for UF_3(c).

Heus and Egan (1966) and Markin et al.(1967) have measured the e.m.f. of cells involving CaF_2 as a solid electrolyte.

For

$$Al(c) + UF_3(c) \rightarrow AlF_3(c) + U(c) \qquad (15)$$

the values for ΔG at 873 K are 4.84±1.0 and 5.40±1.0 kcal/mol, respectively, leading to $\Delta H°_{15}$ = -3.73±1.5 and -3.16±1.5 kcal/mol at 298 K and $\Delta Hf°$ for UF_3(c) = -357.3±2.0 and -357.8±2.0 kcal/mol, respectively.

The above relationship (15) was combined with other experimental reactions of Heus and Egan, and Markin et al. to obtain the relationship of UF_3(c) to MgF_2(c), which on the NBS Technical Note Scale, was less dependent upon their F^-(aq, std.). The following relationship is obtained which can be used with the CODATA $\Delta Hf°$ MgF_2(c):

$$4/3U(c) + 2MgF_2(c) \rightarrow 2Mg(c) + 4/3UF_3(c) \qquad (16)$$

and from the Heus and Egan values ΔG at 873 K = 50.73, so that $\Delta H°_{16}$ = 62.09±1.5 and $\Delta Hf°$ = -356.5±2.0 kcal/mol. From Markin et al.: ΔG at 873 K = 50.27, $\Delta H°_{16}$ = 61.63±1.5 and $\Delta Hf°$ for UF_3(c) = -356.8±2.0 kcal/mol.

These two relationships indicate that the measured ΔG's are good within their experimental uncertainty of 1.0 kcal/mol. Because of the uncertainty in $-(G-H_{298})/T$ for UF_3(c) and the uncertainties in $\Delta Hf°$ of AlF_3(c) and MgF_2(c), the assigned uncertainties on the UF_3 values are ±2.0 kcal/mol.

Markin et al. have also determined the relationship between UF_3(c) and UF_4(c).

$$4UF_3(c) \rightarrow 3UF_4(c) + U(c) \qquad (17)$$

$$\Delta G_{873K} = 62.20 \text{ and } \Delta H° = 61.86\pm4.0 \text{ kcal/mol (3rd law)}$$

This relationship will be used with the results of Heus and Egan, and Markin et al. to calculate the ΔHf°'s of UF_4(c). The calculated ΔH_{11} then is ~ -98 kcal/mol.

B. The Measurements on the Enthalpy of Formation of UF_4(c)

1. Room Temperature Calorimetry

Khanaev (1968) has made a series of measurements at 323 K on the ΔH_{soln}'s. UF_4(c, monoclinic) = -3.11±.02 kcal and UCl_4(c) = -17.91±.05 kcal in various HCl-H_3BO_3 aqueous solutions, and on the various $\Delta H_{mix.}$'s to obtain the relationship between UCl_4(c) and UF_4(c).

The summation of the measured reactions leads to:

$$UF_4(c) + 4HCl(aq) \rightarrow UCl_4(c) + 4HF(aq); \ \Delta H_1 = 49.77\pm0.15 \text{ kcal/mol} \quad (1)$$

where ΔH_1 includes the correction from ΔH at 323 K = 51.20±0.13 kcal/mol using a ΔCp = 58 cal/mol·K.

The concentrations for HCl(aq) and HF(aq) are the same as for the similar cycles for UF_3(c) by Khanaev and Khripin (1970), so that ΔHf° UF_4(c) = -452.3±0.9 kcal/mol.

As indicated in the discussion on the ΔHf° UF_3(c), the results of Hayman (1967) on the fluorination of UF_4(c) lead to ΔHf° UF_4 values of -453.7±0.7 (if a systematic error is assumed in all their measurements) or -456.4±0.5 kcal/mol (if only ΔH_{13} is in error).

The available information on $UF_4 \cdot 2.5H_2O$(c) and the various reported hydrates, as well as on the other forms of UF_4(c), must be considered.

The $\Delta Hf°$ $UF_4 \cdot 2.5H_2O(c)$ may be obtained from the Maltsev et al. (1960) calorimetric measurements involving the precipitation of $UF_4 \cdot 2.5H_2O(c)$ at 293 K. Their measured reactions (kcal/mol) are:

$$UCl_4(c) + 250HCl(aq) \rightarrow [UCl_4 + 250HCl]aq; \ \Delta H_2 = -43.47 \pm 0.10 \qquad (2)$$

$$[UCl_4 + 250HCl]aq + 18HF(aq) + 2.5H_2O(aq) \rightarrow UF_4 \cdot 2.5H_2O(c) + [254HCl + 14HF]aq; \ \Delta H_3 = -20.96 \pm 0.33 \qquad (3)$$

$$[250HCl + 18HF]aq \rightarrow 250HCl(aq) + 18HF(aq); \ \Delta H_4 = 5.30 \pm 0.12 \qquad (4)$$

The summation, $\Delta H_5 = \Delta H_2 + \Delta H_3 + \Delta H_4 = -59.15 \pm 0.4$ is for:

$$UCl_4(c) + [250HCl + 18HF]aq + 2.5H_2O(aq) \rightarrow [254HCl + 14HF]aq + UF_4 \cdot 2.5H_2O(c) \qquad (5)$$

The authors have calculated

$$4HF(g) + [254HCl + 14HF]aq \rightarrow 4HCl(g) + [250HCl + 18HF]aq; \ \Delta H_6 = 4x(5.68 \pm 0.50) \qquad (6)$$

using unevaluated literature data for the ΔH_{soln} $HF(g) \rightarrow HF(aq)$ and ΔH_{soln} $HCl(g) \rightarrow HCl(aq)$ to obtain:

$$4HF(g) + 4HCl(aq) \rightarrow 4HCl(g) + 4HF(aq); \ \Delta H_7 = 5.68x4 \qquad (7)$$

This ΔH was assumed to be equal to their ΔH_6.

This approach leads to:

$$UCl_4(c) + 4HF(g) + 2.5H_2O(l) \rightarrow UF_4 \cdot 2.5H_2O(c) + 4HCl(g); \ \Delta H_8 = -36.43 \pm 2.1 \qquad (8)$$

which corrected to 298 K ($\Delta C_p = -24$ cal/mol·K) is -36.55±2.1 kcal and $\Delta Hf°$ $UF_4 \cdot 2.5H_2O(c) = -623.9 \pm 3.0$ kcal/mol.

The $\Delta H_{hydration}$, which will be discussed and evaluated separately, for:

$$UF_4(c) + 2.5H_2O(l) \rightarrow UF_4 \cdot 2.5H_2O(c) \qquad (9)$$

is ~ -10 kcal/mol $UF_4(c)$. This results in a ΔHf° $UF_4(c)$ = -443 kcal/mol which is not reasonable.

A better approach would be to use the experimental summation, (4) which contains a mixture of HF and HCl on both sides of the equation differing only by the removal of 4HF(aq) and the addition of 4HCl(aq) and assume that the differentials, $\Delta\overline{H}f$ for the HCl, HF, and H_2O at the appropriate concentrations are to be used; the assumption, of course, is that the $\Delta\overline{H}f$ of HCl(aq) and HF(aq) would be the same as in pure solutions.

Schematically, then, and corrected to 298 K:

$$UCl_4(c) + 4HF(aq) + 2.5H_2O(aq) \rightarrow UF_4 \cdot 2.5H_2O(c) + 4HCl(aq); \quad \Delta H_{10} = -59.68 \pm 0.5 \text{ kcal/mol} \qquad (10)$$

With the differential ΔHf°'s for $HCl(10.04H_2O)$, H_2O, and $HF(160H_2O)$, the resultant ΔHf° $UF_4 \cdot 2.5H_2O(c)$ = -633.2±1.0 kcal/mol which means that ΔHf° $UF_4(c)$ is ~ -452.4 kcal/mol.

2. High Temperature Equilibria

Briggs (1960) has reported the K's in the range 622 to 955 K for the equilibrium:

$$UO_2(c) + 4HF(g) \rightarrow UF_4(c) + 2H_2O(g). \qquad (11)$$

The ΔH = -50.6 kcal/mol $UF_4(c)$ at the mean T results in ΔH° = -50.84 kcal/mol and ΔHf° = -455.88 kcal/mol. The third law value for ΔH° = -51.90±0.92 results in ΔHf° = -456.99 kcal.

The earlier measurements were evaluated by Rand and Kubaschewski (1963) who cite $\Delta G_{11} = -50{,}000 + 57.7T$ cal mol^{-1} for the range 700 to 900 K. This results in a 3rd law $\Delta H° = -50.12$ and $\Delta Hf°$ $UF_4(c) = -455.1$ kcal/mol. The other measurements cited by Rand and Kubaschewski are:

(1) Johns and Walsh (1945) (temperature range 873-1073 K)

2nd law $\Delta H = -42.83$; $\Delta Hf° = -447.82$ kcal/mol

3rd law $\Delta H = -56.46 \pm 2.8$; $\Delta Hf° = -461.45$

(2) Domange and Wohlhuter (1949) (temperature range 374-773 K)

2nd law $\Delta H = -27.4$

3rd law $\Delta H = -49.1 \pm 9.0$

These two sets are given no further consideration.

3. Room Temperature Aqueous Equilibria

Vdovenko et al. (1963) reported for the following equilibria:

$U^{+4}(aq) + F^-(aq) \rightarrow UF^{3+}(aq)$; log K = 7.15 (12)
$U^{+4}(aq) + 2F^-(aq) \rightarrow UF_2^{2+}(aq)$; log K = 12.4 (13)
$U^{+4}(aq) + 3F^-(aq) \rightarrow UF_3^{+}(aq)$; log K = 17.7 (14)
$U^{+4}(aq) + 4F^-(aq) \rightarrow UF_4(aq)$; log K = 23.1 (extrap. value) (15)

Savage and Browne (1960) reported:

$UF_4 \cdot 2.5H_2O(c) \rightarrow UF_4(aq)$; $K = 1.09 \times 10^{-4}$ molal (16)
$UF_4(aq) \rightarrow UF_3^{+}(aq) + F^-(aq)$; $K = 5.4 \times 10^{-5}$ molal (17)
$UF_3^{+}(aq) \rightarrow UF_2^{+2}(aq) + F^-(aq)$; $K = 5.9 \times 10^{-5}$ molal (18)

From the combination of (16) and (15) we obtain:

$$UF_4 \cdot 2.5H_2O(c) \rightarrow U^{+4}(aq) + 4F^-(aq) + 2.5H_2O(l); \quad \Delta G°_{19} = +36.9 \text{ kcal/mol} \tag{19}$$

which results in $\Delta Gf°$ $UF_4 \cdot 2.5H_2O(c) = -574.9$ kcal/mol.

If it is assumed that S° $UF_4 \cdot 2.5H_2O(c)$ = 60.0±2.0 cal/mol·K, then the calculated ΔHf° for $UF_4 \cdot 2.5H_2O(c)$ = -631.0 kcal/mol and ΔHf° $UF_4(c) \approx -450.2$ kcal/mol.

Other combinations for the equilibria (19) are possible from various combinations of the Vdovenko et al. data with the Savage and Brown data, such as $\Delta G°_{19} = +35.4$ from (16) + (17) - (14) which would result in -629.5 kcal/mol for ΔHf° $UF_4 \cdot 2.5H_2O(c)$ and ΔHf° $UF_4(c)$ = -448.7 kcal/mol.

4. High Temperature EMF Measurements

As indicated under $UF_3(c)$, Markin et al. (1967) have determined the relationship between $UF_3(c)$ and $UF_4(c)$, as:

$$\Delta G_{873\ K} = 62.20\ \text{kcal/mol}$$

for

$$4UF_3(c) \rightarrow 3UF_4(c) + U(c) \tag{20}$$

Their results and Heus and Egan's (1966) EMF measurements on $UF_3(c)$ can then be converted to relationships involving $UF_4(c)$ and $MgF_2(c)$, and $UF_4(c)$ and $AlF_3(c)$ negating the added uncertainty of the estimated thermal functions of $UF_3(c)$ on the reactions involving $UF_3(c)$.

Then for:

$$Al(c) + 3/4UF_4(c) \rightarrow AlF_3(c) + 3/4U(c) \tag{21}$$

from Heus and Egan, ΔH° = -19.2 kcal/mol and ΔHf° = -455.7±1.0 kcal/mol, and from Markin et al., ΔH = -18.6 and ΔHf° = -456.5±1.0 kcal/mol.

Similarly for:

$$U(c) + 2MgF_2(c) \rightarrow 2Mg(c) + UF_4(c) \qquad (22)$$

from Heus and Egan, ΔH° = 82.7 kcal and ΔHf° = -454.7±1.0 kcal/mol; from Markin et al ΔH° = 82.3 and ΔHf° = -455.1±1.0 kcal/mol.

C. The Selection of Values for the Enthalpies of Formation of $UF_3(c)$ and $UF_4(c)$

As can be seen from the range of values for ΔHf°'s for $UF_3(c)$ and $UF_4(c)$, Table 1, the selected values can not be considered definitive; however a reasonable presentation of the relationships can be made with ΔHf° $UF_4(c)$ = -455.5±1.0 kcal/mol.

$$\Delta(\Delta Hf^\circ\ UF_3(c) - \Delta Hf^\circ\ UF_4(c)) = 98.2 \pm 1.0 \text{ kcal/mol}$$
$$\Delta Hf^\circ\ UF_3(c) = -357.3 \pm 1.5 \text{kcal/mol}$$

The data derived from the aqueous equilibria measurements are suspect; the hydrate system is a complex one; the K's given are not true equilibrium constants.

The more disturbing values are those from the Khanaev measurements; many reactions are involved in their paths to $UF_3(c)$ and $UF_4(c)$ from $UO_2Cl_2(c)$ and $UCl_4(c)$; it does not appear reasonable to assume that all the measurements are in error and that these errors are additive, particularly since the relationship between $UCl_4(c)$ and $UO_2Cl_2(c)$ is in excellent agreement with that from the selected values for ΔHf°'s $UCl_4(c)$ and $UO_2Cl_2(c)$. One of the reactions in common for both compounds is the $\Delta H_{mix.}$ of $HF(1.33H_2O)$ with the appropriate solution; if the ΔH mix. should be 0.7 kcal/mol HF more negative, the $\Delta(\Delta Hf^\circ\ UF_3 - \Delta Hf^\circ\ UF_4)$ would become 98.2 in agreement with the Markin et al (1967) EMF measurements and would result in

ΔHf° of UF_3(c) and UF_4(c) ≈ -357 and -455 kcal/mol, respectively. The $UF_4 \cdot 2.5H_2O$ value may have a similar error in ΔH mix. Obviously all of this is conjecture.

D. The Enthalpy of Hydration of UF_4(c, monoclinic) to $UF_4 \cdot 2.5H_2O$(c, orthorhombic)

As indicated in C, from the Maltsev et al. (1960) reactions involving the precipitation of $UF_4 \cdot 2.5H_2O(c)$ from UCl_4-HCl solutions, ΔHf° $UF_4 \cdot 2.5H_2O(c)$ = -633.2±1.0 kcal/mol.

Gagarinskii and Khanaev (1967) have measured the ΔH's of solution of UF_4(c, monoclinic) and $UF_4 \cdot 2.5H_2O(c)$ at 323 K and 298 K to the same final solution.

Their measurements are:

$$UF_4(c) + [166.5HCl + 3H_3BO_3] \rightarrow [UCl_4 + 3H_2O + HBF_4 + 162.5HCl + 2H_3BO_3]aq;\ \Delta H_{23} \quad (23)$$

$$[UCl_4 + 3H_2O + HBF_4 + 162.5HCl + 2H_3BO_3]aq + 2.5H_2O(liq) \rightarrow [UCl_4 + 5.5H_2O + HBF_4 + 162.5HCl + 2H_3BO_3]aq;\ \Delta H_{24} \quad (24)$$

$$UF_4 \cdot 2.5H_2O(c) + [166.5HCl + 3H_3BO_3]aq \rightarrow [UCl_4 + 5.5H_2O + HBF_4 + 162.5HCl + 2H_3BO_3];\ \Delta H_{25} \quad (25)$$

then for:

$$UF_4(c) + 2.5H_2O(liq) \rightarrow UF_4 \cdot 2.5H_2O(c);\ \Delta H_{26} \quad (26)$$

$$\Delta H_{26} = \Delta H_{23} + \Delta H_{24} - \Delta H_{25}$$

At 323 K: ΔH_{23} = -2.74±0.02 kcal

ΔH_{24} = -2.629±0.001

ΔH_{25} = +5.13±0.01

ΔH_{26} = -10.50 ± .025 kcal

$$
\begin{aligned}
\text{At 298 K: } \Delta H_{23} &= -4.73 \pm 0.05 \text{ kcal} \\
\Delta H_{24} &= -2.405 \pm 0.003 \\
\Delta H_{25} &= +3.21 \pm 0.03 \\
\hline
\Delta H_{26} &= -10.34 \pm .06
\end{aligned}
$$

Correcting ΔH_{26} from 323 K to 298 K ($\Delta C_p = -22$ cal/mol·K) results in $\Delta H_{26} = -9.94$ kcal/mol. A weighted average for ΔH_{26} at 298 K, then, is -10.2±0.2 kcal/mol.

From an inspection of the values calculated from $\Delta Hf°$ $UF_4(c)$ and $\Delta Hf°$ $UF_4 \cdot 2.5H_2O(c)$ from the Khanaev measurements and the Maltsev et al. measurements, one can calculate:

$$\Delta H_{26} = -633.2 + 2.5 \times 68.315 + 452.3 = -10.11 \text{ kcal}$$

which indicates a consistent cycle.

Popov et al. (1957) reported the $\Delta H_{\text{hydration}}$ of $UF_4(c)$ at 293 K to be -8.21±0.02 kcal/mol UF_4. The samples of UF_4 were obtained by dehydrating the crystalline $UF_4 \cdot 2.5H_2O(c)$ in vacuo, gradually heating to 498 K.

In addition to this Popov and Gagarinskii (1957) reported from tensimetric data

$$UF_4 \cdot 2.5H_2O(c) \rightarrow UF_4(c) + 2.5H_2O(g) \text{ (293-318 K)}; \qquad (27)$$
$$\log P_{\text{atm}} = 7{,}154 - 2{,}920/T$$

so that for the process given:

$$
\begin{aligned}
\Delta H &= 13.36 \times 2.5 = 33.4 \text{ kcal} \\
\Delta G &= 3.60 \times 2.5 = 9.0 \text{ kcal} \\
\Delta S &= 32.7 \times 2.5 = 81.75 \text{ cal}
\end{aligned}
$$

This would result in $\Delta H_{26} = -33.4 + 2.5 \times 10.52^{*} = -7.1$ kcal/mol of $UF_4 \cdot 2.5H_2O(c)$.

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* ΔH_{vap} $H_2O(l)$ = 10.52 kcal/mol at 298 K.

This is clearly in error. In addition ΔS = 32.7 cal/mol $H_2O \cdot K$ is low; one would expect ΔS = 35-36 cal/mol $H_2O \cdot K$. There is a possibility of a lower hydrate forming.

If it is assumed that the $\Delta G°$ is reasonable but that the slope is in error, then ΔH_{26} = -(9.0 + 35x2.5x.29815) + 2.5x10.52 = -8.7 kcal/mol $UF_4 \cdot 2.5H_2O(c)$, in somewhat better agreement with the Popov et al (1957) ΔH_{26}.

We have selected ΔH hydration from the results of Gagarinskii and Khanaev (1967), = -10.2±0.2 kcal/mol, since these direct solution measurements are on well characterized samples. This results in $\Delta Hf°$ $UF_4 \cdot 2.5H_2O(c)$ = -636.5±0.2 kcal/mol (relative to $\Delta Hf°$ $UF_4(c)$).

The previously mentioned $\Delta Hf°$ = -633.2 kcal/mol from Maltsev et al. (1960 may suffer from incomplete precipitation to $UF_4 \cdot 2.5H_2O(c)$; more probable is an error in the ΔH_{mix} involving HF(aq); this would cancel in the derived $\Delta H_{hydration}$ (obtained using the ΔHf $UF_4(c)$ from Khanaev (1968)).

The estimated S° $UF_4 \cdot 2.5H_2O(c)$ = 60±2.0 cal/mol·K is obtained from the measured S° $UF_4(c)$ plus an estimate for the contribution of the 2.5H_2O's (2.5 x 9.5).

The calculated and accepted $\Delta Gf°$ = -580.4 kcal/mol is obtained from the selected $\Delta Hf°$ and the $\Delta Sf°$ = -188.2±2.0 cal/mol·K.

The $\Delta Gf°$ obtained from the aqueous K's (see Section C) are in poor agreement.

E. Lower Hydrates of UF_4 and the Various Metastable Forms of UF_4

Gagarinskii and Khanaev (1967) have also prepared and measured the ΔH soln. of various lower hydrates and metastable forms. These lower hydrates and their dehydration products are ill-defined. The values derived for the $\Delta H_{\text{hydration}}$ UF_4(c, monoclinic) to the lower hydrates are inconsistent, i.e.,

$$UF_4(c) + 1.5H_2O(l) \rightarrow UF_4 \cdot 1.5H_2O(c); \; \Delta H = -5.1 \text{ kcal/mol}$$

but

$$UF_4(c) + 1.33H_2O(l) \rightarrow UF_4 \cdot 1.33H_2O(c); \; \Delta H = -7.44 \text{ kcal/mol.}$$

The metastable forms of UF_4(c) are formed from the lower hydrates and are irreversibly converted to the monoclinic. Again, they are not well defined.

An earlier paper by Gagarinskii and Mashirev (1959) also reports on the lower hydrates.

Table 1

The Enthalpies of Formation of UF_3(c) and UF_4(c)

Investigator	ΔHf° UF_3(c) kcal/mol	Method	Key Dependency for UF_3(c)	Key Dependency for UF_4(c)	ΔHf UF_4(c) kcal/mol	Δ(UF_3-UF_4) calc. from ΔHf UF_3 & UF_4 kcal/mol
Khanaev (1968)		Solution calorimetry, 323 K		UCl_4(c), HF(aq)	-452.3±0.9	97.5±1.2
Khanaev and Khripin (1970)	-354.94 ~±0.8	Solution calorimetry, 323 K	UO_2Cl_2(c), HF(aq) $FeCl_2$(c)-$FeCl_3$(c)			
" "	-354.67 ~±0.8	" "	UCl_4(c), HF(aq) $FeCl_2$(c)-$FeCl_3$(c)			
Hayman (1967) or	-357.08 ±0.75	Fluorination of U(c) and UF_3(c) to UF_6(g)	none	none	-454.65±0.7	96.6±0.5
Hayman (1967)	-359.86 ±0.6	Fluorination of UF_3(c) to UF_6(g)	ΔHf° UF_6(g)=-513.25	ΔHf° UF_6(g)=-513.25	-456.43±0.5	96.6±0.5
Heus and Egan (1966)	-357.3 ~±2.0	EMF, 873 K	AlF_3(c)	AlF_3(c)	-455.7±1.5*	98.4
Markin et al (1967)	-357.8 ~±2.0	" "	"	"	-456.4±1.5*	98.6
Heus and Egan (1966)	-356.5 ~±2.0	EMF, 873 K	MgF_2(c)	MgF_2(c)	-454.7±1.5*	98.2
Markin et al (1967)	-356.80 ~±2.0	" "	"	"	-455.1±1.5*	98.3

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*Obtained from Markin et al (1967) $4UF_3(c) \rightarrow 3UF_4(c) + U(c)$, ΔH° = 61.86±4.0 kcal

$UF_4(g)$

Hildenbrand (1976) has calculated the thermal functions for $UF_4(g)$ using the estimates of Tumanov (1968) where a tetrahedral structure was assumed and the vibrational frequencies were estimated on that basis. These are the assumed parameters:

$\nu_1 = 555\ \mathrm{cm}^{-1}$ (1)
$\nu_2 = 147$ " (2)
$\nu_3 = 566$ " (3)
$\nu_4 = 177$ " (3)
T_d model, tetrahedron
$\sigma = 12$
Singlet ground state
r U-F = 2.08Å

However, an analysis of the vapor pressure of $UF_4(c)$ and (l) indicates a serious discrepancy in calculated ΔH's of sublimation from 2nd and 3rd law analyses (which also shows a trend with temperature). The trend can be removed and agreement with the 2nd law values can be made by increasing S° and $-(G-H_{298})/T$ by 8.2 cal/mol·K (see Table 2 ΔH°_{subl} $UF_4(c)$ to (g)). One can account for about 3.7 cal/mol·K of this difference if $UF_4(g)$ has the less symmetrical C_{2v} structure; it had been assumed that the rest was due to a large electronic partition function. However, Gurvich et al. (1977) have indicated that this would not resolve the remaining 4 cal/mol·K discrepancy. For convenience the thermal functions are tabulated but with S° and $-(G-H_{298})/T$ increased by 8.2 cal/mol·K.

Table 2 shows the available vapor pressure measurements on UF_4(c) and (1), the ΔH and ΔS at the mean temperature, the 2nd law ΔH_{298} calculated from the $\Delta(H-H_{298})_T$ for the gas and the condensed phases, and the increment in S° needed to resolve the discrepancy between the 2nd law ΔH_{298} and 3rd law ΔH_{298} (calculated using S° at 298 K = 80.18 cal/mol•K from the unadjusted thermal functions for UF_4(g)). From these measurements the selections at 298 K are:

$$\Delta H^\circ_{subl} = 75.4 \pm 0.5 \text{ kcal/mol}$$

$$\Delta S^\circ_{subl} = 80.2 - 36.25 + 8.2 = 52.1 \pm 1.5 \text{ cal/mol·K}$$

leading to ΔHf° UF_4(g) = -380.1±1.2 kcal/mol. The ΔGf° = -373.9±2.0 kcal/mol is calculated from the ΔHf° and the tabulated S° = 88.4 cal/mol•K.

Table 2

ΔH°_{subl} $UF_4(c) \rightarrow UF_4(g)$

Investigator	Temp. Range	Method	$\Delta\bar{H}_T$ kcal/mol	$\bar{T}$ K	ΔH_{298} 2nd law kcal/mol	ΔH_{298} 3rd law kcal/mol	$\Delta S_{\bar{T}}$ cal/mol·K	X^{**} cal/mol·K
Lange and Blankenship (1960)	1314-1579*	Static and b.p. technique	55.62	1430	74.7	64.3	32.52	7.2
Hildenbrand (1976)	1040-1108	Mass spec., torsion effusion	71.8	1050	76.2	67.1	45.3	8.5
Akishin and Khodeev (1961)	920-1040	Mass spec., effusion	71.45	1000	75.55	65.7	45.8	8.9
Popov et al. (1959b)	1150-1273	Flow	69.02	1210	74.5	66.8	42.0	6.3
Johnsson (1947)	1120-1275	Static, diaphragm	70.84	1185	76.1	64.3	45.75	10.1
Chudinov and Choporov (1968)	830-1280	Effusion	65.3	1050	69.7	65.9	40.1	3.4

[*] Liquid above 1309 K; $\Delta S_{fusion} = 8.58$ cal/mol·K

[**] To be added to all S° values of T.F. $UF_4(g)$ to obtain 2nd and 3rd law agreement.

$UF_n(c)$ (n = 4.25, 4.5, 5)

Katz and Rabinowitch (1951) and Agron (1958) reported on the properties of $UF_{4.25}(c)$, $UF_{4.5}(c)$, $UF_5(c,\alpha)$ and $UF_5(c,\beta)$. Although the α-form of UF_5 is the stable form above 398 K (under 1.76 mm $UF_6(g)$), the α-form has not been converted to the β-form at lower temperature. To affect complete conversion of the β-form to the α-form requires 12 hrs heating at 458 K. Both α and β forms have tetragonal crystal symmetry.

Brickwedde (1951) measured the C_p of $UF_5(c,\alpha)$ which contained only 83 weight % UF_5. The reported S° UF_5 at 298 K was 45±3 cal/mol·K. This value lies between the values for $UF_5(c,\alpha)$ and $UF_5(c,\beta)$ which are derived from the disproportionation reactions of Agron (1958) on $UF_5(\alpha)$, $UF_5(\beta)$, $UF_{4.5}(c)$ and $UF_{4.25}(c)$. The values for S° $UF_{4.5}$ and S° $UF_{4.25}$ were estimated by Rand and Kubaschewski (1963).

Rand and Kubaschewski (1963) evaluated the disproportionation reactions of Agron (1958) modifying the experimental data (382-621 K) by using their estimated S°'s for $UF_{4.5}(c)$ and $UF_{4.25}(c)$ and a ΔC_p = -11 cal/mol·K*. The following relationships are accepted:

$$8UF_{4.25}(c) \rightarrow 7UF_4(c) + UF_6(g) \qquad (1)$$

$$\Delta G^\circ = 33{,}400 - 116.5T + 25.3T \log T \text{ cal/mol } UF_6(g)$$

(502-621 K)

at 298 K

ΔH° = 30.1 kcal/mol $UF_6(g)$

ΔG° = 17.4 kcal/mol $UF_6(g)$

ΔS° = 42.7 cal/mol·K $UF_6(g)$

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* A slightly better ΔC_p for the disproportionations, -5 cal/mol·K, would result in negligible differences in the ΔHf°'s.

$$7UF_{4.5}(c) \rightarrow 6UF_{4.25}(c) + UF_6(g) \qquad (2)$$

$$\Delta G^\circ = 31{,}100 - 114.4T + 25.3\ T \log T \text{ cal/mol } UF_4(g)$$

$$(533 - 590 \text{ K})$$

at 298 K

$$\Delta H^\circ = 27.8 \text{ kcal/mol } UF_6(g)$$

$$\Delta G^\circ = 15.7 \text{ kcal/mol } UF_6(g)$$

$$\Delta S^\circ = 40.7 \text{ cal/mol·K } UF_6(g)$$

For the disproportionations of α-$UF_5(c)$ and β-$UF_5(c)$, however, Rand and Kubaschewskii did not distinguish between the two forms, so that the original measurements of Agron then were refit (with a $\Delta C_p = -11$ cal/mol·K) to obtain:

$$3UF_5(c,\alpha) \rightarrow 2UF_{4.5}(c) + UF_6(g) \qquad (3)$$

$$\Delta G^\circ = 18{,}300 - 99.8T + 25.3T \log T \text{ cal/mol}$$

$$(382 - 469 \text{ K})$$

at 298 K

$$\Delta H^\circ = 15.0 \text{ kcal/mol } UF_6(g)$$

$$\Delta G^\circ = 7.3 \text{ kcal/mol } UF_6(g)$$

$$\Delta S^\circ = 26.1 \text{ cal/mol·K } UF_6(g)$$

$$3UF_5(c,\beta) \rightarrow 2UF_{4.5}(c) + UF_6(g) \qquad (4)$$

$$\Delta G^\circ = 24{,}000 - 114.0T + 25.3T \log T \text{ cal/mol}$$

$$(384 - 423 \text{ K})$$

at 298 K

$$\Delta H^\circ = 20.7 \text{ kcal/mol } UF_6(g)$$

$$\Delta G^\circ = 8.7 \text{ kcal/mol } UF_6(g)$$

$$\Delta S^\circ = 40.4 \text{ cal/mol·K } UF_6(g)$$

These equations result in the tabulated values (Section III).

Then, from (3) and (4) for:

$$UF_5(c,\beta) \rightarrow UF_5(c,\alpha) \qquad (5)$$

at 298 K

$$\Delta H = 1.9 \text{ kcal/mol}$$

$$\Delta G = 0.5 \text{ kcal/mol}$$

$$\Delta S = 4.8 \text{ cal/mol·K}$$

$UF_5(g)$

Krohn et al. (1976) estimated the vibrational assignment for $UF_5(g)$ on the basis of the C_{4v} pyramidal structure ($\sigma = 4$). Hildenbrand (1976) used these with the U-F bond length = 1.995 Å and a doublet electronic ground state to calculate the thermal functions for $UF_5(g)$. These functions are accepted as modified below.

Hildenbrand (1976) using high temperature mass spectrometry studied the gaseous equilibrium (range 1012-1158 K):

$$Ag(g) + UF_5(g) \rightarrow AgF(g) + UF_4(g) \qquad (1)$$

The experimental $\Delta S°_{1100\ K} = 8.9 \pm 1.0$ cal/mol·K results in S° $UF_5(g) \approx$ 131.1 cal/mol·K, at 1100 K, ~ 3 cal/mol·K higher than the calculated S° = 128 cal/mol·K. The tabulated S and $-(G-H_{298})/T$ have been increased by these 3 cal/mol·K. These are to be considered approximate functions.

The 2nd law $\Delta H = 15.6 \pm 0.6$ kcal/mol corrects to $\Delta H°_1 = 16.9 \pm 1.5$ kcal/mol. Using:

$$AgF(g) \rightarrow Ag(g) + F(g); \ \Delta H°_2 = 84.8 \pm 4.0 \text{ kcal/mol} \qquad (2)$$

from Clements and Barrow (1968), and Hildenbrand's determination:

$$UF_4(c) \rightarrow UF_4(g); \ \Delta H°_3 = 76.2 \text{ kcal/mol} \qquad (3)$$

the following is obtained:

$$UF_5(g) \rightarrow UF_4(c) + F(g); \ \Delta H°_4 = 25.5 \pm 4.5 \text{ kcal/mol} \qquad (4)$$

The resultant $\Delta Hf°$ $UF_5(g) = -462. \pm 5.0$ kcal/mol.

From electron impact threshold measurements Hildenbrand also reports:

$$UF_6(g) \rightarrow UF_5(g) + F(g) \qquad (6)$$

$$D^\circ_0 = 2.955 \text{ e.v. or } 68.0\pm0.2 \text{ kcal/mol}$$

so that $\Delta H^\circ_{298} \approx 69$ kcal/mol and ΔHf° $UF_5(g) = -463.3\pm3.3$ kcal/mol.

Wolf et al. (1965) determined the vapor pressure of the α form of $UF_5(c)$ from 555 K to the experimentally determined melting point, 621° K as well as that of the liquid to 685°K by measurements of the transpiration rates, using UF_6 as the carrier gas to prevent disproportionation of the UF_5. The following vapor pressure equations were derived:

$UF_5(c,\alpha)$:

$$\log P(\text{atm}) = -(8001\pm664)/T + (11.113\pm1.119), (555\text{-}621 \text{ K})$$

$UF_5(\text{liq})$:

$$\log P(\text{atm}) = -(5388\pm803)/T + (6.938\pm1.236), (621\text{-}685 \text{ K})$$

The calculated mean ΔH_{subl} and ΔS°_{subl} at 580 K = 36.6±3.0 kcal/mol and 50.8±4.5 cal/mol·K. Correcting to 298 using an estimated $\Delta C_p = -7$ cal/mol·K results in $\Delta H^\circ = 38.6\pm3.2$ and $\Delta S^\circ = 55.6\pm5.0$, leading to ΔHf° $UF_5(g) = -456\pm3.6$ kcal/mol and $S^\circ = 104\pm5.4$ cal/mol·K. The entropy appears particularly high. One would not expect S° $UF_5(g)$, even including an electronic contribution, to be greater than 94 cal/mol·K. In addition, the calculated $\Delta S_{fusion} = 19$ cal/mol·K appears high; one would expect $\Delta S_{fusion} = 12\text{-}14$ cal/mol·K.

A third law analysis of the vapor pressure measurements on the crystal, however, results in $\Delta H^\circ_{subl} = 32.6$ kcal/mol. At 600 K, $-\Delta(G-H_{298})/T = 44.0$ cal/mol·K, based on the adjusted $-(G-H_{298})/T$ for $UF_5(g)$, S° $UF_5(c,\alpha) = 47.7$ and an estimate for $-(G-H_{298}/T)_{600\text{ K}}$ for $UF_5(c,\alpha)$. This ΔH°_{subl} results in $\Delta Hf^\circ \approx -462$ kcal/mol for $UF_5(g)$ in agreement with the Hildenbrand measurements.

The Gibbs energy of formation has been calculated from ΔHf° and ΔSf°.

UF_6(c)

The S° , C_p° and $(H-H_0)_T$ values tabulated by Brickwedde et al. (1948) from their C_p measurements on the crystal and liquid (14-370 K) are accepted. These measurements also define the triple point (337.20 K) and ΔH_{fusion} = 4.588±0.045 kcal/mol.

In addition, there are measurements by Llewellyn (1953) in the range 213-373 K.

The ΔHf° UF_6(c) has recently been redetermined by Johnson (1977) by direct fluorination of U(c) to be -525.13±0.44 kcal/mol. Although still to be considered preliminary, this new determination confirms the value = -525.1±0.5 kcal/mol recommended by Parker (1976b)from the key network analyses and the $UO_3(c,\gamma)$ - UF_6(c) - HF(aq) - UO_2F_2(c) cycles. These values supercede the value -522.6±0.4 kcal/mol that had been considered to be definitive.

The analysis which indicated that the value -522.6 kcal/mol for UF_6(c) was questionable and that a direct redetermination was needed to substantiate the indirect value, -525.1 kcal/mol, is presented historically in order to indicate how values considered reliable become suspect through a detailed analysis of the network. The analysis includes much of the preliminary evaluation of ΔHf° UO_2F_2(c) and ΔHf° UO_2F_2(aq, in HF) which brought the problem into focus.

A. The Initially Accepted ΔHf° UF_6(c) and ΔHf° UF_6(g)

There were two determinations of the enthalpy of fluorination of U(c) to UF_6(c) and UF_6(g) that were in good agreement with one another and were considered definitive for ΔHf° UF_6(c) and ΔHf° UF_6(g).

The first of these is by Settle et al. (1963) using bomb calorimetry

$U(c) + 3F_2(g) \rightarrow UF_6(c)$; $\Delta H_1 = -522.64 \pm 0.43$ kcal/mol (1)

Hayman (1967) in a flow calorimeter obtained:

$U(c) + 3F_2(g) \rightarrow UF_6(g)$; $\Delta H_2 = -510.47 \pm 0.64$ kcal/mol (2)

From the analysis of the vapor pressure measurements (see $UF_6(g)$):

$UF_6(c) \rightarrow UF_6(g)$; $\Delta H°_3 = 11.85 \pm 0.10$ kcal/mol (3)

so that $\Delta H_1^\circ = -522.32 \pm 0.65$ kcal/mol from Hayman's data.

These measurements led to the accepted $\Delta Hf°$ $UF_6(c) = -522.6 \pm 0.4$ and $\Delta Hf°$ $UF_6(g) = -522.6 + 11.85 = -510.75 \pm 0.4$ kcal/mol.

B. The Inconsistency in Paths and How it Affected $\Delta Hf°$ $UO_2F_2(c)$ and $\Delta Hf°$ UO_2F_2(in HF)

The analysis of the data on the $\Delta Hf°$ $UO_2F_2(c)$ involves the ΔHf of the aqueous species. The measurements on the reaction of $UO_3(c,\gamma)$ in HF(aq) to form a species for convenience called UO_2F_2(aq, in HF) will be cited first. The measured reactions are of the form:

$UO_3(c,\gamma) + 2HF(\text{aq, in excess}) \rightarrow UO_2F_2(\text{aq, in HF}) + H_2O(\text{aq, in HF})$

Since all the measurements on the ΔH_r of $UO_3(c,\gamma)$ were made in excess HF of varying concentration and in varying UO_3/HF ratios we have corrected for the dilution of the excess HF in the final solution, either by using the appropriate φ_L[*] values for the initial and final concentrations, or by using the differentials $\bar{L}_2$[*] and $\bar{L}_1$ if there is no appreciable concentration change for HF(aq).

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[*] All values listed by Parker et al. (1976) for the integral and differential ΔHf's $HF(nH_2O)$ should be made more negative by 0.07 kcal/mol. The value listed for $\Delta Hf°$ HF(aq, std. state) = -80.15 kcal/mol is correct.

Table 3

The Reaction of $UO_3(c,\gamma)$ in HF(aq)

	ΔH_m kcal/mol	ΔH_r kcal/mol	Initial HF soln.	Descriptive state of UO_2F_2 formed	ΔHf $UO_2F_2(aq)$ in descriptive state
Calculated*		-19.32*	∞H_2O, 0 HF	aq. std. state	-403.8±0.5*
Vidavskii et al. (1965)	-24.56±.11	-18.308	6(HF+267H_2O)	4(HF+400H_2O)	-402.79±0.45
Cordfunke and Ouweltjes (1976)	-25.31±.08	-19.052	~48(HF+264H_2O)	~46(HF+276H_2O)	-403.54±0.4
O'Hare and Johnson (1976)	-25.38±.09	-19.140	27.3(HF+115.25 H_2O)	25.3(HF+124.4 H_2O)	-403.62±0.4
Vidavskii and Ippolitova(1971)	-25.63±.08	-19.293	19(HF+20H_2O)	17(HF+22.4H_2O)	-403.78±0.4

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* Calculated from the ΔHf F^-(aq, std. state) and $\Delta Hf°$ UO_2^{2+}(aq, std. state)

Table 3 shows the measured ΔH_m and the corrected ΔH_r for the reaction,

$$UO_3(c,\gamma) + 2HF(aq,\ std.\ state) \rightarrow H_2O(1) + UO_2F_2(aq,\ in\ HF),$$

the initial composition of the HF solution, the descriptive state for the UO_2F_2 in the final solution and the calculated ΔHf UO_2F_2 for that state.

As can be seen, the results are in good agreement with one another, although the ΔHf calculated from Vidavskii et al. (1965) is 0.75 to 1.0 kcal/mol more positive than the others. The solution is also more concentrated with respect to the UO_2F_2.

Similarly, information on ΔHf UO_2F_2(aq, in HF) from the reaction of UF_6(c) in H_2O(1) or in a solution of HF(aq) may be obtained. The measured reactions are of the form:

$$UF_6(c) + 2H_2O(1)\ or\ (in\ HF\ soln.) \rightarrow UO_2F_2(aq,\ in\ HF\ soln.) + 4HF(soln.)$$

The reactions have been corrected where necessary to 298 K and to the form:

$$UF_6(c) + 2H_2O(1) \rightarrow UO_2F_2(aq,\ in\ HF) + 4HF(aq,\ std.\ state)$$

by correcting as for the reaction of $UO_3(c,\gamma)$ in a solution of HF.

Table 4

The Reaction of UF_6(c) in H_2O

	ΔH_m kcal/mol	ΔH_r	Initial Soln.	Descriptive state of UO_2F_2 formed	ΔHf UO_2F_2 in descriptive state
Popov et al. (1957)	-49.73* ±0.30	-61.874	1602H_2O	4(HF+400H_2O)	-400.50 ±0.8
O'Hare and Johnson(1976)	-49.918 ±0.07	-62.35	21.33(HF+ 147.80H_2O)	25.33(HF + 124.4H_2O)	-400.98 ±0.75

*Corrected from ΔH_m= -50.22±0.30 at 305 K assuming ΔC_p = -70 cal/mol·K

The two values are in good agreement with one another, and show the same effect as noted earlier, but the values calculated from the two tables differ by ~ 2.5 kcal/mol.

ΔHf UO_2F_2(aq, in HF) from UF_6	from γUO_3(c)	Descriptive State	Difference in Paths UF_6-UO_3
-400.50	-402.79	4(HF+400H_2O)	2.29
-400.98	-403.62	25.33(HF+124.4H_2O)	2.64

The following measurements have been made on the $\Delta H_{soln.}$ UO_2F_2(c) in HF and in H_2O(1) corrected to 298 where necessary.

	ΔH_{soln} kcal/mol	Solution
Suponitskii et al. (1971)	-7.12	571H_2O
Popov et al. (1957)	-7.89±0.2*	4(HF+400H_2O)
Cordfunke and Ouweltjes (1976)	-8.10±0.05	47.6(HF+264H_2O)

These values are also in agreement with one another. Obviously the values calculated for ΔHf° UO_2F_2(c) from the two available paths will reflect the 2.5 kcal discrepancy, i.e. ΔHf° UO_2F_2(c) = -402.79 + 7.89 = -394.90±0.50 kcal/mol and -403.54 + 8.10 = -395.44±0.40 kcal/mol from the UO_3(c,γ) path and the appropriate ΔH_{soln} UO_2F_2(c), and ΔHf° UO_2F_2(c) = -400.50 + 7.89 = -392.61±0.85 kcal/mol from the UF_6(c) path and the appropriate ΔH_{soln} UO_2F_2(c).

At this point it is essential to explore the possible causes of the difference.

1. There is a major error in either the experimental measurements involving the reaction of UF_6(c) or those of UO_3(c,γ). This is

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*Corrected from $\Delta H_{soln.}$ = -8.10 at 305 K assuming ΔC_p = -30 cal/mol·K.

highly unlikely since the agreement within each set (differing in their origin) is good.

2. The UO_3(c,γ) used for the measurements is not the same form as that for which ΔHf° = -292.5±0.3. However, O'Hare confirmed that the sample of UO_3(c,γ) used by O'Hare and Johnson (1976) was the same as that used by Fitzgibbon et al. (1967) in their determination of ΔHf° UO_3(c,γ) from solution calorimetry involving UO_3(c,γ), UO_2(c) and U_3O_8(c) since they confirmed these solution measurements.
3. The value used for UO_3(c,γ) = -292.5±0.3 kcal/mole is too negative by ~2.5 kcal/mol. This does not seem possible unless a corresponding change is made in UO_2(c) and an even larger change is made in U_3O_8(c). If UO_2(c) and UO_3(c,γ) were changed significantly the good agreement obtained for the ΔHf° values for (1) UCl_4(c) [only partly dependent on ΔHf UO_2(c)], (see section on UCl_4(c)); (2) UO_2Cl_2(c) [partly dependent on UCl_4(c) and partly dependent on UO_3(c,γ)], (see section on UO_2Cl_2(c)); and (3) UO_2^{2+}(aq, std. state) [partly dependent on UO_2Cl_2(c) and partly dependent on $UO_2(NO_3)_2 \cdot 6H_2O$(c) which is completely dependent on UO_3(c,γ)], (see Fuger and Oetting (1976)) would disappear.
4. The value used for UF_6(c) should be made more negative than -522.6 by this 2.5 kcal/mol. As shown in A on the ΔHf°'s for UF_6(c) and UF_6(g), there is confirmation for -522.6 kcal/mol. However, a more negative value for UF_6(c) and UF_6(g) would lower the value for $\Delta H°_{subl.}$ U(c) derived from UN(c) and US(c) and would bring them into better agreement with the accepted $\Delta H°_{subl}$ = 127 kcal/mol (Oetting et al. (1976)).

5. Neither the ΔHf° $UO_3(c,\gamma)$ nor the ΔHf° $UF_6(c)$ are seriously in error, but the auxiliary values for ΔHf HF(aq) are. Since the $UF_6(c)$-$UO_3(c,\gamma)$ relation involves six HF(aq), this shift of 0.4 kcal/mol HF would account for the discrepancy in paths. However, the ΔHf HF(aq) values listed by Parker et al. (1976) from the Johnson et al. (1973) determinations are consistent with the CODATA (1975) ΔHf° F^-(aq, std. state) = -80.15±0.16 kcal/mol which was fixed from various cycles, five of which were in agreement (within ±0.1 kcal).

6. None of the above, but an erroneous assumption is being made.

The first three possibilities are at present rejected. It is more difficult to assess the remaining three; however, these 3 possibilities all involve the reaction of $UF_6(c)$, either because the accepted ΔHf° $UF_6(c)$ is erroneous, or because of the greater dependency on the value for ΔHf° F^-(aq, std. state), or because the assumption on final solutions is not warranted.

The better path, then, to $UO_2F_2(c)$ and UO_2F_2(aq, in HF) is from the relationship to $UO_3(c,\gamma)$, which results in -394.90±0.5 and -395.44±0.4 kcal/mol for ΔHf° $UO_2F_2(c)$ rather than from the $UF_6(c)$ path which results in -392.6±0.85 kcal/mol.

C. The decision to change the ΔHf°'s UF_6 (c) and UF_6(g)

As is indicated in B, either the ΔHf° UF_6 is suspect or to a lesser extent ΔHf HF(aq, std. state). However, if one goes through the uranium key network the more positive ΔHf° HF(aq, std. state) (= -79.75 kcal/mol) required here would not resolve other inconsistencies. (See $UF_3(c)$ and $UF_4(c)$) where a more negative ΔHf° HF(aq, std. state) would be required to resolve the inconsistencies. In addition, on a practical note, many more new cycles would have to be considered before one could say with certainty that the CODATA ΔHf HF(aq, std. state) is too negative by 0.4 kcal/mol (the UF_6(c)-UO_3(c,γ) cycle from the combination of Popov et al. (1957) and Vidavskii et al. (1965) had been considered by the CODATA task force).

The most likely values then, by the process of elimination, are ΔHf°'s UF_6(c) and UF_6(g). In order to substantiate this the following was done:

It was assumed that the fluorinations of U(c) to UF_6(c) and (g) were in error but that the ΔH's of fluorination of UN(c), US(c) to UF_6 were correct.

The high temperature decomposition reactions of US(c) and UN(c) were considered and the most reasonable reactions used. The ΔHf° U(g) = 127^{+2}_{-1} kcal/mol from Oetting et al.(1976) was used in each reaction to obtain values for ΔHf° of US(c) and UN(c) which were then used in the fluorination reactions to obtain values for ΔHf° UF_6(c) and ΔHf° UF_6(g).

The reactions are:

$$UN(c) \rightarrow U(g) + 1/2N_2(g);\ \Delta H^\circ_1 = 200.7 \pm 1.0 \text{ kcal/mol} \quad (1)$$

(avg. of 2nd and 3rd law)

from Hoenig (1971), so that ΔHf° UN(c) = -73.7±1.8 kcal/mol and ΔHf°

$UN_{0.9957}$ = -73.6±1.8 kcal/mol.

$UN_{0.9957}(c) + 3F_2(g) \rightarrow UF_6(c) + 0.9957/2N_2(g)$;

ΔH_2 = -451.86±0.3 kcal/mol (2)

from O'Hare et al. (1967) (corrected for composition), so that ΔHf° $UF_6(c)$ = -525.5±1.9 kcal/mol.

$US(c) \rightarrow U(g) + S(g)$; ΔH_2 = 269.6±2.0 kcal/mol from Nater (1969) (3)

so that ΔHf° US(c) = -76.4±2.5 and ΔHf° $US_{1.011}(c)$ = -76.8±2.5 kcal/mol.

$US_{1.011}(c) + 6.033F_2(g) \rightarrow UF_6(g) + 1.011SF_6(g)$;

ΔH_4 = -732.59±2.0 kcal/mol from O'Hare et al. (1967) (4)

with ΔHf° $UF_6(g)$ = -514.4±3.2 kcal/mol and ΔHf° $UF_6(c)$ = -526.3±3.2 kcal/mol. These two paths lend support to more negative values for ΔHf° $UF_6(c)$ and ΔHf° $UF_6(g)$. These are obtained from the UF_6-UO_3 cycles, so that ΔHf° $UF_6(c)$ = -522.6 - 2.29 = -524.89±0.6 kcal/mol from the Popov-Vidavskii cycle and -522.6 - 2.64 = -525.24±0.5 kcal/mol from the O'Hare and Johnson cycle, resulting in a selected ΔHf° $UF_6(c)$ = -525.1±0.5 kcal/mol.

D. Confirmation From the Direct Enthalpy of Fluorination

Obviously confirmation for this new value was needed. The new measurements of Johnson (1977) on the direct fluorination to $UF_6(c)$ cited previously = -525.13±0.44[*] kcal/mol lends support to the indirect value[**].

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[*] A recalculation by Johnson (1979) using the values for the ΔHf°'s for $UF_3(c)$ and $UF_4(c)$ and the ΔH°_{subl} $UF_6(c)$ selected in this evaluation results in ΔHf°$UF_6(c)$ = -525.28±0.44 kcal/mol.

[**] One should also note that the new direct determination lends support to the CODATA ΔHf° HF(aq, std. state) and ΔHf° F^-(aq, std. state) = -80.15 kcal/mol.

We can now with certainty assign $\Delta Hf°$ $UF_6(c)$ = -525.1±0.4 kcal/mol and $\Delta Hf°$ $UF_6(g)$ = -525.1 + 11.85 = -513.25±0.4 kcal/mol.

There is at present no explanation for the two earlier direct fluorination reactions, in agreement with one another, being in error.

The Gibbs energy of formation has been calculated from the $\Delta Hf°$ and the $\Delta Sf°$.

$\underline{UF_6(g)}$

The ΔH°_{subl} = 11.85±0.10 kcal/mol and the ΔG°_{subl} = 1.14 kcal/mol result in $\Delta S^\circ_{subl.}$ = 35.95±0.3 cal/mol·K which leads to S° $UF_6(g)$ = 90.3±0.45 cal/mol·K.

The thermal functions for the ideal gas may also be calculated from spectroscopic data. The frequency assignment by Claasen (1959) 667(1), 535(2), 623(3), 181(3), 202(3), 140(3) cm^{-1} based on the measurements of Gaunt (1953), Claasen et al. (1956), Burke et al. (1952), and Bigeleisen et al. (1948), for the octahedron (symmetry = 24), with r-U-F 1.999Å from Seip (1965) results in S° = 90.23 cal/mol·K in excellent agreement with the experimentally derived S°.

The more recent assignment of McDowell et al. (1974) 672(1), 540(2), 634(3), 186(3), 200(3), 143(3) cm^{-1} results in S° = 89.93 cal/mol·K.

A table of thermal functions based on Claasen et al.'s (1956) assignment is presented here (Section V).

The ΔHf° of $UF_6(g)$ is derived from the selected ΔH°_{subl} = 11.85±0.10 kcal/mol for:

$$UF_6(c) \rightarrow UF_6(g). \qquad (1)$$

This is obtained from both the calorimetric determinations of ΔH°_{vap} (277-363 K) of Masi (1949) and those calculated from the various vapor pressure measurements, all in excellent agreement. This results in ΔHf° $UF_6(g)$ = -513.25±0.4 kcal/mol.

As indicated under $UF_6(c)$, Hayman (1967) obtained $\Delta H_2 = -510.5 \pm 0.7$ kcal/mol for:

$$U(c) + 3F_2(g) \rightarrow UF_6(g) \qquad (2)$$

This has been shown to be in error.

The $\Delta G°_1 = 1.14$ kcal/mol, results in $\Delta Gf°$ $UF_6(g) = -493.26$ kcal/mol.

The various vapor pressure measurements on the solid and liquid are in good agreement and can be represented by the equations of Oliver et al.(1953):

$UF_6(c)$

$$\log P(atm) = 3.50282 + 0.0075377t - 942.76/(t+183.416)$$
$$(273\text{-}337\ K)$$

$UF_6(l)$

$$\log P(atm) = 4.11383 - 1126.288/(t+221.963)$$
$$(337\text{-}390\ K)$$

$UF_6(l)$

$$\log P(atm) = 4.80988 - 1683.165/(t+302.148)$$
$$(390\text{-}500\ K)$$

The triple point calculated here is 337.20 K with P(mm) = 1139.6. This calculated triple point is in excellent agreement with that directly determined by Brickwedde et al. (1948) as 337.202 K with $\Delta H_{fusion} = 4.588$ kcal/mol, $\Delta S° = 13.61$ cal/mol·K.

For $UF_6(l) \rightarrow UF_6(g)$:

at T = 337.202 K $\qquad \Delta H°_{vap} = 6.84$ kcal/mol

The sublimation temperature (1 atm.) is at 329.69 K.

For convenience Masi's (1949) smoothed ΔH°_{vap} for the condensed phases (273-370 K) are tabulated. These values are within 50 cal/mol of the recommended values given here.

TABLE 5

Enthalpies of Vaporization of UF_6

T, K	ΔH cal/mole
crystal	
273.15	12,023
280	11,988
290	11,929
298.15	11,872
300	11,858
310	11,772
320	11,666
330	11,537
337.20	11,429
liquid	
337.20	6859
340	6817
350	6671
360	6533
370	6404

See Rand and Kubaschewski (1963) for citations to the individual investigations for the vapor pressure measurements.

3.102 U-F-O Compounds

UOF_2(c) and $UOF_2 \cdot H_2O$(c)

S° UOF_2(c) has been estimated as 28.5±1.0 cal/mol·K based on a comparison of the S°'s of UCl_4(c), UF_4(c), $UOCl_2$(c), UO_2Cl_2(c), UO_2F_2(c), UO_2(c), and UO_3(c). The S° $UOF_2 \cdot H_2O$(c) is derived from the estimated ΔS_5 discussed in the following section.

Vdovenko et al. (1967) isolated a black crystal hydrate which corresponded to $UOF_2 \cdot H_2O$(c). In (1969) they measured its enthalpy of reaction in HCl(aq) at 293 K. Their measured reactions are:

$$UOF_2 \cdot H_2O(c) + 254HCl(aq) \rightarrow [UF_2Cl_2 + 252HCl + 2H_2O]aq; \quad \Delta H_1 = -5.42 \pm 0.04 \text{ kcal/mol} \quad (1)$$

$$[UCl_4 + 250HCl]aq + 2HF(aq) \rightarrow [UF_2Cl_2 + 252HCl]aq; \quad \Delta H_2 = -7.90 \pm 0.05 \text{ kcal/mol} \quad (2)$$

The concentrations used correspond to those used by Maltsev et al. (1960) in their determination of $\Delta Hf°$ $UF_4 \cdot 2.5H_2O$(c) and use is made of the Maltsev et al. reaction:

$$UCl_4(c) + 250HCl(aq) \rightarrow [UCl_4 + 250HCl]aq; \quad \Delta H_3 = -43.47 \pm 0.10 \quad (3)$$

to complete the cycle. From these reactions the following summation is obtained:

$$UCl_4(c) + 2H_2O(aq) + 2HF(40\% \text{ soln.}) \rightarrow UOF_2 \cdot H_2O(c) + 4HCl(5N\ HCl); \quad \Delta H_4 = -46.68 \pm 0.2^{*} \text{ kcal/mol } UCl_4(c) \quad (4)$$

From the individual reactions in the two papers involved it is clear that the ΔHf of the HF 40% soln. HF·1.667H_2O) to be used is an

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[*] Corrected to 298 K, assuming ΔC_p = -145 cal/mol·K.

integral quantity = -76.42 kcal/mol but the ΔHf's of HCl and H_2O in 5N HCl solution, HCl($10H_2O$), are differential quantities.

The resultant ΔHf° $UOF_2 \cdot H_2O(c)$ = -430.7±0.8 kcal/mol.

In addition, the H_2O vapor pressure (283 to 363 K) over $UOF_2 \cdot H_2O$ was determined by Vdovenko et al. (1969). For:

$$UOF_2 \cdot H_2O(c) \rightarrow UOF_2(c) + H_2O(g); \qquad (5)$$

at 298 K they report a calculated ΔH_5 = 11.1 kcal/mol $H_2O(g)$

ΔG_5 = 2.82 kcal/mol $H_2O(g)$

ΔS_5 = 27.8 cal/mol·K

Use of the calculated ΔH_5 = 11.1 kcal/mol results in ΔHf° $UOF_2(c)$ = -361.8 kcal/mol. This would mean that for the reaction:

$$2UOF_2(c) \rightarrow UO_2(c) + UF_4(c) \qquad (6)$$

$$\Delta H > 8 \text{ kcal/mol } UF_4{}^{*} \text{ and } \Delta G > 9 \text{ kcal/mol } UF_4$$

This would indicate that the stability of $UOF_2(c)$ is greater than that of $UOCl_2(c)$ (ΔH and ΔG for the comparable chloride reaction are 7.2 and 7.4 kcal/mol $UCl_4(c)$, respectively). This is questionable. In addition the calculated ΔS and ΔH for reaction (5) are low. One would expect ΔS_5 to be ~ 35 e.u. If the measured pressure at 298 K is used ($\Delta G°_5$ = 2.82 kcal/mol) with the estimate ΔS_5 = 35 cal/mol·K, ΔH_5 = 13.3 kcal/mol $H_2O(g)$. This results in ΔHf° $UOF_2(c)$ = -359.6±1.5 kcal and results in, for (6), $\Delta H < 6$ kcal/mol UF_4*.

The Gibbs energies of formation have been calculated from the ΔHf°'s and ΔSf°'s.

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* $\Delta H > 8$ and $\Delta H < 6$ are used because of the uncertainty in the ΔHf° $UF_4(c)$.

$UO_2F_2(c)$

Wacker and Cheney (1947) measured the heat capacity from 13 K to 418 K. The tabulated S°, $C_p°$ and $H-H_0$ are obtained from their smoothed values. Kelley and King (1961) cite the above measurements in their tabulation; however, they report $S°_{298} = 33.40$ cal/mol·K. This appears to be an error in transcription.

Cordfunke et al. (1978) determined the high-temperature enthalpy from 375 to 811 K relative to 298 K. The results are expressed as:

$$H_T-H_{298} = 29.53T + 0.5833\text{x}10^{-3}T^2 + 5.193\text{x}10^5T^{-1} - 10{,}598 \text{ cal/mol}$$

(298-811 K)

This equation results in values for H_T-H_{298} in good agreement (lower by ∿ .03 kcal/mol at 400 K) with those tabulated by Wacker and Cheney (1947) but leads to a calculated $C_p°$ at 298.15 K ∿0.6 cal/mol·K lower than that obtained from the direct $C_p°$ determinations which are, at present, preferred for the low-temperature properties.

Purity of the Wacker and Cheney sample, however, may be the problem.

As indicated in the discussion of ΔHf° $UF_6(c)$, from

$$UO_3(c,\gamma) + 2HF(aq, \text{ std. state}) \rightarrow UO_2F_2(c) + H_2O(l)$$

ΔHf° $UO_2F_2(c) = -394.90\pm0.50$ kcal/mol from the combination of the Popov et al. (1957) ΔH_{soln} $UO_2F_2(c)$ in $4(HF + 400H_2O)$ and the Vidavskii et al. (1965) ΔHf° $UO_2F_2(aq)$ in the same final solution. Also ΔHf° $UO_2F_2(c) = -395.44\pm0.35$ from the Cordfunke and Ouweltjes (1976) values.

From the Popov et al. (1957) UF_6-UO_2F_2 cycle ΔHf° = -403.0[*] + 7.89 = -395.11±0.6 kcal/mol.

The selected value of ΔHf° UO_2F_2(c) = -395.2±0.3 kcal/mol.

In addition to the measurements described above, Knacke et al. (1969) reported a ΔH = 90.7 kcal/mol UF_6(g) and ΔS° = 62.3 cal/mol UF_6(g) in the range 1033 K to 1073 K for the decomposition:

$$3UO_2F_2(c) \rightarrow 2/3U_3O_8(c) + UF_6(g) + 1/3O_2(g)$$

With a ΔC_p = -3.7 cal/mol·K, ΔH° = 94.0 kcal/mol and ΔS° = 66 cal/mol·K. This ΔH results in ΔHf° UO_2F_2(c) = -392.3 kcal/mol and S° UO_2F_2(c) = 28.6 cal/mol·K, in sharp disagreement with the measured low temperature value. In addition, if one uses the measured low temperature S°'s and the ΔG° at 1040 K, the resultant $\Delta H°_{298}$ = 80.2 kcal/mol and ΔHf° = -387.7 kcal/mol, even further off. No weight can be given to these measurements. There is a possibility that the products of the decomposition are not as written.

The Gibbs energy of formation has been calculated from the accepted ΔHf° and the ΔSf°.

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[*] i.e., -400.5 - 2.5 where -2.5 = -525.1 - 522.6.

UO_2F_2(aq, in HF)

The various values for the ΔHf° UO_2F_2(aq, in HF) cited in the discussion under UF_6(c) from the ΔH°'s of reaction of UF_6, γUO_3 and UO_2F_2(c) in HF can now be consolidated. The major effect appears to be the concentration of the HF solution.

Final smoothed values are:

ΔH_{soln} UO_2F_2(c) kcal/mol	ΔHf UO_2F_2(solution) kcal/mol	Descriptive State
-8.6	-403.8	aq. std. state
-7.12	-402.32	in $570H_2O$
-7.85	-403.05	in 4(HF + $400H_2O$)
-8.20±.10	-403.40	in 47(HF + $276H_2O$)
-8.35	-403.55	in 25(HF + $124.4H_2O$)
-8.58	-403.78	in 17(HF + $22.4H_2O$)

$UO_2F_2 \cdot nH_2O$(c)

Suponitskii et al (1971) report the following ΔH's soln. in $571H_2O$:

	ΔH, kcal/mol
UO_2F_2 (c)	-7.12±.11
$UO_2F_2 \cdot 1.6H_2O$(c)	-2.05±.07
$UO_2F_2 \cdot 3H_2O$(c)	-1.46±.06
$UO_2F_2 \cdot 4H_2O$(c)	-1.35±.02

Tsvetkov et al (1972) report from tensimetric measurements:

Reaction	ΔH kcal/mol H_2O(g)	ΔG°_{298} kcal/mol H_2O(g)
1	12.8±0.8	2.32±0.08
2	12.6±0.8	2.54±0.07
3	10.7±1.2	2.54±0.08
4	13.3±1.4	3.25±0.10
5	11.7±1.9	3.25±0.12
6	13.3±2.2	3.93±0.13
7	11.3±2.4	3.93±0.15

for the following:

$$UO_2F_2\cdot 4H_2O(c) \rightleftharpoons UO_2F_2\cdot 3H_2O(c) + H_2O(g) \quad (1)$$
$$UO_2F_2\cdot 3H_2O(c) \rightleftharpoons UO_2F_2\cdot 2.18H_2O(c) + 0.82H_2O(g) \quad (2)$$
$$UO_2F_2\cdot 2.18H_2O(c) \rightleftharpoons UO_2F_2\cdot 1.75H_2O(c) + 0.43H_2O(g) \quad (3)$$
$$UO_2F_2\cdot 1.75H_2O(c) \rightleftharpoons UO_2F_2\cdot 1.18H_2O(c) + 0.57H_2O(g) \quad (4)$$
$$UO_2F_2\cdot 1.18H_2O(c) \rightleftharpoons UO_2F_2\cdot 0.85H_2O(c) + 0.33H_2O(g) \quad (5)$$
$$UO_2F_2\cdot 0.85H_2O(c) \rightleftharpoons UO_2F_2\cdot 0.25H_2O(c) + 0.60H_2O(g) \quad (6)$$
$$UO_2F_2\cdot 0.25H_2O(c) \rightleftharpoons UO_2F_2(c) + 0.25H_2O(g) \quad (7)$$

Then for:

$$UO_2F_2\cdot nH_2O(c) \rightarrow UO_2F_2(c) + nH_2O(l)$$

we obtain:

n	ΔH kcal/mol Suponitskii	ΔH kcal/mol	ΔG kcal/mol Tsvetkov et al	S° cal/mol·K
4	5.77	7.54	3.45	13.7
3	5.66	5.46	3.14	7.8
2	5.36	3.97	2.73	4.2
1.6	5.07			
1.0		2.09	1.7	1.3

ΔH = 5.6±1.0 kcal/mol is accepted for:

$$UO_2F_2\cdot 3H_2O(c) \rightarrow UO_2F_2(c) + 3H_2O(l)$$

leading to ΔHf° $UO_2F_2\cdot 3H_2O(c)$ = -605.8±1.0 kcal/mol. No values are given for the others because of the disagreement and the imprecise states of the hydrates.

$UOF(OH)(c)$ and $UOF(OH)\cdot 0.5H_2O(c)$

Vdovenko et al. (1970a) prepared a black finely crystalline precipitate (by the addition of alkali to an aqueous solution containing UF^{3+}) which has the composition $UOF(OH)\cdot 0.5H_2O(c)$. They also measured the thermal properties at 293 K, i.e. in 5N HCl (1970b).

$$UOF(OH)\cdot 0.5H_2O(c) + 254HCl(aq) \rightarrow [UFCl_3 + 251HCl + 2.5H_2O]aq; \quad \Delta H_1 = -13.84\pm 0.15 \text{ kcal} \qquad (1)$$

and

$$[UCl_4 + 250HCl]aq + HF(aq) \rightarrow [UFCl_3 + 251HCl]aq; \quad \Delta H_2 = -4.6\pm 0.1 \text{ kcal/mol} \qquad (2)$$

The concentrations appear to correspond, as in their similar solution measurements on $UOF_2\cdot H_2O(c)$, to those used by Maltsev et al. (1960) in their determination of ΔHf° $UF_4\cdot 2.5H_2O(c)$ and use is made of the Maltsev et al. reaction:

$$UCl_4(c) + 250HCl(aq) \rightarrow [UCl_4 + 250HCl]aq; \quad \Delta H_3 = -43.47\pm 0.1 \text{ kcal} \qquad (3)$$

so that

$$UCl_4(c) + HF(40\% \text{ soln.}) + 2.5H_2O(aq) \rightarrow UOF(OH)\cdot 0.5H_2O(c) + 4HCl(aq); \qquad (4)$$

$$\Delta H_4 = -34.8\pm 0.6^{*}\text{kcal/mol}$$

With the integral ΔHf° HF(40% soln., $HF(1.667H_2O)$) = -76.42 kcal/mol and the differential $\Delta\bar{H}f$'s for HCl and H_2O in a 5N HCl solution, i.e. $HCl(10H_2O)$ ΔHf° = -376.7±1.5 kcal/mol for the hemihydrate.

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[*] Corrected to 298 K, assuming $\Delta C_p = -120$ cal/mol·K.

Vdovenko et al. (1970b) also measured the vapor pressure (283-363 K) and reported for:

$$UOF(OH) \cdot 0.5H_2O(c) \rightarrow UOF(OH)(c) + 0.5H_2O(g); \qquad (5)$$

$$\Delta H_5 = 10.4 \text{ kcal/mol } H_2O(g) \text{ and } \Delta S_5 = 25.6 \text{ cal/mol } H_2O(g) \cdot K$$

If one assumes (5) to be the process, one would expect ΔS to be 35-36 cal/mol·K. If this ΔS is used and one assumes the $\Delta G°$ is reasonable ≈ 2.8 kcal/mol, a $\Delta H \approx 13.2$ kcal/mol $H_2O(g)$ is obtained, and $\Delta Hf°$ $UOF(OH)(c) \approx -341 \pm 3.0$ kcal/mol.

$UO_2(OH)F\cdot H_2O(c)$ and $UO_2(OH)F\cdot 2H_2O(c)$

Tsvetkov et al. (1973) observed the existence, in the UO_3-HF-H_2O system, of two hydrates of a basic salt of variable composition; they are $UO_2(OH)_xF_{2-x}\cdot 2H_2O$ and $UO_2(OH)_xF_{2-x}\cdot H_2O$, where $x = 0.3$-1.2. The thermodynamic characteristics have been determined by DTA.

They report the following for the case when $x = 1$.

$$UO_2(OH)F\cdot H_2O(c) \rightarrow 1/2UO_2F_2(c) + 1/2UO_3\cdot H_2O(c) + H_2O(g) \qquad (1)$$
$$\log P(atm) = (7.60\pm 0.84) - (3100\pm 246)/T \quad (303\text{-}408\ K)$$

$$UO_2(OH)F\cdot 2H_2O(c) \rightarrow UO_2(OH)F\cdot H_2O(c) + H_2O(g) \qquad (2)$$
$$\log P(atm) = (6.23\pm 0.52) - (2360\pm 141)/T \quad (303\text{-}379\ K)$$

The calculated values at 298 K are:

For reaction (1) $\Delta H_1 = 14.2$ kcal/mol $H_2O(g)$
$\Delta G^\circ_1 = 3.82$ kcal/mol $H_2O(g)$
$\Delta S^\circ_1 = 34.8$ cal/mol $H_2O(g)$

for reaction (2) $\Delta H_2 = 10.8$ kcal/mol $H_2O(g)$
$\Delta G^\circ_2 = 2.3$ kcal/mol $H_2O(g)$
$\Delta S^\circ_2 = 28.5$ cal/mol $H_2O(g)$

The formation properties of $UO_2(OH)F\cdot H_2O(c)$ are obtained from the values for reaction (1) since the formation properties of $UO_2F_2(c)$ and $UO_3\cdot H_2O(c)^*$ are known.

For reaction (2), the ΔH and ΔS° are unreasonable. The normal $\Delta S^\circ_{dehyd} \approx 35$-$36$ cal/mol $H_2O(g)$. A more reasonable $\Delta H = 13.0$ kcal/mol results from using the measured $\Delta G^\circ_2 = 1.11$ kcal/mol at $T = 340$ K and the estimated $\Delta S^\circ = 35$ cal/mol.

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* ΔHf° $UO_3\cdot H_2O(c,\beta) = -366.5\pm 0.2$ kcal/mol from Cordfunke and O'Hare (1978) is used. Parker (1976) recommends -366.6 ± 0.3 kcal/mol.

Then for the dehydration

$$UO_2(OH)F \cdot 2H_2O(c) \rightarrow UO_2(OH)F \cdot H_2O(c) + H_2O(g) \qquad (2)$$

$$\Delta G^\circ = 13,000 - 35T \text{ (cal/mol)} \quad (298\text{-}380 \text{ K})$$

and

$$\log P(\text{atm}) = 7.65 - 2,840/T.$$

3.103 U-Cl Compounds

$UCl_3(c)$

The 298 K values for S° and $H-H_0$ are taken from Katz and Rabinowitch's (1951) tabulation of the smoothed thermal functions obtained from the low temperature specific heat measurements of Ferguson and Prather (1944) (15-380 K) made on samples of unknown purity. They are considered accurate to 0.5%. The measurements extrapolated to 0 K assuming no abnormal behavior results in S° = 38.0 cal/mol·K; however, as pointed out by MacWood (1958), the UCl_3 curve appears unusual between 15-20 K, appearing to approach a minimum at ~ 10 K. If this is so, then a better value for S° $UCl_3(c)$ would be between 38.0 and 40.75 cal/mol·K where R ln 4 = 2.75 is the total magnetic entropy present in $UCl_3(c)$. However, until more definitive measurements are made, S° = 38.0±0.3 cal/mol·K is accepted.

Ginnings and Corruccini (1947) measured the heat content relative to 273 K in the range 273-998 K using a higher purity sample (~ 99.8%) than Ferguson and Prather. In the overlapping range, 273-373 K, the derived C_p's are 0.5% lower.

Kelley (1960) tabulated the $C_p°$, $(S-S_{298})_T$ and $(H-H_{298})_T$ from the Ginnings and Corruccini results which, with the low temperature S°, results in the thermal functions to 1000 K. The results can be expressed as:

$$H_T-H_{298\ K} = 20.98T + 3.72\times10^{-3}T^2 - 1.16\times10^5T^{-1} - 6{,}197 \quad \text{cal/mol}$$

$$(298\text{-}1{,}000\ K)$$

Fontana (1947) and (1958) measured the following:

$$UCl_3(c) + [1/2UO_2^{2+} + 2H^+] \text{ in } 0.5m\ HClO_4 \rightarrow [3/2U^{4+} + 3Cl^- + H_2O] \text{ in } 0.5m\ HClO_4;\ \Delta H_1 = -69.07\pm0.5 \text{ kcal/mol} \quad (1)$$

With the values for the ΔHf's for U^{4+} (0.5m $HClO_4$) and UO_2^{2+} (0.5m $HClO_4$) from Fuger and Oetting (1976) and the assumption that the enthalpy of formation of the Cl^- in 0.5m $HClO_4$ is the same as in 0.5m HCl, ΔHf° $UCl_3(c)$ = -207.3±1.3 kcal/mol is calculated.

However, since Fontana made a whole series of calorimetric oxidation reduction measurements on $UCl_3(c)$, $UCl_4(c)$, and $U^{4+} \rightarrow UO_2^{2+}$ (see Fuger and Oetting (1976)), another way of treating the above measurements would be to rearrange his reactions and obtain the $\Delta H_{soln.}$ $UCl_3(c)$:

$$UCl_3(c) \rightarrow [U^{3+} + 3Cl^-] \text{ in } 0.5m\ HClO_4;\ \Delta H_2 = -28.97\pm0.5 \text{ kcal/mol} \quad (2)$$

Assuming ΔHf° U^{3+} (in 0.5m $HClO_4$) ≈ ΔHf° U^{3+}(aq, std. state), one obtains ΔHf° $UCl_3(c)$ = -206.5±1.3 kcal/mol.

Another approach, which minimizes the assumptions regarding the value to be used for the formation of Cl^- in 0.5m $HClO_4$ and ties ΔHf° $UCl_3(c)$ to ΔHf° $UCl_4(c)$ is through the rearrangement of Fontana's' reactions to:

$$UCl_3(c) + HCl(\text{in } 0.5m\ HClO_4) \rightarrow UCl_4(c) + 1/2H_2(g);\ \Delta H_3 = +3.01\pm0.6 \text{ kcal/mol} \quad (3)$$

Although, again the partial $\Delta\bar{H}f$ of HCl is to be used, the solution now involves only one mole of HCl, an introduction of only ~ 0.1 kcal uncertainty. The resultant ΔHf° $UCl_3(c)$ = -207.0±0.9 kcal/mol.

The experimental calorimetric results of Barkelew given by MacWood (1958) result in:

$$UCl_3(c) + Cl_2(g) \rightarrow UCl_4(c);\ \Delta H_4 = -38.1 \text{ kcal/mol} \qquad (4)$$

and $\Delta Hf°\ UCl_3(c) = -205.4 \pm 2.0$ kcal/mol.

MacWood (1958) also tabulates the K's from Altman (1944) and Gregory (1945) for the UCl_4 hydrogen reduction equilibrium (673 to 823 K). The third law $\Delta H°$ values for the reaction:

$$UCl_4(c) + 1/2H_2(g) \rightarrow UCl_3(c) + HCl(g) \qquad (5)$$

are:

Altman $\Delta H°_5 = 14.36 \pm 0.1$ kcal/mol $UCl_4(c)$
Gregory $\Delta H°_5 = 14.38 \pm 0.3$ kcal/mol $UCl_4(c)$

The value obtained for $\Delta Hf°\ UCl_3(c)$ from the data of Altman and Gregory is -207.0 ± 0.7 in excellent agreement with the calorimetric value from Fontana's results. However, as MacWood (1958) points out, if a value for $S° = 40.5$ cal/mol·K is used for $UCl_3(c)$, then the 3rd law $\Delta H° = 16.21$ kcal/mol and $\Delta Hf°\ UCl_3(c)$ from Altman and Gregory is -205.2 kcal/mol in better agreement with the calorimetric value of -205.4 from Barkelew and MacWood. At present, the value -207.0 ± 1.0 is accepted.

A value of -29.5 ± 0.6 kcal/mol (Fuger (1976)) for $\Delta H°$ soln $UCl_3(c)$ at infinite dilution can be estimated from the experimental $\Delta H_{soln.}$ $PuCl_3(c)$ and $AmCl_3(c)$. This value with the $\Delta Hf°\ U^{3+}$(aq, std. state) results in $\Delta Hf°\ UCl_3(c) = -207.2 \pm 1.1$ in support of -207.0 ± 1.0 kcal/mol.

There are other measurements pertaining to $UCl_3(c)$.

Hardy-Grens (1964) reported pressure measurements for the decomposition of $UCl_3(c)$. The assumed reaction is:

$$4/3UCl_3(c) \rightarrow UCl_4(g) + 1/3U(c) \qquad (6)$$

The reported $\Delta G°$ (1030 to 1173 K) is 52,900 - 27.9T cal/mol $UCl_4(g)$ with $\Delta H°_{298}$ = 57.7 kcal/mol (assuming ΔC_p = -6 cal/mol·K) and $\Delta S°_{298}$ = 35.8 cal/mol·K, resulting in -188.3 kcal/mol for $\Delta Hf°$ $UCl_3(c)$ and S° $UCl_3(c)$ = 51 cal/mol·K.

Similarly Shchukarev et al. (1956) reported, in the temperature range 863 to 1063 K:

$$\Delta G = 51{,}000 - 27.5T \text{ cal/mol}$$

This results in ΔH_{298} = 55.0 kcal/mol $UCl_4(g)$ and $\Delta Hf°$ = -186.3 kcal/mol for $UCl_3(c)$.

These two sets of measurements are in reasonable agreement with one another but differ with both the calorimetric values and the UCl_4-H_2 reduction equilibria values. It may be that the measurements made do not pertain to the disproportionation process.

The tabulated $\Delta Gf°$ is obtained from the accepted $\Delta Hf°$ and $\Delta Sf°$.

UCl_4(c)

The low temperature heat capacities (15-355 K) have been measured by Ferguson et al. (1944a). The $C_p°$, $(H-H_0)_T$ and S° at 298 K are taken from Katz and Rabinowitch's (1951) tabulated values. It is appropriate at this point to point out that the S° UCl_4 at 298.15 K (47.1_4) has been listed in various places as 47.4 cal/mol·K [for example Rand and Kubaschewski (1963) and Rossini et al. (1952)]. There is no evidence that a reevaluation of the low temperature C_p and S° was made. It would appear to be an error in transcription.

Ginnings and Corruccini (1947) measured the heat content of UCl_4(c) in the range 700 K to 273 K. Popov et al. (1959a) measured the C_p from 450 K to 920 K (above the melting point). A reasonable presentation of the high temperature measurements has been made by Rand and Kubaschewski (1963):

$$UCl_4(c) \quad C_p = 27.2 + 8.57\times10^{-3}T - 0.79\times10^{5}T^{-2} \ \text{cal/mol·K} \quad (400\text{-}800\ K)$$

$$UCl_4(l) \quad C_p = 25.8 + 14.4\times10^{-3}T \ \text{cal/mol·K} \quad (890\text{-}920\ K)$$

In combination with the vapor pressure measurements (see UCl_4(g)) the following is accepted:

at the melting point, 863 K (Mueller (1948)):

$$UCl_4(c) \rightarrow UCl_4(l)$$
$$\Delta H = 10.9 \ \text{kcal/mol}$$
$$\Delta S = 12.6 \ \text{cal/mol·K}$$

UCl_4(c) is a key compound in the evaluation of a consistent set of thermodynamic data for the uranium compounds, and until 1971 the

$\Delta Hf°$ had been considered to be firmly established as -251 kcal/mol. [See Rand and Kubaschewski (1963), Rossini et al. (1952), Brewer et al. (1945)]. However, an inconsistency noted by Rand and Kubaschewski existed in the paths to $\Delta Hf°$ UO_2^{2+}(aq, std. state) and the various forms of UO_3(c). These inconsistencies can now be traced primarily to the $\Delta Hf°$'s of UCl_4(c) and UO_2Cl_2(c).

These early measurements and subsequent ones in support of the above mentioned value for $\Delta Hf°$ have been recalculated and are listed below. They are given no further consideration for the selection of $\Delta Hf°$ UCl_4(c).

These values* were obtained from measurements of U(c) and UCl_4(c) in excess HCl so that:

$$U(c) + 4HCl(aq) \rightarrow UCl_4(aq\text{ in excess } HCl) + 2H_2(g);\ \Delta H_1 \quad (1)$$

$$UCl_4(c) \rightarrow UCl_4(aq\text{ in } HCl);\ \Delta H_2 \quad (2)$$

and by difference:

$$U(c) + 4HCl(aq) \rightarrow UCl_4(c) + 2H_2(g);\ \Delta H_3 \quad (3)$$

$$\Delta H_3 = \Delta H_1 - \Delta H_2 = \Delta Hf°\ UCl_4(c) - 4\Delta Hf\ HCl(aq)$$

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* The measurements of Barkelew were for oxidation in HCl-$FeCl_3$ soln., but by difference ΔH_3 is for the same reaction.

Investigator	T K of measurement	Conc. HCl, $HCl\cdot nH_2O$	$\Delta Hf°$ $UCl_4(c)$ kcal/mol
Smith et al. (1969)	298	8.13	-251.0
Argue et al. (1961)	298	8.13	-250.5±0.6
Barkelew [MacWood (1946)]	273	*	-249.8*
Biltz and Fendius (1928)	273	8.	-248.2**

Fitzgibbon et al. (1971) redetermined the $\Delta Hf°$ $UCl_4(c)$ by two independent paths, and obtained significantly different results from those tabulated above. Their measurements were confirmed by Cordfunke et al. (1976); the resultant newly established $\Delta Hf°$ $UCl_4(c)$ = -243.5±0.6 kcal/mol has resolved many of the earlier inconsistencies in the uranium network of key values. Measurements by Fitzgibbon et al. also offer a reasonable explanation for the more negative values arrived at earlier.

One of Fitzgibbon's paths is a repeat of the above; i.e., reactions (1) and (2) for which ΔH_1 = -137.5±0.5 kcal/mol when m_{HCl} = 4.35, or $HCl:(12.76H_2O)$ and ΔH_1 = -136.2±1.0 kcal/mol when m_{HCl} = 6.83, or $HCl:(8.13H_2O)$, and ΔH_2 = -45.7±0.5 and -39.3±0.5 kcal/mol, respectively.

Using the differentials $\Delta\bar{H}f$ HCl $(12.76H_2O)$ = -37.856 kcal/mol and $\Delta\bar{H}f$ HCl $(8.13H_2O)$ = -36.671 kcal/mol, values of -243.22±0.70 and -243.58±1.1 kcal/mol are obtained for $\Delta Hf°$ $UCl_4(c)$.

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* Barkelew used a 12M $HCl\text{-}FeCl_3$ solution and experimentally determined the $\Delta\bar{H}f$ HCl in this medium at 273 K as -33.0 kcal/mol; certain auxiliary components needed revising so that $\Delta\bar{H}f$ HCl for use in the Barkelew $HCl\text{-}FeCl_3$ medium is -32.7 kcal/mol.

** Earlier evaluations had $\Delta Hf°$ = -251, in exact agreement with Barkelew (MacWood); an erroneous interpretation of $\Delta Hf°$ HCl and the experimental ΔH mix had been made.

The ΔH's for the individual reactions, particularly (1), are significantly less negative than the earlier measurements. It would appear, as explained by Fitzgibbon et al., that the earlier measurements for the reaction of U(c) with HCl(aq) were not for process (1). Probably not all dissolved oxygen had been eliminated; nor had a scavenger been used (SiF_2^{2-} in the acid) to prevent the formation of insoluble residues from the reaction of U(c) in HCl solutions.

The other path, which confirms the above values is dependent upon UO_2(c). Fitzgibbon's experimental measurements, and those of Cordfunke et al. (1976) who repeated the measurements are cited in the following Table 6.

Table 6

The Enthalpy of Formation of UCl_4(c) from UO_2(c)

Soln. A refers to 1.502M H_2SO_4; Soln. B refers to 1.502M H_2SO_4 + 0.0350M $Ce(SO_4)_2$

	Reaction	Fitzgibbon	Cordfunke*
(4)	$UO_2(c) + 2Ce(SO_4)_2 \cdot Soln.B \rightarrow UO_2SO_4 \cdot Soln.B + Ce_2(SO_4)_3 \cdot Soln.B$	-53.16±0.4	-53.92±0.06
(5)	$U(C_2H_3O_2)_4(c) + 2Ce(SO_4)_2 \cdot Soln.B + 2H_2O \cdot Soln.B \rightarrow UO_2SO_4 \cdot Soln.B + Ce_2(SO_4)_3 \cdot Soln.B + 4HC_2H_3O_2 \cdot Soln.B$	-45.34±0.7	-45.70±0.53
(6)	$4HC_2H_3O_2 \cdot Soln.B \rightarrow 4HC_2H_3O_2 \cdot Soln.A$	-0.12±0.1	
(7)	$U(C_2H_3O_2)_4(c) + H_2SO_4 \cdot Soln.A \rightarrow U(SO_4)_2 \cdot Soln.A + 4HC_2H_3O_2 \cdot Soln.A$	-8.446±0.1	-8.58±0.05
(8)	$UCl_4(c) + 2H_2SO_4 \cdot Soln.A \rightarrow U(SO_4)_2 \cdot Soln.A + 4HCl \cdot Soln.A$	-49.958±0.6	-50.94±0.20
(9)	$4(HCl \cdot 3.61H_2O) + Soln.A \rightarrow 4(HCl \cdot 3.16H_2O) \cdot Soln.A^*$	-10.64±0.2	-1.18±0.04*
(10)	$14.44H_2O(1) + Soln.A \rightarrow 14.44H_2O \cdot Soln.A^*$	-0.2±0.1	-0.49±0.20*
(11)	$2H_2O(1) + Soln.B \rightarrow 2H_2O \cdot Soln.B$		

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* For the Cordfunke results the H_2SO_4 concentration is 1.505M and the H_2O/HCl ratio is 10.01; Reaction (10) involves 40.04 moles H_2O.

The summation results in:

$$UO_2(c) + 4HCl(aq) \rightarrow UCl_4(c) + 2H_2O(l)\,;\ \Delta H_{12} \qquad (12)$$

and ΔH_{12} = 23.37±0.9 and 33.55±0.60 kcal/mol, respectively. With $\Delta Hf°\ UO_2(c)$ = -259.3±0.2 based on the combustion work of Huber and Holley (1969) and the integral values for $\Delta Hf°$ HCl(aq), $\Delta Hf°$ = -243.95±1.1 (Fitzgibbon) and -243.27±0.65 kcal/mol (Cordfunke).

A weighted average from these four values results in the selected $\Delta Hf°\ UCl_4(c)$ = -243.5±0.6 kcal/mol.

These two paths to $\Delta Hf°\ UCl_4(c)$, one independent of other uranium compounds and one dependent upon $\Delta Hf°\ UO_2(c)$, are mutually consistent; i.e., the $\Delta Hf°\ UCl_4(c)$, independent of other uranium compounds supports a $\Delta Hf°\ UO_2(c)$ = -259.3±0.2 kcal/mol.

The Gibbs energy of formation has been calculated from the $\Delta Hf°$ and $\Delta Sf°$.

UCl_4 in Various Aqueous Media

The concern here is with the bulk ΔH_{soln}, that is, the ΔH_{soln} of $UCl_4(c)$ in various aqueous media to form the real solution, which in HCl may be highly complexed and in dilute HCl and $HClO_4$, a partly hydrolyzed one, correcting only for the presence of the foreign silicate ion when present, temperature (if not at 298.15 K) and possible impurities if known.

In all measurements cited here the concentration of the UCl_4 in solution is below .01m. There is at present insufficient experimental information to correlate the ΔH_{soln} UCl_4 as a function of m_{UCl_4}.

1. Measurements in HCl

In Fuger and Oetting (1976) the measurements were corrected and extrapolated from HCl and $HClO_4$ solutions in order to obtain the ΔHf°, ΔGf°, and S° for U^{4+}(aq, std. state). For convenience they are repeated here (uncorrected for hydrolysis) along with additional measurements.

Investigator	Conc. m, moles HCl/kg H_2O	ΔH_{soln} kcal/mol
Biltz and Fendius (1928)	7.2	-39.4*
Kilner (see Brewer et al. (1958))	7.2	-36.2
Smith et al. (1969)	6.90	-40.0
Fitzgibbon et al. (1971)	6.82	-38.9
Argue et al. (1961)	6.82	-42.7
Maltsev et al. (1960)	5.53	-43.47**
Fitzgibbon et al. (1971)	4.35	-45.3
Hearne and White (1957)	2.08	-51.53
Fuger and Brown (1970)	1.02	-54.46
Argue et al. (1961)	1.02	-57.0

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* Measurements at 273 K, uncorrected.

** Measurements at 293 K, uncorrected.

2. Measurements in $HClO_4$

Investigator	Conc. m, moles $HClO_4$/kg H_2O	ΔH_{soln} kcal/mol
Argue et al. (1961)[**]	.01	-54.6[*]
	.05	-57.3
	0.135	-55.6
	0.200	-59.1
	1.02	-61.0
Fontana (1947)	0	-44.7
	0.1	-52.7
	0.5	-55.7
	2.0	-53.6

3. Measurements in Acid-Salt Mixtures

Investigator	Solvent	ΔH_{soln} kcal/mol
Fontana (1947) [concentration $UCl_4 \sim 5\times10^{-3}$m]	0.1m $HClO_4$, 0.4m $LiClO_4$	-54.22
Hearne and White (1957) [concentration $UCl_4 \sim 5\times10^{-4}$]	HCl-LiCl with constant $\mu=2.0$ $[H^+] = 2.0$	-51.53±0.7
	1.6	-54.40
	1.2	-56.10
	1.0	-56.89
	0.6	-57.15
	0.4	-57.96
	0.2	-58.31
	0.1	-58.43
	0.04	-58.50
	0.02	-58.46

The final smoothed values recommended for ΔH_{soln} of UCl_4(c) as a function of m of HCl and $HClO_4$ are given in Tables 7 and 8.

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[*] Corrected for polymerization of U(IV).

[**] Measurements by Argue are for molar concentrations.

Table 7

Recommended Values of ΔH_{soln} $UCl_4(c)$ in HCl

Conc. m, moles HCl/kg H_2O	ΔH_{soln} $UCl_4(c)$	ΔHf UCl_4(aq, in HCl)
	kcal/mol	
1.0	-54.6	-298.1
2.0	-51.5	-295.0
3.0	-48.8	-292.3
4.0	-46.2	-289.7
5.0	-43.7	-287.2
6.0	-41.3	-284.8
7.0	-39.25	-282.7

Table 8

Recommended Values of ΔH_{soln} UCl_4 (c) in $HClO_4$

Conc. m moles $HClO_4$/kg H_2O	ΔH_{soln} $UCl_4(c)$	ΔHf UCl_4(aq, in $HClO_4$)
	kcal/mol	
0	-44.7	-288.5[*]
0.1	-52.7	-296.2
0.5	-55.7	-299.2
1.0	-55.1	-298.6
2.0	-53.6	-297.1

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[*] This represents the 'real' ΔH_{soln} in H_2O, i.e. the hydrolyzed solution, not to be confused with the ΔH°_{soln} = (-141.3 - 4x39.933) + 243.5 = -57.5 kcal/mol for the ideal unhydrolyzed solution [U^{+4} + $4Cl^-$]. The difference between the two ΔH's soln. is a measure of $\Delta H_{hydrolysis}$.

$UCl_4(g)$

The vapor pressure measurements of Choporov and Chudinov (1968) (650-750 K; Knudsen effusion) on $UCl_4(c)$ are in good agreement with the evaluation of Rand and Kubaschewski (1963); a readjustment, however, of the parameters of the ΔG expressions for $UCl_4(l)$ (which retains the fit of the experimental measurements of Young and Grady (1958), Gregory (1948), and Jenkins and Anderson (1948)) has been made in order to obtain slightly better agreement with the measurements of Popov et al (1959a) who, from C_p measurements, calculated the ΔH = 11.9 kcal/mol of all transformations between 834 and 882 K (including fusion).

The adjusted expressions are:

$$UCl_4(c) \rightarrow UCl_4(g) \qquad (1)$$

$$\Delta G_1 = 51{,}900 - 93.0T + 13.8\, T \log T \text{ cal/mol} \quad (298\text{-}863\text{ K})$$

at 298 K:

$$\Delta G^\circ_1 = 34.3 \text{ kcal/mol}$$
$$\Delta H^\circ_1 = 50.1 \text{ kcal/mol}$$
$$\Delta S^\circ_1 = 52.9 \text{ cal/mol}\cdot\text{K}$$

$$UCl_4(l) \rightarrow UCl_4(g) \qquad (2)$$

$$\Delta G_2 = 47{,}000 - 134.8T + 29.9\, T \log T \text{ cal/mol} \quad (863\text{-}1063\text{ K})$$

at 1063 K:

$$\Delta G = 0$$
$$\Delta H = 33.2 \text{ kcal/mol}$$
$$\Delta S^\circ = 31.2 \text{ cal/mol}\cdot\text{K}$$

The calculated tabulated values for ΔHf°, ΔGf° and S° for $UCl_4(g)$ are obtained from the sublimation process.

The earlier measurements are cited by Rand and Kubaschewski.

$UCl_5(c)$ and $UCl_6(c)$

The low temperature thermal functions of $UCl_6(c)$, 0-350 K, from the specific heat measurements of Ferguson and Rand (1945), have been tabulated by Katz and Rabinowitch (1951).

S° $UCl_5(c)$ at 298.15 K has been estimated from the measured values for $UCl_4(c)$ and $UCl_6(c)$.

The enthalpies of formation of $UCl_5(c)$ and $UCl_6(c)$ are discussed together.

MacWood (1958), reporting on the experimental results of Barkelew, cites the ΔH's at 273 K for the oxidation of $UCl_4(c)$ ($\Delta H = -24.1 \pm 0.1$ kcal/mol), $UCl_5(c)$ ($\Delta H = -33.9 \pm 0.1$ kcal/mol) and $UCl_6(c)$ ($\Delta H = -44.6 \pm 0.1$ kcal/mol) in 12N HCl, 10% $FeCl_3$ solutions, so that:

$$UCl_4(c) + FeCl_3(aq) \rightarrow UCl_5(c) + FeCl_2(aq);\ \Delta H_1 = 9.8 \pm 0.15 \text{ kcal/mol} \quad (1)$$

$$UCl_5(c) + FeCl_3(soln) \rightarrow UCl_6(c) + FeCl_2(soln);\ \Delta H_2 = 10.7 \pm 0.15 \text{ kcal/mol} \quad (2)$$

Using the relationship:

$$FeCl_2(soln) + Cl_2(g) \rightarrow FeCl_3(soln);\ \Delta H_3 = -20.2 \pm 0.5 \text{ kcal/mol} \quad (3)$$

which incorporates the Barkelew experimental components and pertains to the specific medium of a 12N HCl, 10% $FeCl_3$ soln. at 273 K, the following relationships are obtained:

$$UCl_4(c) + 1/2Cl_2(g) \rightarrow UCl_5(c);\ \Delta H_{1a} = -10.4 \pm 0.6 \text{ kcal/mol} \quad (1a)$$

and

$$UCl_5(c) + 1/2Cl_2(g) \rightarrow UCl_6(c);\ \Delta H_{2a} = -9.4 \pm 0.6 \text{ kcal/mol} \quad (2a)$$

More recently Gross et al. (1971) reported the direct chlorination of U(c) with $Cl_2(l)$, so that:

$$U(c) + 5/2Cl_2(g) \rightarrow UCl_5(c); \Delta H_4 = -247.8 \pm 1.0 \text{ kcal/mol} \qquad (4)$$

which results in $\Delta H_{1a} = -4.3 \pm 1.2$ kcal/mol.

Obviously there is a major disagreement in the relationships for $UCl_5(c)$ and $UCl_6(c)$. If, from Gross et al., $\Delta Hf°\ UCl_5(c) = -247.8$ kcal/mol one would expect $\Delta H_{2a} \approx -4$ and $\Delta Hf°\ UCl_6(c) \approx -252$ kcal/mol, as opposed to $\Delta Hf°\ UCl_5(c) = -253.9$ and $\Delta Hf°\ UCl_6(c) = -263.3$ kcal/mol from the MacWood-Barkelew measurements. Although the Gross et al. measurements appear to be definitive for $UCl_5(c)$, the overall picture they present appears unreasonable, as compared to the other halides.

The Barkelew measurements for ΔH of oxidation of U(c) in this medium are known to be in error; however, some of the other measurements appear reasonable and lead to calculated values for ΔHf° that are in agreement (within 2 kcal/mol) with the presently accepted values, such as $UCl_3(c)$, $UBr_4(c)$, $UOCl_2(c)$ and $UOBr_2(c)$. It may be that ΔH_3 is erroneous, and that a better value is ≈ -19 kcal/mol for these conditions. See Rand and Kubaschewski (1963) for the variation of ΔH_3* with HCl concentration. Use of -19 kcal/mol for ΔH_3 results in: $\Delta H_{1a} = -9.2$ kcal/mol and $\Delta Hf°\ UCl_5(c) = -252.7$ kcal/mol; and $\Delta H_{2a} = -8.2$ kcal/mol and $\Delta Hf°\ UCl_6(c) = -260.9$ kcal/mol. These values have been rounded. Further work is necessary on the UCl_4-UCl_5-UCl_6 relationships.

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* Use of $\Delta H_3 \approx -19$ kcal/mol would result in $\Delta Hf°\ UCl_3(c) = -206.6$ kcal/mol from the MacWood-Barkelew investigation, in better agreement with the selected ΔHf° = -207.0.

The Gibbs energies of formation have been calculated from the selected $\Delta Hf°$'s and the calculated $\Delta Sf°$'s.

$UCl_6(g)$

Rand and Kubaschewski (1963) reviewed the vapor pressure data through 1961 and reported $\Delta H°_{subl}$ 298.15 K to be 18.8 kcal/mol and $\Delta S° = 35.1$ cal/mol·K.

The $\Delta Gf°$ $UCl_6(g)$ is derived from the $\Delta G°_{subl}$.

$U_2Cl_{10}(g)$

Gruen and McBeth (1969) studied the reaction of $UCl_4(c)$ with $Cl_2(g)$ (450-650 K) spectrophotometrically; the uranium pentachloride was found to vaporize as a dimer molecule.

For the reaction:

$$2UCl_4(c) + Cl_2(g) \rightarrow U_2Cl_{10}(g);$$

$$\Delta G = 15{,}130 - 15.4T \text{ cal/mol} \quad (450\text{-}650 \text{ K})$$

The Uranium Pentachloride-Aluminum Chloride Vapor Complex

Gruen and McBeth (1969) studied the reaction of $UCl_4(c)$ with $AlCl_3(c)$ and $Cl_2(g)$ spectrophotometrically; they report:

$$UCl_4(c) + 1/2Al_2Cl_6(g) + 1/2Cl_2(g) \rightarrow UCl_5 \cdot AlCl_3(g)$$

$$\Delta G = 8{,}910 - 10.7T \text{ cal/mol} \quad (440\text{-}630 \text{ K})$$

and

$$UCl_4(c) + Al_2Cl_6(g) \rightarrow UCl_4 \cdot Al_2Cl_6(g)$$

$$\Delta G = 15{,}780 - 15.3T \text{ cal/mol} \quad (600\text{-}800 \text{ K})$$

3.104 U-Cl-O Compounds

UOCl(c) and UOBr(c)

Katz and Rabinowitch (1951) tabulate the K's of Gregory (1945) for the supposed equilibrium of the H_2 reduction of UOX_2, where X = Cl or Br. It was assumed that the products were UOX(c) and HX(g). No analyses of the products were made.

The K's lead to the following for:

$$UOX_2(c) + 1/2H_2(g) \rightarrow UOX(c) + HX(g)$$

X	ΔH_T kcal/mol HX	ΔG_T kcal/mol HX	ΔS_T cal/mol·K	T
Cl	10.6	6.0	6.9	673
Br	10.1	6.1	6.0	673

If it is assumed that the ΔC_p's are negligible, the resultant ΔHf°'s for UOCl(c) and UOBr(c) are -222 and -213 kcal/mol, respectively; however, the resultant calculated S°'s are 11 cal/mol·K for UOCl(c) and 12 cal/mol·K for UOBr(c), obviously impossible values. Reasonable values for S° UOCl(c) and S° UOBr(c) are ~ 24 and ~ 27 cal/mol·K, respectively (based on a comparison of the measured S°'s for U(c), UO_2(c), UCl_3(c), UCl_4(c), $UOCl_2$, UO_2Cl_2 and $UOBr_2$(c)).

If it is assumed that the measured K's are reasonable, but the T dependency is in error, then, with the estimated S°'s for UOCl and UOBr (and assuming $\Delta C_p \approx 0$) one obtains ΔS = 20 cal/mol·K and ΔH = 19.5 kcal/mol for the UOCl(c) equilibrium and ΔS = 21 cal/mol·K and ΔH = 20.2 kcal/mol for the UOBr(c) equilibrium. These ΔH's result in ΔHf° UOCl(c) = -213 kcal/mol and ΔHf° UOBr(c) = -203 kcal/mol. However, these ΔHf° values still appear unreasonable in comparison with the relationships derived for the PuOCl(c)-$PuCl_3$(c), PuOBr(c)-$PuBr_3$(c), and AmOCl(c)-$AmCl_3$(c) systems from Fuger (1976). No recommendations are made at this time.

$UOCl_2$(c)

Greenberg and Westrum (1956b) measured the heat capacity from 11.7 to 348 K (also some measurements from 5 to 10 K of lower precision). Thermal anomalies were not observed. The extrapolation below 10°K was made assuming the absence of magnetic transformation below 5 K. Their tabulated values are accepted.

Rand and Kubaschewski (1963) evaluated the earlier measurements (700 to 800 K) on the equilibria:

$$2UOCl_2(c) \rightarrow UO_2(c) + UCl_4(g) \qquad (1)$$

and arrived at ΔH_1 = 57.1 kcal/mol UCl_4, with perfect agreement on $\Delta S°$ from the experimental ΔS_1 at 750 K (46.4 cal/mol·K) and that obtained from the calorimetric S°'s for $UOCl_2$(c) and UO_2(c), and the calculated S° UCl_4(g) obtained from the $\Delta S°_{subl}$ UCl_4(c) and a ΔC_p = -6 cal/mol·K. These earlier measurements will not be cited here, or reinterpreted. The resultant $\Delta Hf°$ $UOCl_2$(c) = -254.9 kcal/mol.

Recently Knacke et al. (1972) reported measurements on the same equilibria (in the range 700 to 1023 K), which result (with a ΔC_p = -6 cal/mol·K) in $\Delta H°_1$ = 57.3 kcal/mol, and $\Delta S°_1$ = 52.4 cal/mol·K, also in perfect agreement with the independently calculated $\Delta S°$. This $\Delta H°$ results in $\Delta Hf°$ $UOCl_2$(c) = -255.0 kcal/mol.

Barkelew, as cited in MacWood (1958), calorimetrically determined the $\Delta Hf°$'s of many of the uranium-halogen containing compounds; however, his determination of $\Delta Hf°$ $UCl_4(c)$ is seriously in error because of the reaction of U(c) in HCl; the $\Delta Hf°$'s of $UCl_5(c)$ and $UCl_6(c)$ agreement with better determinations. Where possible, little weight is given to the determination, even if it is in agreement with better determinations, but calculations will continue to be made of the $\Delta Hf°$'s from the Barkelew data, possibly giving alternative ways of handling his data, in order to apply this knowledge to compounds where other data are scanty or non-existent.

Barkelew's measurements on $UOCl_2$ are viewed in this regard.

Since the measurement of the oxidation of U(c) in a 12N HCl, 10% $FeCl_3$ is seriously in error, Barkelew's $\Delta H = -16.7$ kcal/mol for the oxidation of $UOCl_2(c)$ in this medium is combined with the oxidation of $UCl_4(c)$ in the same medium, $\Delta H = -24.1$ kcal/mol. Since the final solutions are the same, UO_2Cl_2 and $FeCl_2$ forming in the medium:

$$UCl_4(c) + H_2O(aq) \rightarrow UOCl_2(c) + 2HCl(aq); \; \Delta H_2 = -7.4 \text{ kcal/mol} \quad (2)$$

Barkelew's values for $\Delta\overline{H}f$'s of HCl and $H_2O(aq)$ in the 12N HCl, 10% $FeCl_3$ medium (which are partly experimental) have been corrected for the presently accepted $\Delta Hf°$ HCl $(3.49H_2O) = -36.05$ kcal/mol and $\Delta Hf°$ $H_2O(l) = -68.315$ kcal/mol and recorrected to 273 K, incorporating the experimental determinations of ΔH_{mix} and ΔH_{diln} to obtain for

$\Delta\bar{H}f$'s HCl and H_2O in the medium at 273 K, -32.7 and -69.45 kcal/mol, respectively. These ΔHf's and -243.6 for ΔHf $UCl_4(c)$ (at 273 K) result in $\Delta Hf°$ $UOCl_2(c)$ = -255.0 at 273 K and -254.9 kcal/mol at 298 K.

The agreement here indicates that the Barkelew-MacWood data on the reaction for $UOCl_2(c)$ can be considered reasonable and can be used in combination with the $\Delta H_{reaction}$ of $UOBr_2(c)$ to obtain $\Delta Hf°$ $UOBr_2(c)$.

The Gibbs energy of formation is derived from the $\Delta Sf°$ and the $\Delta Hf°$.

UO_2Cl_2(c)

The low temperature heat capacities (6-350 K) have been measured by Greenberg and Westrum (1956a). The smoothed thermodynamic functions are accepted. Prins[*] (1973) determined the high-temperature enthalpy from 392 to 696 K relative to 298 K. The results are expressed as:

$$H_T-H_{298} = 22.93T + 5.562\times10^{-3}T^2 + 0.4643\times10^5T^{-1} - 7{,}494 \quad \text{cal/mol}$$
$$(298 - 700\ \text{K})$$

These functions join the low temperature results smoothly.

The recent measurements of Cordfunke et al. (1976) have clarified the situation regarding the ΔHf° UO_2Cl_2(c). Two different cycles existed prior to this time for obtaining ΔHf°, both involving ΔHf° UCl_4(c). Rand and Kubaschewski (1963) obtained ΔHf° = -302.9 kcal/mol (based on ΔHf° UCl_4(c) = -251.3) from the Shchukarev et al. (1958a) path which at that time was the only available one: a complete recalculation using presently accepted auxiliary ΔHf°'s and ΔHf° UCl_4(c) = -243.5 kcal/mol results in ΔHf° UO_2Cl_2(c) = -292.0±2.0 kcal/mol. The more recent cycle[**] from Khanaev and Khripin (1970) results in -297.0 ±1.0 kcal/mol.

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[*] More recently Cordfunke et al. (1978) reported measurements in the range 366 to 649 K relative to 298 K:

$$H_T-H_{298} = 27.55T + 2.178\times10^{-3}T^2 + 2.729\times10^5T^{-1} - 9323 \text{ cal/mol}$$

At 500 K and 700 K, H_T-H_{298} are 1% and 0.2% higher than those of Prins (1973).

[**] Another value for ΔHf° UO_2Cl_2(c) can be derived, = -291.5 kcal/mol, if one uses the ΔHf° Na_3UO_4(c) from the mass spectrometric studies of Battles et al. (1972) in the thermochemical cycle from O'Hare et al. (1972) involving Na_3UO_4(c) and UO_2Cl_2(c). Since this ΔHf° Na_3UO_4(c) has a high uncertainty, a better approach is to obtain ΔHf° UO_2Cl_2(c) from the other thermochemical cycles and to obtain ΔHf° Na_3UO_4(c) from the O'Hare measurements as has been done by Cordfunke and O'Hare (1977).

Cordfunke et al. determined the ΔHf° relative to ΔHf° $UO_3(c,\gamma)$ and determined ΔHf° $UO_2Cl_2(c)$ = -297.1±0.3 and also repeated the "Shchukarev" cycle and obtained -297.9±0.9 kcal/mol.

The thermochemical cycles studied are presented, beginning with the Cordfunke "γUO_3" cycle, which is the most straightforward of the four available cycles. The measurements have been made in excess 5.545 molal HCl solutions.

$$\gamma\text{-}UO_3(s) + 2HCl(aq,\ excess) \rightarrow UO_2Cl_2(in\ HCl) + H_2O(in\ HCl);\quad \Delta H_1 = -15.53\pm0.07\ kcal/mol \qquad (1)$$

$$UO_2Cl_2(s) \rightarrow UO_2Cl_2(aq,\ HCl);\ \Delta H_2 = -17.06\pm0.05\ kcal/mol \qquad (2)$$

so that:

$$UO_3(c,\gamma) + 2HCl(aq,\ excess) \rightarrow UO_2Cl_2(c) + H_2O(in\ HCl);\quad \Delta H_3 = 1.53\pm0.09\ kcal/mol \qquad (3)$$

With the differentials, $\Delta\overline{H}f$ $HCl(10.01H_2O)$ and $\Delta\overline{H}f$ H_2O in HCl $10.01H_2O)$ = -37.291±0.01 and -68.440±0.001 kcal/mol, respectively, ΔHf° $UO_2Cl_2(c)$ = -297.12±0.3 kcal/mol.

The second of Cordfunke's cycles, the "Shchukarev cycle", and the original Shchukarev results are tabulated.

TABLE 9
The "Shchukarev cycle" for the Enthalpy of Formation of $UO_2Cl_2(c)$

Reaction	ΔH kcal/mol (Cordfunke)	(Shchukarev)
(4) $UCl_4(c) + 2FeCl_3(soln.) + 2H_2O(soln.) \rightarrow UO_2Cl_2(soln.) + 2FeCl_2(soln.) + 4HCl(soln.)$	-45.11±0.37	-45.50±0.10
(5) $UO_2Cl_2(c) \rightarrow UO_2Cl_2(soln.)$	-24.56±0.17	-25.44±0.07
(6) $2FeCl_3(c) \rightarrow 2FeCl_3(soln.)$	-64.64±0.15	-61.14±0.54
(7) $2FeCl_2(c) \rightarrow 2FeCl_2(soln.)$	-36.74±0.11	-

The solution refers to 1.98 mass percent of HCl, i.e. $HCl(100.6H_2O)$ containing 0.5 mass percent of $FeCl_3$, i.e. $FeCl_3(1800H_2O)$.

From the Cordfunke Measurements:

$$UCl_4(c) + 2FeCl_3(c) + 2H_2O(soln.) \rightarrow 2FeCl_2(c) + 4HCl(soln.) + UO_2Cl_2(c);\ \Delta H_8 = -48.45\pm0.45 \text{ kcal/mol} \quad (8)$$

Using auxiliary values for $\Delta Hf°$ $FeCl_3(c)$, $\Delta Hf°$ $FeCl_2(c)$ $\Delta\bar{H}f$ $HCl(100.6H_2O)$ and $\Delta\bar{H}f$ H_2O in HCl 100.6H_2O) from Parker et al. (1976), $\Delta Hf°$ $UO_2Cl_2(c) = -297.89\pm0.9^*$ kcal/mol.

From the Shchukarev measurements:

$$UCl_4(c) + 2FeCl_3(c) + 2H_2O(soln.) \rightarrow UO_2Cl_2(c) + 2FeCl_2(soln.) + 4HCl(soln.);\ \Delta H_{8a} = -81.20\pm0.55 \text{ kcal/mol} \quad (8a)$$

The value for $\Delta Hf°$ $FeCl_2(soln.) = -101.2$ kcal/mol from Wagman et al. (1969) used to obtain the $\Delta Hf°$ $UO_2Cl_2(c) = -292.0$ cited previously was probably not appropriate for this solution; a larger uncertainty (±2.0 kcal/mol) was therefore assigned to the calculated $\Delta Hf°$. Also Shchukarev's value for ΔH_6 differs considerably from that reported by Cordfunke, although the measurements for reactions (4) and (5) are in reasonable accord. If the measurements of Shchukarev for ΔH_4 and ΔH_5 are combined with Cordfunke's values for ΔH_6 and ΔH_7, $\Delta H_8 = -47.96\pm0.8$ kcal/mol is obtained, which results in $\Delta Hf° = -297.67$ ±1.0 kcal/mol, in good agreement with the two Cordfunke values and that derived from the Khanaev and Khripin work cited earlier.

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[*] Cordfunke et al. (1976) at the same time measured the $\Delta Hf°$ $UCl_4(c) = -243.27\pm0.65$, relative to $\Delta Hf°$ $UO_2(c)$. This value was used to be consistent with Cordfunke's cycle.

A detailed analysis of the Khanaev and Khripin measurement is given under the discussion for UF_3(c) where the summation equations are:

$$UO_2Cl_2(c) + 3FeCl_2(c) + 3HF(aq) + HCl(aq) \rightarrow 2H_2O(liq) + 3FeCl_3(c) + UF_3(c);\ \Delta H_9 = +29.54 \pm 0.32 \text{ kcal/mol} \quad (9)$$

and

$$FeCl_2(c) + UCl_4(c) + 3HF(aq) \rightarrow FeCl_3(c) + UF_3(c) + 3HCl(aq);\ \Delta H_{10} = -5.564 \pm 0.20 \quad (10)$$

By difference reaction (8) is obtained with $\Delta H_8 = -35.104 \pm 0.50$ kcal/mol. However, here the H_2O/HCl ratio is 3.91 and the integral $\Delta Hf°$ HCl(aq) = -36.449 kcal/mol is needed, resulting in the earlier mentioned $\Delta Hf° = -296.98 \pm 1.0$ kcal/mol.

$\Delta Hf°$ UO_2Cl_2(c) = $-297.2_3 \pm 0.3$ is the selected value.

$\Delta Gf°$ has been calculated from $\Delta Hf°$ and $\Delta Sf°$.

UO_2Cl_2(in HCl solutions)

There are scattered values in the literature for the ΔH_{soln} of $UO_2Cl_2(c)$ in HCl solutions. The following table summarizes the available measurements. In all cases the concentration of the UO_2Cl_2, although different in each case, is below 1×10^{-3} molal.

Table 10

The Enthalpy of Solution of UO_2Cl_2 in HCl

	m_{HCl} mol$(KgH_2O)^{-1}$	ΔH_{soln} kcal/mol
Fitzgibbon et al (1971)	6.82	-15.34±0.5
Cordfunke et al (1976)	5.55	-17.06±0.1
Prins (1973)	5.55	-17.30±0.23
Fitzgibbon et al (1971)	4.35	-18.75±0.5
O'Hare and Hoekstra (1974)	1.0	-22.18±0.15*
Shchukarev et al (1958a)	0.552 (0.5% $FeCl_3$)	-25.44±0.07
Cordfunke et al (1976)	0.552 (0.5% $FeCl_3$)	-24.56±0.17
O'Hare et al (1972)	0.25 (containing NaCl)	-24.27±0.07
O'Hare and Hoekstra (1973)	"	-24.19±0.09
Cordfunke (1975)	5.6×10^{-4}	-26.03±0.03

Lipilina and Samoilov (1954) measured the ΔH_{soln} of the trihydrate (using one mole of the salt in 50 moles H_2O) as a function of the HCl concentration. The experimental ΔH's have been corrected for

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* Revised from original -22.49±0.13 as explained by O'Hare et al (1976).

the dilution of $3H_2O(aq)$. These results are tabulated.

Table 11

The Enthalpy of Solution of $UO_2Cl_2 \cdot 3H_2O(c)$ in HCl

m_{HCl}	ΔH_{exp} kcal/mol	ΔH corrected kcal/mol
0.80	-8.86	-8.86
0.97	-8.75	-8.74
1.55	-7.78	-7.75
1.98	-6.95	-6.91
4.44	-2.80	-2.56

In addition Prins measured ΔH_{soln} in 5.55 molal HCl (concentration of $UO_2Cl_2 \sim .03\ mol \cdot kg^{-1}$) = -2.41±0.01 kcal/mol, which corrected for the $3H_2O(aq)$ formed = -2.04 ±.01 kcal/mol.

As can be seen from the tabulated results the data on the ΔH_{soln} $UO_2Cl_2(c)$ below one molal HCl are discordant; the measurements (m = 4.4 to 0.8) for $UO_2Cl_2 \cdot 3H_2O(c)$ appear to be reasonable (the concentration of the UO_2Cl_2, though, is much greater). From a smoothed plot of the $UO_2Cl_2 \cdot 3H_2O$ data we obtain at m = 4.40 ΔH_{soln} = -2.65 kcal/mol. From the $UO_2Cl_2(c)$ data (m = 4.35 to 6.82) we obtain ΔH_{soln} = -18.65 kcal/mol for m = 4.4 If the difference in the concentrations of UO_2Cl_2 (in HCl) is ignored, a $\Delta H_{hydration}$ = -16.0 kcal/mol is obtained for:

$$UO_2Cl_2(c) + 3H_2O(l) \rightarrow UO_2Cl_2 \cdot 3H_2O(c)$$

If, however, it is assumed that $\Delta\varphi_L(\varphi_L\ 1.11m - \varphi_L\ m < 0.001) = +0.5$ kcal/mol, estimated on the basis of the behavior of $BaCl_2$ (Parker et al (1971)), ΔH = -15.5 kcal/mol. This confirms the $\Delta H_{hydration}$ = -15.3±0.23 from Prins (1973) measurements. In view of this confirmation, all measurements on $UO_2Cl_2(c)$ and $UO_2Cl_2 \cdot 3H_2O(c)$ have been merged to obtain a set of smoothed values for ΔH_{soln} $UO_2Cl_2(c)$ as a function of the HCl concentration (Table 12). The $UO_2Cl_2 \cdot 3H_2O(c)$ measurements were converted using the ΔH hydration = 15.3 and $\Delta\varphi_L$ = 0.5 kcal/mol. The corresponding values for the ΔHf's of UO_2Cl_2 ($m<10^{-3}$ and m = 1.11) are also given in Table 12. This approach supports the Cordfunke and Shchukarev measurements in the dilute region and is in agreement with a $\Delta H°$ = 26.3 kcal/mol.

Table 12

The Recommended ΔH_{soln} $UO_2Cl_2(c)$ in HCl

m HCl	ΔH soln $UO_2Cl_2(c)$ m $UO_2Cl_2<10^{-3}$	ΔHf UO_2Cl_2 $m<10^{-3}$ kcal/mol	ΔHf UO_2Cl_2 m=1.11
10^{-3}	-26.0	-323.2	-322.7
0.5	-25.2	-322.4	-321.9
1.0	-24.3	-321.5	-321.0
1.5	-23.4	-320.6	-320.1
2.0	-22.6	-319.8	-319.3
2.5	-21.7	-318.9	-318.4
3.0	-20.9	-318.1	-317.6
3.5	-20.1	-317.3	-316.8
4.0	-19.3	-316.5	-316.0
4.5	-18.6	-315.8	-315.3
5.0	-17.8	-315.0	-314.5
5.5	-17.1	-314.3	-313.8
6.0	-16.4	-313.6	-313.1
6.5	-15.7	-312.9	-312.4
7.0	-15.1	-312.3	-311.8

The Heat Capacity of Aqueous UO_2Cl_2 Solutions

Kapustinskii and Lipilina (1955) measured the specific heat of various aqueous solutions in the concentration range m = 0.9 to 0.14

mols (kg $H_2O)^{-1}$. A graph of φ_C (the apparent molal heat capacity) vs. $m^{1/2}$ results in the following tabulated values:

m UO_2Cl_2	φ_C cal/mol·K
0.2	-33.0
0.3	-28.0
0.4	-23.0
0.5	-18.5
0.6	-14.0
0.7	-10.0
0.8	-7.0
0.9	-3.0
1.0	0

$UO_2Cl_2 \cdot H_2O(c)$ and $UO_2Cl_2 \cdot 3H_2O(c)$

The S°'s at 298 K have been estimated from the known S° $UO_2Cl_2(c)$, the estimated contributions of the additional H_2O and the Gibbs energies of formation.

There are two self contained sets of measurements on the ΔH's solution of the two hydrates and the anhydrous $UO_2Cl_2(c)$, those of Prins (1973) [measurements in 5N HCl], and those of Shchukarev et al (1959b) [measurements in H_2O]. The following summarizes the measurements and the calculated enthalpies of dehydration for:

$$UO_2Cl_2 \cdot nH_2O(c) \rightarrow UO_2Cl_2(c) + nH_2O(liq)$$

Hydrate	Prins ΔH_{soln} (in 5N HCl) kcal/mol	Shchukarev et al (1959b); ΔH_{soln} (in H_2O) kcal/mol	Prins $\Delta H_{dehydration}$ kcal/mol	Shchukarev $\Delta H_{dehydration}$ kcal/mol	
3	-2.41±0.01	-10.00±0.11	15.26±0.23*	13.86±0.17	(1)
1	-10.19±0.3	-13.32±0.23	7.24±0.38*	10.54±0.26	(2)
0	-17.30±0.23	-23.86±0.13	-	-	

As is obvious the results are not in agreement. Other information, though, is available which supports the Prins measurements. A detailed analysis is given elsewhere of the measurements of ΔH_{soln} of $UO_2Cl_2(c)$ in varying concentrations of HCl [from different laboratories], and the Lipilina and Samoilov (1954) measurements of the ΔH_{soln} of the trihydrate in HCl solutions over the range m_{HCl} = 0.8 to 4.4, where the molal concentration of UO_2Cl_2 is 1.1 (a much higher concentration of UO_2Cl_2 than for the measurements on the anhydrous). Exclusive

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* Corrected for the formation of $H_2O(aq)$ in 5N HCl, $H_2O(liq) \rightarrow H_2O(aq)$; ΔH = -0.125 kcal/mol.

of the Prins measurements they also result in a ΔH dehydration = 15.1 to 15.6 kcal/mol, confirming the Prins (1973) relationship for the trihydrate complete dehydration. In addition, the individual measurements from Prins are in agreement with other ΔH_{soln} measurements.

Now, ΔH_3 can also be obtained:

$$UO_2Cl_2 \cdot 3H_2O(c) \rightarrow UO_2Cl_2 \cdot H_2O(c) + 2H_2O(l) \qquad (3)$$

which from Prins' measurements is = 8.02±0.3 kcal/mol and from Shchukarev's measurements is = 3.32±0.25 kcal/mol. Cordfunke (1965) represents his vapor pressure measurements for:

$$UO_2Cl_2 \cdot 3H_2O(c) \rightarrow UO_2Cl_2 \cdot H_2O(c) + 2H_2O(g) \qquad (4)$$

as

$$\log P_{atm} = -3{,}406 \pm 32/T + 8.497 \pm 0.10.$$

This converts to:

$$\Delta G^\circ_4 = 31{,}170 - 77.76T \text{ cal/mol}$$

with $\Delta H^\circ_4 = 31.2 \pm 0.3$ kcal/mol and $\Delta S^\circ_4 = 77.8$ cal/mol·K. Converting to equation (3) using for $H_2O(l) \rightarrow H_2O(g)$, $\Delta H^\circ = 10.52 \pm 0.01$ kcal/mol and $\Delta S^\circ = +28.4$ cal/mol·K, we obtain $\Delta H^\circ_3 = +10.6$ kcal/mol and $\Delta S^\circ_3 = 21.0$ cal/mol·K. Obviously this derived value for ΔH does not confirm either the Prins measurements or Shchukarev's; the ΔS° for the decomposition of a hydrate should be $\approx$ 33-36 cal/mol·$H_2O(g)$·K and $\approx$ 5-8 cal/mol·$H_2O(l)$·K. The derived ΔS°_3 is 5-8 cal/mol·K too high. If the assumption is made that the measured pressure is reasonably correct, i.e., $\log P_{atm} = -2.93$, then $\Delta G^\circ_4 = 7.98 \pm 0.1$ kcal and with the estimate $\Delta S^\circ_4 = 71$ cal/mol·K, $\Delta H_4 = 29.1$ kcal and $\Delta H_3 =$ 8.1 kcal, in excellent agreement with the Prins determination.

The Prins' values for the dehydrations result in ΔHf° $UO_2Cl_2 \cdot 3H_2O(c)$ = -517.4±0.4 kcal/mol and ΔHf° $UO_2Cl_2 \cdot H_2O(c)$ = -372.8±0.5 kcal/mol.

With an estimate of 46±2 cal/mol·K for S° $UO_2Cl_2 \cdot H_2O(c)$, ΔSf° $UO_2Cl_2 \cdot H_2O(c)$ = -124.0 cal/mol·K which in combination with ΔHf° $UO_2Cl_2 \cdot H_2O(c)$ = -372.8±0.5 kcal/mol results in ΔGf° = -335.8±0.8 kcal/mol.

The experimental $\Delta G^\circ_4 = 7.98 \pm 0.1$ kcal/mol, results in ΔGf° $UO_2Cl_2 \cdot 3H_2O(c)$ = -453.0±0.8 kcal/mol. The calculated S° $UO_2Cl_2 \cdot 3H_2O(c)$ = 65.4 cal/mol·K is rounded to 65±2 cal/mol·K.

The experimental vapor pressure measurements of Cordfunke (1965), with modifications, have been used to obtain the following equation:

$$UO_2Cl_2 \cdot 3H_2O(c) \rightarrow UO_2Cl_2 \cdot H_2O(c) + 2H_2O(g)$$

$$\Delta G^\circ = 29{,}040 - 70.6T \text{ cal/mol}$$

so that:

$$\log P_{atm} = -3{,}170/T + 7.71$$

$UO_2Cl_2(g)$

Cordfunke and Prins (1974) chlorinated $U_3O_8(c)$ (1140-1330 K). Volatile UO_2Cl_2 is formed. The transpiration method was used to measure the pressure of $UO_2Cl_2(g)$ formed.

The equilibrium:

$$U_3O_8(c) + 3Cl_2(g) \rightarrow 3UO_2Cl_2(g) + O_2(g)$$

can be expressed by:

$$\Delta G_T^\circ = 142{,}300 \pm 1600 - (67.8 \pm 1.3)T \text{ cal/mol } O_2 \text{ (1140-1330 K)}$$

A ΔC_p = -10 cal/mol·K is assumed so that at 298 K, ΔH = 151.5 kcal/mol and ΔS = 82 cal/mol·K, resulting in ΔHf° = -234±3 kcal/mol and S° = 87±4 cal/mol·K. The S appears low and is not tabulated as a recommended value.

The results of Sietz cited by Kangro (1963) are not in agreement.

$UOCl_3$(c) and $UOBr_3$(c)

An estimate is given for $UOCl_3$(c) S° = 41±2 based on the measured S° for UCl_3(c), UCl_4(c), $UOCl_2$(c), and UO_2Cl_2(c).

Similarly for $UOBr_3$(c) from the above pattern and the measured $UOBr_2$(c), S° = 49±3 cal/mol is estimated.

Shchukarev et al. have determined the ΔH's of reaction of $UOCl_3$(c) = -28.55±0.13 (1958a) and $UOBr_3$(c) = -45.42±0.21 kcal/mol (1958b) in 2% HCl, 0.5%$FeCl_3$ solution, as well as UCl_4(c). [See discussion on UO_2Cl_2(c).]

The reactions of $UOCl_3$(c) and $UOBr_3$(c) involve oxidation to the (VI) state, e.g.,

$$UOCl_3(c) + FeCl_3(aq) + H_2O(aq) \rightarrow UO_2Cl_2(aq) + 2HCl(aq) + FeCl_2(aq)$$

as does the reaction of UCl_4(c), so that

$$UOCl_3(c) + FeCl_2(c) + 2HCl(aq) \rightarrow UCl_4(c) + FeCl_3(c) + H_2O(aq)^*; \quad (1)$$

$$\Delta H_1 = 30.90 \pm 0.22 \text{ kcal/mol}$$

and ΔHf° $UOCl_3$(c) = -277.5±0.8 kcal/mol.

The difference between Shchukarev's measurements on $UOCl_3$(c) and $UOBr_3$(c) yie

$$UOCl_3(c) + 3HBr(aq) \rightarrow UOBr_3(c) + 3HCl(aq); \ \Delta H_2 = 16.87 \pm 0.25 \text{kcal/mol} \quad (2)$$

and ΔHf° $UOBr_3$(c) = -228.2±0.84 kcal/mol

The value for $UOCl_3$(c) appears to be reasonable; however, the value for $UOBr_3$(c) appears questionable; one would expect, if ΔHf° $UOCl_3$(c) is correct, ΔHf° $UOBr_3$(c) ≈ -238 kcal/mol. Since there is

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[*] As in the case of UO_2Cl_2(c) the Cordfunke et al. (1976) measurements on $FeCl_2$(c)-$FeCl_3$(c) are used.

no other information at present to resolve this, the uncertainties have been enlarged to ±5 kcal/mol.

$(UO_2)_2Cl_3(c)$

Cordfunke et al. (1977) have prepared a new oxide-chloride by two different methods, one the thermal decomposition of $UO_2Cl_2(c)$ in vacuum at ~ 723 K, and the other by heating mixtures of $UO_2(c)$ and $UO_2Cl_2(c)$ (in a molar ratio of 1:3) ~ 773 K. They have characterized this black-brown solid as $(UO_2)_2Cl_3(c)$ with an orthorhombic unit cell and have determined its ΔH solution in 1.505M H_2SO_4, (-46.025 ±0.8 kcal/mol).

Previously Cordfunke et al. (1976) had determined the ΔH_{soln} of $UCl_4(c)$ (-50.94±0.20) and $HCl(10.01H_2O)$ (-0.245±0.01) and Cordfunke and Ouweltjes (1977) had determined the ΔH_{soln} of $UO_3(c,\gamma)$ (-20.13±0.04 kcal/mol), all in 1.505M H_2SO_4.

A summation (after correction for dilution effects to the same final solutions) results in:

$$3UO_3(c,\gamma) + UCl_4(c) + 2HCl(aq)^* \rightarrow 2(UO_2)_2Cl_3(c) + H_2O(l);$$

$$\Delta H = -19.64 \pm 0.3 \text{ kcal/mol } UCl_4$$

The recommended value is derived from this reaction.

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[*] The integral $\Delta Hf°$ HCl $10.01H_2O$

$UO_2(OH)Cl\cdot 2H_2O(c)$

Prins (1973) measured the ΔH_{soln} of $UO_2(OH)Cl\cdot 2H_2O(c)$ in excess $HCl(10.01H_2O)$ = -2.04±0.07 kcal/mol. With his ΔH_{soln} $UO_2Cl_2\cdot 3H_2O(c)$ = -2.4±0.01 kcal/mol, one obtains the relationship:

$$UO_2(OH)Cl\cdot 2H_2O(c) + HCl(aq) \rightarrow UO_2Cl_2\cdot 3H_2O(c);\ \Delta H = 0.37\pm 0.07 \text{ kcal/mol}$$

from which $\Delta Hf^\circ = -480.5\pm 0.4$ kcal/mol.

3.105 U-Cl-F Compounds

$UF_3Cl(c)$, $UF_2Cl_2(c)$, and $UFCl_3(c)$

The tabulated values for S°, $C_p°$ and $H-H_0$ are obtained from the thermal functions estimated by Maslov (1964) on the basis of $UF_4(c)$ and $UCl_4(c)$ (0-350 K).

No enthalpy or Gibbs energy of formation data are available.

3.106 U-Br Compounds

$UBr_3(c)$

Krestov (1972) has estimated the C_p as a function of the temperature as:

$$C_p = 24.1 + 6.3\text{x}10^{-3}T \text{ cal/mol·K} \quad (298\text{-}1000 \text{ K}).$$

MacWood (1958) cites the measurements of Altman (1944) and Gregory (1945) in the range 648-798 K on the H_2 reduction equilibrium:

$$UBr_4(c) + 1/2H_2(g) \rightarrow UBr_3(c) + HBr(g) \qquad (1)$$

From the K's as a function of T, a second law $\Delta H°_1 = 16.0$ kcal/mol ($\Delta Hf°$ $UBr_3(c) = -167.0$ kcal/mol) is obtained which is in agreement with the calorimetric determinations cited below, so that this $\Delta H°$ in conjunction with the $\Sigma(H-H_{298})_T$, $\Sigma(S-S_{298})_T$ and the K's are used to obtain $S°$ $UBr_4(c)$-$S°$ $UBr_3(c) = 11.0$ cal/mol, resulting in $S°$ $UBr_3(c) = 46\pm2$ cal/mol·K.

MacWood (1958) reporting on the measurements of Barkelew cites the ΔH's for reaction of $UBr_3(c)$ (= -49.5 kcal/mol) and $UCl_3(c)$ (= -42.0 kcal/mol) in solutions of 12N HCl, 10% $FeCl_3$. In both of these solutions the uranium is oxidized to the hexavalent state so that one can write:

$$UBr_3(c) + 3HCl(aq) \rightarrow UCl_3(c) + 3HBr(aq); \; \Delta H_2 = -7.5 \text{ kcal/mol} \qquad (2)$$

with $\Delta\overline{H}f°$ HCl(aq) = -32.7 and $\Delta\overline{H}f$ HBr(aq) = -22.0 kcal/mol which are consistent with Barkelew's experimental components, $\Delta Hf°$ $UBr_3(c)$ = -167.4 kcal/mol.

One can also use the measurement of $UBr_4(c)$ in the same media ($\Delta H = -33.1$ kcal/mol) to obtain the relationship:

$$UBr_3(c) + HBr(aq) + FeCl_3(aq) \rightarrow UBr_4(c) + FeCl_2(aq) + HCl(aq);$$
$$\Delta H_3 = -16.4 \text{ kcal/mol} \qquad (3)$$

With the Barkelew relationship (△H = -20.2 kcal/mol) cited previously (see UCl_5(c) and UCl_6(c)) for the $FeCl_2$-$FeCl_3$ relationship, △Hf° UBr_3(c) = -165.8 kcal/mol. This provides a crosscheck.

As cited previously, the high temperature equilibrium studies result in △Hf° = -167.0 kcal/mol. The selected value is △Hf° = -167.0±1.0 kcal/mol.

The Gibbs energy of formation is derived from the selected △Hf° and △Sf° = -20.6 cal/mol·K.

$UBr_3(g)$

Rand and Kubaschewski (1963), using the information given by Katz and Rabinowitch (1951) on the vapor pressure of $UBr_3(c,l)$ (measurements by Altman and by Webster), obtained the following:

$$UBr_3(c) \rightarrow UBr_4(g)$$

$$\Delta G = 75{,}100 - 91.8T + 13.8T \log T \quad \text{cal/mol}$$

$$(298 \text{ to } 1000 \text{ K})$$

at 298 K: $\Delta H = 73.4$ kcal/mol

$\Delta S = 51.6$ cal/mol·K

$\Delta G = 58.0$ kcal/mol

$$UBr_3(l) \rightarrow UBr_3(g)$$

$$\Delta G = 68{,}600 - 112.8T + 23.0T \log T \quad \text{cal/mol}$$

$$(1000 \text{ to } 1810 \text{ K})$$

$\Delta G = 0$ at 1810 K

and

$\Delta H = 50.5$ kcal/mol

$\Delta S = 27.9$ cal/mol·K

At 1000 K: $UBr_3(c) \rightarrow UBr_3(l)$

$\Delta H = 10.5$ kcal/mol

$\Delta S = 10.5$ cal/mol·K

These values are accepted.

UBr_4(c)

S° has been estimated as 57.0±2.0 cal/mol. Krestov (1972) has estimated the C_p UBr_4(c) as:

$$C_p = 28.5 + .0071T \text{ cal/mol}\cdot\text{K } (298\text{-}792 \text{ K})$$

From the discussion on UBr_4(g) we have, at the melting point, 792 K:

$$\Delta H_{fusion} = 11.6 \text{ kcal/mol}$$
$$\Delta S_{fusion} = 14.6 \text{ cal/mol}\cdot\text{K}$$
$$C_p(1) = 41 \text{ cal/mol}\cdot\text{K}$$

Fuger and Brown (1973) measured ΔH's of soln. of UBr_4(c) and UCl_4(c) in 1M HCl solutions , i.e., $HCl(54.4H_2O)$ of -63.24±0.09 and -54.46±0.23 kcal/mol, respectively. From these measurements the following is obtained:

$$UBr_4(c) + 4HCl(aq) \rightarrow UCl_4(c) + 4HBr(aq);\ \Delta H_1 = -8.78\pm0.25 \text{ kcal/mol} \quad (1)$$

It is assumed that the formation of HBr in a 1M HCl solution is equivalent to the formation of an additional mole of HBr in an HBr 1M solution. Using differential $\Delta\overline{H}f$'s, then for HCl and HBr of -39.284 and -28.53 kcal/mol, respectively, ΔHf° of UBr_4(c) = -191.70 ±0.7 kcal/mol.

Shchukarev et al (1959a) measured the ΔH for the reaction of UBr_4(c) wit 2% HCl, 0.5%$FeCl_3$ solution as -53.27±0.36 kcal/mol. In an earlier report (1958a) they measured the ΔH for reaction of UCl_4(c) as -45.50±0.10 kcal/mol in a similar solution. These reactions involve oxidation to UO_2Cl_2 (in HCl) as:

$$UBr_4(c) + 2FeCl_3(aq) + 2H_2O(1) \rightarrow UO_2Cl_2(aq) + 2FeCl_2(aq) + 4HBr(aq)$$

By difference, though, one obtains ΔH_1 = -7.77±0.37 kcal/mol and with the same assumptions as earlier regarding the use of the differentials and with $\Delta\overline{H}f$ HCl(100H_2O) and $\Delta\overline{H}f$ HBr(100H_2O) = -39.489 and -28.692 kcal/mol, respectively, $\Delta Hf°$ HBr_4(c) = $-192.5_4 \pm 0.8$.

Similarly, Vdovenko et al (1973) obtain ΔH for UBr_4(c) to be -54.32±0.1, and -45.34±0.1 for UCl_4(c), from which ΔH_1 = -8.98±0.14 and $\Delta Hf°$ = -191.4±0.6 kcal/mol.

MacWood (1958), reporting on the measurements of Barkelew (1946) cites the ΔH's at 273 K of the reaction of UCl_4(c) and UBr_4(c) in 12N HCl, 10% $FeCl_3$ solutions, from which ΔH_1 = -9.0 kcal/mol. With their values for $\Delta\overline{H}f$'s of HCl and HBr = -32.7 and -22.0 kcal/mol, respectively (these values for the differentials at 273 K incorporate the Barkelew experimental components), $\Delta Hf°$ = -191.8±2.0 kcal/mol.

A weighted average results in $\Delta Hf°$ = -191.7±0.6 kcal/mol.

The $\Delta Sf°$ = -27.77 cal/mol·K and the $\Delta Hf°$ results in $\Delta Gf°$ = -183.4±0.9 kcal/mol.

$UBr_4(g)$

Rand and Kubaschewski (1963) reviewed the vapor pressure data on the crystal and liquid and using an estimated $\Delta C_p = -6$ cal/mol·K obtained for the sublimation process, (from the excellent agreement in the measurements of Thompson and Schelberg (573 K - 723 K; effusion) and Nottorf and Powell (723-773; gas saturation) given by Katz and Rabinowitch (1951)):

$$UBr_4(c) \rightarrow UBr_4(g)$$

$$\Delta G° = 49{,}400 - 92.7T + 13.8\ T \log T \text{ cal/mol}$$

These results lead to, at 298.15 K:

$$\Delta H° = 47.6 \text{ kcal/mol}$$
$$\Delta G° = 31.9 \text{ kcal/mol}$$
$$\Delta S° = 52.6 \text{ cal/mol·K}$$

These values are accepted in the absence of newer data.

A similar equation, with $\Delta C_p = -11$ for the vaporization process

$$UBr_4(l) \rightarrow UBr_4(g)$$

results in ΔH_{fusion} at the melting point, 792 K, = 13.2 kcal/mol and a $\Delta S_{fusion} = 16.5$ cal/mol·K.

In view of the large ΔS_{fusion} a reexamination of the vapor pressure data was made using the measurements of Gregory (815-1033 K; boiling point), and Nottorf and Powell (798-898; gas saturation) as given by Mueller (1948). The measurements (although there is some scatter) are in agreement, and with $\Delta C_p = -13$ cal/mol·K, the following is obtained:

$$\Delta G° = 43{,}300 - 131.9T + 29.9T \log T \text{ cal/mol}$$

$\Delta G° = 0$ at 1040 K, $\Delta H = 29.8$ kcal/mol and $\Delta S = 28.6$ cal/mol·K.

At 792 K (melting point):

$$\Delta H = 11.6 \text{ kcal/mol}$$
$$\Delta S = 14.6 \text{ cal/mol·K}$$

UBr_5(c)

Krestov's (1972) estimated $C_p = 36.0 + 8.0 \times 10^{-3} T$ cal/mol·K is accepted. The S° was estimated as 70±3 cal/mol·K. These values result in a reasonable fit of the Blair and Ihle (1973) thermal decomposition measurements of UBr_5(c) to a third law plot.

The thermal decomposition of UBr_5(c) was studied in the range 298-400 K.

$$UBr_5(c) \rightarrow UBr_4(c) + 1/2Br_2(g)$$

The decomposition is reversible below 353 K. Above this temperature the compound decomposes irreversibly into UBr_4(c) and Br_2(l). From the vapor pressure measurements below 383 K a third law $\Delta H° = 6.0$ kcal/mol ($\Delta Hf° = -194.0$ kcal/mol). A second law $\Delta H = 5.4$ kcal/mol ($\Delta Hf° = -193.4$ kcal/mol). The average $\Delta Hf°$ UBr_5(c) = -193.7±2.0 kcal/mol is selected. The $\Delta Gf°$ is calculated from the $\Delta Hf°$ and the estimated $\Delta Sf°$.

3.107 U-Br-O Compounds

UOBr(c)

See UOCl(c)

$UOBr_2(c)$

The S°, C_p°, and $H-H_0$ are from Greenberg and Westrum's (1956b) tabulation from their heat capacity measurements from 5 K to 339 K.

Mueller (1948) reported the vapor pressure measurements of $UBr_4(g)$ over $UOBr_2(c)$ from the results of Gregory. For the range 710 to 960 K,

$$\log P(\text{atm}) = -10{,}870/T + 8.32$$

$\Delta H = 49.7$ kcal/mol UBr_4 at the mean temperature for:

$$2UOBr_2(c) \rightarrow UBr_4(g) + UO_2(c) \qquad (1)$$

which, with $\Delta C_p = -6$ cal/mol·K results in $\Delta H_1 = 52.9$ kcal/mol and $\Delta Hf° = -228.2$ kcal/mol. However, the $\Delta S_1° = 38.1$ cal/mol·K at the mean temperature results in a $\Delta S°_1$ at 298 K = 44 cal/mol·K, whereas the value calculated from the S°'s of $UO_2(c)$, $UOBr_2(c)$ and $UBr_4(g)$ [obtained from $\Delta S°_{subl}$ and an estimate for S° $UBr_4(c)$] results in $\Delta S_1°$ = 53 cal/mol·K. The difference in ΔS° is too great to be rationalized; the S° $UBr_4(g)$ accepted here does not appear to be appreciably too high since 110 cal/mol·K is reasonable with regard to S° $UCl_4(g)$ obtained from $\Delta S°_{subl}$ $UCl_4(c)$ which is in excellent agreement with the value obtained from the comparable $UOCl_2(c)$ decomposition to $UCl_4(g)$.

In addition, using the $\Delta Hf°$ $UOBr_2(c)$ = -228.2 kcal/mol for

$$2UOBr_2(c) \rightarrow UO_2(c) + UBr_4(c), \qquad (2)$$

ΔH_2= 5.4 kcal/mol $UBr_4(c)$ which indicates a lower stability for $UOBr_2(c)$ than for $UOCl_2(c)$. Again this does not seem reasonable.

For these reasons the Gregory data has been rearranged by:

1. Assuming that his pressure measurements are reasonable, with log P(atm) = -4.47 at 850 K (obtained from his equation).
2. Assuming $\Delta S°_1$ at 850 K ≈ 47 cal/mol·K (using the $\Delta S°_1$ at 298 K 53 cal/mol·K and $\Delta C_p°$ = -6 cal/mol·K).
3. Recalculating ΔH_1 at 850 K to be 57.3 kcal/mol from the above listed values for log P and $\Delta S°$ results in $\Delta H°_1$ at 298 K = 60.6 kcal/mol.

The resultant $\Delta Hf°$ $UOBr_2(c)$ = -232.0 kcal/mol.

The Barkelew (1946) measurements on the oxidation reactions of (1) $UOBr_2(c)$ and (2) $UOCl_2(c)$ in a 12N HCl, 10% $FeCl_3$ aqueous solution at 273 K are now considered. As indicated in the discussion on $UOCl_2(c)$ the values obtained for the $\Delta Hf°$ $UOCl_2(c)$ from the Barkelew data are in reasonable agreement with the preferred data, although the sample of $UOCl_2(c)$ used was not of high purity.

The ΔH of oxidation of $UOBr_2(c)$ in a 12N HCl, 10% $FeCl_3$ aqueous solution = -16.3 kcal/mol. This reaction was paired with the comparable reaction of $UOCl_2(c)$, ΔH = -16.7 kcal/mol, to obtain ΔH_3 at 273 K = -0.4 kcal/mol for

$$UOCl_2(c) + 2HBr(aq) \rightarrow UOBr_2(c) + 2HCl(aq). \qquad (3)$$

As for the differential $\Delta\overline{H}f$ HCl(aq), the Barkelew value for the differential $\Delta\overline{H}f$ of HBr(aq) in a 12N HCl, $FeCl_3$ aqueous solution has been recalculated equal to -22.03 kcal/mol at 273 K (this value incorporated Barkelew's experimental components), so that $\Delta Hf°$ at 273 K = -234.2 for $UOBr_2(c)$ and $\Delta Hf°$ at 298 K = -234.1 kcal/mol.

None of these values by themselves can be considered good. However, the recalculations have brought them, from very different paths, into reasonable agreement.

$\Delta Hf°$ $UOBr_2(c)$ has been taken to be -232.7±2.0 kcal/mol. This value results in ΔH_3 = 14.4 kcal/mol $UBr_4(c)$.

The $\Delta Gf°$ is calculated from the $\Delta Hf°$ and S°.

$UO_2Br_2\cdot nH_2O$(c) (n = 0, 1, 3)

The entropy for UO_2Br_2(c) at 298 K is estimated on the basis of the values for $UOCl_2$(c), $UOBr_2$(c), and UO_2Cl_2(c); those for the hydrates using a contribution to S° of 9.4 cal/mol·K per mole of H_2O.

Recently Cordfunke et al. (1978) determined the enthalpy of UO_2Br_2(c) in the range 345 to 454 K relative to 298 K. The results are expressed as:

$$H_T-H_{298} = 24.92T + 4.534\times10^{-3}T^2 - 7833 \text{ cal/mol}$$
$$(298 - 460 \text{ K})$$

The values for the ΔHf°'s are obtained from the recent measurements of Prins et al. (1978) on the ΔH's of solution of UO_3(c,γ), $UO_2Br_2\cdot0.024H_2O$(c) $UO_2Br_2\cdot1.05H_2O$(c) and $UO_2Br_2\cdot2.92H_2O$(c) in excess HBr($14.63H_2O$). The ΔH's are given, corrected to the appropriate hydrates.

Compound	ΔH_{soln} kcal/mol	
UO_3(c,γ)	-17.88±0.05	(1)
UO_2Br_2(c)	-25.38±0.10	(2)
$UO_2Br_2\cdot H_2O$(c)	-17.61±0.15	(3)
$UO_2Br_2\cdot3H_2O$(c)	-10.43±0.20	(4)

The ΔHf° UO_2Br_2(c) = -271.84±0.32 is obtained from the summation:

$UO_3(c,\gamma) + 2HBr(aq) \rightarrow UO_2Br_2(c) + H_2O(aq)$; $\Delta H_5 = 7.50\pm0.11$ kcal/mol (5)

using the differentials, $\Delta\overline{H}f°$ HBr(aq) = -27.60 kcal/mol and $\Delta\overline{H}f°$ H_2O(aq) = -68.361 kcal/mol.

For the ΔH's of hydration:

$UO_2Br_2(c) + H_2O(l) \rightarrow UO_2Br_2\cdot H_2O(c)$; $\Delta H_6 = -7.82\pm0.18$ kcal/mol (6)

$UO_2Br_2(c) + 3H_2O(l) \rightarrow UO_2Br_2\cdot3H_2O(c)$; $\Delta H_7 = -15.09\pm0.22$ kcal/mol (7) from which ΔHf° $UO_2Br_2 \cdot H_2O(c)$ = -347.97±0.34 kcal/mol and ΔHf° $UO_2Br_2 \cdot 3H_2O(c)$ = -491.88±0.36 kcal/mol.

The ΔH's of hydration for $UO_2Br_2(c)$ and $UO_2Cl_2(c)$ appear to be essentially the same.

The earlier measurements of Shchukarev et al. (1958a) on ΔH_{soln} $UO_2Cl_2(c)$ = -25.44±0.07 and (1958b) on ΔH_{soln} $UO_2Br_2(c)$ = -31.23±0.2 kcal/mol in 2% HCl, 0.5% $FeCl_3$ aqueous solutions lead to:

$$UO_2Cl_2(c) + 2HBr(aq) \rightarrow UO_2Br_2(c) + 2HCl(aq);$$
$$\Delta H_8 = 5.79 \pm 0.5^{*} \text{ kcal/mol} \qquad (8)$$

which, with the differentials for the formation of $HX(100H_2O)$, $\Delta\overline{H}f$ HCl = -39.489 and $\Delta\overline{H}f$ HBr = -28.689 kcal/mol, results in ΔHf° UO_2Br_2 = -269.8 kcal/mol, in poor agreement with the Prins et al. results.

From the Shchukarev et al. (1959b) ΔH_{soln} measurements of the anhydrous $UO_2Br_2(c)$ and the two hydrates in H_2O, ΔH_6 = -8.9 kcal/mol and ΔH_7 = -11.8 kcal/mol, also in poor agreement with the Prins et al. results.

The Shchukarev et al. (1958a, 1958b, 1959b) measurements on the $UO_2Br_2 \cdot nH_2O$ system are suspect and are rejected for the following reasons:

1. The ΔH_{soln} $FeCl_3(c)$ in a solution of 2% HCl by Shchukarev et al. (1958a) has been found to be in error.
2. The ΔH's of hydration of $UO_2Cl_2(c)$ to the two hydrates from Shchukarev et al. (1959b) appear to be incorrect. See $UO_2Cl_2 \cdot H_2O(c)$ and $UO_2Cl_2 \cdot 3H_2O(c)$.
3. A comparison of the ΔH's of solution of UO_2Br_2 in a solution of 2% HCl, 0.5% $FeCl_3$ (1958b) and in $H_2O(l)$ (1959b)

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[*] See $UO_2Cl_2(c)$ discussion on the "Shchukarev" cycle.

with those for $UO_2Cl_2(c)$ indicates an inconsistency which may be caused by erroneous measurements on $UO_2Br_2(c)$. The Prins measurements, in contrast, offer a consistent picture on the behavior of $UO_2Cl_2 \cdot nH_2O(c)$ and $UO_2Br_2 \cdot nH_2O(c)$.

The ΔGf°'s have been calculated from the ΔHf°'s and the ΔSf°'s.

$UOBr_3(c)$

See $UOCl_3(c)$

$UO_2(OH)Br \cdot 2H_2O(c)$

Prins et al. (1978) measured the $\Delta H_{soln} = -6.67 \pm 0.01$ kcal/mol of $UO_2(OH)Br \cdot 2H_2O(c)$ in $HBr(14.63H_2O)$. Combining this with their measurement for ΔH_{soln} of $UO_3(c,\gamma)$ in $HBr(14.63H_2O) = -17.88 \pm 0.05$ one obtains:

$$UO_3(c,\gamma) + HBr(aq) + 2H_2O(aq) \rightarrow UO_2(OH)Br \cdot 2H_2O(c);\ \Delta H = -11.21 \pm 0.05$$

and $\Delta Hf° = -468.0_3 \pm 0.3$ kcal/mol.

The differential $\Delta\bar{H}f$'s to be used are $\Delta\bar{H}f$ $HBr(14.63H_2O) = -27.60$ and $\Delta\bar{H}f$ $H_2O(aq) = -68.361$ kcal/mol.

3.108 U-Br-Cl Compounds

$UCl_{3-x}Br_x$(c) (x=1,2) and $UCl_{4-x}Br_x$(c) (x=1,2,3)

MacWood (1958) reports the K's for: (1) the H_2 reduction of various $UCl_{4-x}Br_x$(c) in the range 650-750 K from the results of Gregory (1945) and (2) the exchange equilibria with HBr(g) in the range 600-773 K from the results of Altman (1944). Examples of these equilibria are:

1. $UCl_{4-x}Br_x(c) + 1/2H_2(g) \rightarrow UCl_{4-x}Br_{x-1}(c) + HBr(g)$

and

$UCl_{4-x}Br_x(c) + 1/2H_2(g) \rightarrow UCl_{3-x}Br_x(c) + HCl(g)$

2. $UCl_{4-x}Br_x(c) + HBr(g) \rightarrow UCl_{3-x}Br_{x+1}(g) + HCl(g)$

These K's and the △H's calculated from the △Hf°'s selected here were used to obtain the S°'s for the various III and IV mixed halides. They are to be considered approximate values.

MacWood also reports the measurements of Barkelew on the △H's of solution in a 12N HCl 10% $FeCl_3$ solution of the mixed halides (III and IV) as well as UCl_3(c), UCl_4(c), UBr_3(c), and UBr_4(c) from which the △Hf°'s can be obtained by summation reactions. Examples follow, as well as the measured △H's of solution.

$UCl_2Br(c) + HCl(aq) \rightarrow UCl_3(c) + HBr(aq);$

$\Delta H = \Delta H_{soln}\ UCl_2Br - \Delta H_{soln}\ UCl_3(c)$

and

$UClBr_3(c) + HBr(aq) \rightarrow UBr_4(c) + HCl(aq);$

$\Delta H = \Delta H_{soln}\ UClBr_3(c) - \Delta H_{soln}\ UBr_4(c)$

	ΔH_{soln} kcal/mol
$UCl_3(c)$	-42.0
$UCl_2Br(c)$	-44.2
$UClBr_2(c)$	-48.2
$UBr_3(c)$	-49.5
$UCl_4(c)$	-24.1
$UCl_3Br(c)$	-25.7
$UCl_2Br_2(c)$	-29.2
$UClBr_3(c)$	-31.8
$UBr_4(c)$	-33.1

3.109 U-I Compounds

$UI_3(c)$

Krestov (1972) has estimated the C_p as a function of temperature

$$C_p = 25.1 + 5.8\times10^{-3}T \text{ cal/mol·K (298-800 K)}$$

MacWood (1958) tabulated the decomposition pressure measurements (523-666 K) of MacWood et al. (1944) for:

$$UI_4(c) \rightarrow UI_3(c) + 1/2I_2(g) \qquad (1)$$

From the values for $\Delta Hf°$ $UI_3(c)$ listed below, $\Delta Hf° = -111.7\pm1.0$ kcal is selected. The resultant $\Delta H°_1 = 19.7\pm0.5$ kcal/mol is used in combination with the above pressure measurements and $\Delta(H-H_{298})_T$ and $\Delta(S-S_{298})_T$ to obtain $\Delta S_1 = 21.8\pm1.0$ cal/mol·K and $\Delta(S°\ UI_4(c)-S°\ UI_3(c))$ = 10 cal/mol·K. $S°\ UI_3(c) = 53\pm2$ appears reasonable in comparison with the measured $S°\ UCl_3(c)$ and $\Delta S°$ (Cl-I). This value for $S°\ UI_3(c)$ in conjunction with the estimated C_p equation completes the tabulated thermal functions.

The second law value for $\Delta H°_1$ from the above decomposition pressure measurements is 18.5±1.0 kcal/mol which results in $\Delta Hf° = -113.0\pm1.2$ kcal/mol.

MacWood (1958) reporting on the measurements of Barkelew (1946) cites the ΔH's reaction of $UI_3(c) = -56.5$ and $UI_4(c) = -44.2$ kcal/mol, respectively, with a solvent of 12N HCl saturated with $I_2(c)$. In these final solutions the uranium is considered to be in (IV) state. Then for the relationship:

$$UI_4(c) \rightarrow UI_3(c) + 1/2I_2(c);\ \Delta H_2 = 12.3\pm0.6 \text{ kcal/mol} \qquad (2)$$

and $\Delta Hf° = -111.7\pm1.0$ kcal/mol.

Tveekrem and Chandrasekharaiah (1968) from cell measurements obtained $\Delta G^\circ_{643\ K}$ = -98.8±0.4 kcal/mol for:

$$U(c) + 3/2I_2(g) \rightarrow UI_3(c) \qquad (3)$$

The third law ΔH° = -131.5±1.0 and ΔHf° = -110.2±1.0 kcal/mol.

The ΔSf° = -0.6 cal/mol·K results in ΔGf° = -111.5±1.2 kcal/mol.

$UI_4(c)$

The S° has been estimated as 63±2 cal/mol based on a comparison of the differences in measured entropies of chlorides and iodides for the polyvalent halides.

Popov et al. (1959a) have measured the C_p of $UI_4(c)$ and (l) from 373 K to 873 K.

Rand and Kubaschewski (1963) used these measurements to obtain for $UI_4(c)$:

$$C_p = 34.8 + 2.38\times10^{-3}T - 4.72\times10^{5}T^{-2} \quad \text{cal/mol·K} \quad (380\text{-}720\ K)$$

The results of Popov et al., for the phase changes have been accepted. (See the discussion of the vapor pressure data for $UI_4(c)$ and (l) under $UI_4(g)$.) The total ΔH for the phase changes of $UI_4(c)$ to $UI_4(l)$ (m.p. ≈ 779 K) is 9.2 kcal/mol. For $UI_4(l)$: C_p = 39.6 cal/mol·K (820-870 K).

The selected C_p° at 298 K is obtained from the extrapolation of the measurements below 473 K. Smoothed tabulated functions are given here incorporating the estimated S°_{298}.

The measurements of Fuger and Brown (1973) on the enthalpies of solution of $UI_4(c)$ (-69.29±0.3 kcal/mol) and $UCl_4(c)$ (-54.46±0.23

kcal/mol) in 1M HCl, i.e., $HCl(54.4H_2O)$ lead to:

$$UI_4(c) + 4HCl(aq) \rightarrow UCl_4(c) + 4HI(aq);\ \Delta H_1 = -14.83 \pm 0.38 \text{ kcal/mol} \quad (1)$$

With the assumption that the differential $\Delta\overline{H}f$ HI(aq) in HCl is the same as in an HI solution = 13.265 kcal/mol and using $\Delta\overline{H}f$ HCl = -39.284, $\Delta Hf° = -124.55 \pm 0.07$ kcal/mol.

In addition, from their measurements in 6M HCl (i.e. $HCl(8.13H_2O)$) $(8.13H_2O)$ of $UI_4(c) = -57.41 \pm 0.07$ and $UBr_4(c) = -49.17 \pm 0.20$, there is:

$$UI_4(c) + 4HBr(aq) \rightarrow UBr_4(c) + 4HI(aq);\ \Delta H_2 = -8.24 \pm 0.21 \quad (2)$$

With the same assumption, i.e., that the differentials, $\Delta\overline{H}f$'s of HBr = -26.103 and HI = -11.202 in HCl are equivalent to the differentials in their own respective solutions, $\Delta Hf° = -123.51 \pm 0.7$ kcal/mol.

The average $\Delta Hf° = -124.0 \pm 0.7$ kcal/mol is accepted.

The calculated $\Delta Sf° = -4.52 \pm 2.0$ cal/mol·K and the $\Delta Hf° = -124.0 \pm 0.7$ results in $\Delta Gf° = -122.7 \pm 0.9$ kcal/mol.

$UI_4(g)$

The vapor pressure of $UI_4(c)$ has been measured by Thompson and Schelberg (as given by Katz and Rabinowitch (1951)); 573-683 K; effusion method and that of $UI_4(l)$ by Gregory (1946); 823-923 K; boiling point measurements against a known pressure of $I_2(g)$ to prevent decomposition of UI_4. These have been reviewed by Rand and Kubaschewski (1963); however, the calculated values obtained for ΔH_{fusion}(16.9 kcal/mol) and ΔS_{fusion}(21.6 cal/mol·K) at the melting point, 779±3 K, (Gregory (1946)) are unreasonable.

Popov et al.'s (1959a) C_p measurements on UI_4 (c) and (l) indicate a total ΔH = 9.2 kcal/mol and ΔS = 12.1 cal/mol·K for the phase changes (ΔH_{trans} = 3.53±0.1 kcal/mol at ~ 723 K, ΔH_{fusion} = 5.64±0.2 at the melting point) which are reasonable although possibly low. This indicates that either one or both sets of vapor pressure measurements are in error.

If the $UI_4(c)$ measurements are correct, S° $UI_4(g) \approx 125$ cal/mol·K at 298 K. If the $UI_4(l)$ measurements are correct, then Gregory's (1946) measurements can be described (with ΔC_p = -15 cal/mol·K) by:

$$UI_4(l) \rightarrow UI_4(g) \qquad (1)$$

$$\Delta G_1 = 47{,}770 - 150.67T + 34.54T \log T \text{ cal/mol}; \quad (792\text{-}1000 \text{ K})$$

and at 900 K:

$$\Delta H_1 = 34.3 \text{ kcal/mol}$$
$$\Delta G_1 = 4.00 \text{ kcal/mol}$$
$$\Delta S_1 = 33.7 \text{ cal/mol·K}$$

Using $\Delta(S-S_{298})_{900}$ from the ThI_4 system = -21.3 cal/mol·K (Wagman et al. (1977)), results in $\Delta S°_1$ at 298 K = 55 cal/mol·K and S° $UI_4(g)$ = 118 cal/mol·K, which appears more reasonable, in a correlation of the S°'s for the Th-U halides, than 125 cal/mol·K. For the vaporization, the expression for ΔG_1 is accepted. The extrapolated boiling point is 1020 K with ΔS_{vap} = 31.9 cal/mol·K. For the sublimation,

$$UI_4(c) \rightarrow UI_4(g), \qquad (2)$$

with ΔH_2 = 34.3 kcal/mol at 900 K and the comparable $\Delta(H-H_{298})_{900}$ = -16.00 kcal/mol from the ThI_4 system (Wagman et al. (1977)) one obtains at 298 K:

$$\Delta H°_2 = 50.3 \text{ kcal/mol}$$
$$\Delta S°_2 = 55.0 \text{ cal/mol·K}$$
$$\Delta G°_2 = 33.9 \text{ kcal/mol}$$

The tabulated values are obtained from these values.

An approximate equation then for this process is:

$$\Delta G_2 = 52{,}400 - 101.9T + 16.1T \log T \text{ cal/mol; } (550\text{-}700 \text{ K})$$

3.110 U-I-Cl-Br Compounds

$UCl_3I(c)$ and $UBr_3I(c)$

MacWood (1958), reporting on the measurements of Barkelew, cites the reactions of $UCl_3I(c)$ ($\Delta H = -28.0$ kcal/mol), $UCl_3(c)$ ($\Delta H = -35.7$ kcal/mol) and $UBr_3I(c)$ ($\Delta H = -36.7$ kcal/mol) with a solvent of 12N HCl saturated with $I_2(c)$ at 273 K. Since the resultant final solutions are considered to contain the U(IV) species, a summation results in:

$$UCl_3(c) + 1/2I_2(c) \rightarrow UCl_3I(c);\ \Delta H_1^* = -7.7 \text{ kcal/mol} \qquad (1)$$

The calculated $\Delta Hf° = -214.7 \pm 2.0$ kcal/mol.

$$UCl_3I(c) + 3HBr(aq) \rightarrow UBr_3I(c) + 3HCl(aq);\ \Delta H_2^* = +8.7 \text{ kcal/mol} \qquad (2)$$

With $\Delta\overline{H}f$ HCl(aq) = -32.7 kcal/mol and $\Delta\overline{H}f$ HBr(aq) = -22.0 kcal/mol which pertain to the particular solutions used by Barkelew and incorporates the experimental components measured by Barkelew, $\Delta Hf°$ $UBr_3I(c) = -173.9 \pm 2.0$ kcal/mol.

These values are accepted.

MacWood (1958) cites the measurements of Davidson et al. (1945) for the I_2 pressure (effusion method) over $UCl_3I(c)$ and $UBr_3I(c)$.

$$UCl_3I(c) \rightarrow UCl_3(c) + 1/2I_2(g) \qquad (3)$$

(472 - 575 K)

$$UBr_3I(c) \rightarrow UBr_3(c) + 1/2I_2(g) \qquad (4)$$

(551 - 655 K)

With the accepted $\Delta Hf°$ $UCl_3I(c)$, $\Delta H_3 = 15.16$ kcal/mol at 298 K and with a $\Delta C_p = -2$ cal/mol·K the equilibrium K's can be fit to:

$$\Delta G°_3 = 15{,}760 + 4.61\ T\log T - 31.5T \quad \text{cal/mol}$$

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[*] The ΔC_p for this is negligible.

This results in $\Delta G°_3$ = 9.8 kcal/mol and $\Delta S°_3$ = 18 cal/mol·K, from which the tabulated values for $\Delta Gf°$ and S° for $UCl_3I(c)$ are obtained.

Similarly $\Delta H°_4$ = 14.0 kcal/mol at 298 K. Here, however, a similar treatment of the K's results in a $\Delta S°_4 \approx 13$ cal/mol which is too low (i.e., the calculated S° $UBr_3I(c)$ = 64 cal/mol·K, too high a value); no improvement is made by adjusting the ΔC_p. In the absence of more information on this system, no recommendation is made for S° or $\Delta Gf°$ for $UBr_3I(c)$.

3.200 U-X Compounds with N

3.201 U-NH_4-F-O Compounds

$(NH_4)_3UO_2F_5$(c) and $NH_4[(UO_2)_2F_5]$(c)

Mukhametshina et al. (1974b) from a series of reactions in 2M HCl reported:

$$3NH_4F(c) + UO_2F_2(c) \rightarrow (NH_4)_3UO_2F_5(c);\ \Delta H_1 = -17.74\pm0.27\ \text{kcal/mol} \qquad (1)$$

which, using ΔHf° NH_4F(c)* = -111.7±0.2 kcal/mol, results in ΔHf° = -748.0±0.7 kcal/mol.

Similarly, Suponitskii et al. (1974) obtained:

$$NH_4(c) + 2UO_2F_2(c) \rightarrow NH_4(UO_2)_2F_5(c);\ \Delta H_2 = -12.99\pm0.50\ \text{kcal/mol} \qquad (2)$$

which results in ΔHf° = -915.1±0.8 kcal/mol.

The above values are accepted, in preference to those which can be derived from the decomposition pressure measurements of Sudarikov et al. (1970) on $(NH_4)_3UO_2F_5$(c), the ammonium dioxopentafluorouranate (VI) and the intermediate compound, $NH_4[(UO_2)_2F_5]$(c), the ammonium tetraoxopentafluordiuranate (VI).

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* . This is compatible with the CODATA selections. It is derived from the following:

(1) Higgins and Westrum (1961) measured the ΔH's soln NH_3(g) = -42.53±0.06 and NH_4F(c) = -14.31±0.03 kcal/mol in HF(l) so that

$$NH_3(g) + HF(l) \rightarrow NH_4F(c);\ \Delta H = -28.22\pm0.07\ \text{kcal/mol}$$

From Johnson et al. (1973) ΔHf° HF(l) = -72.55±0.06 kcal/mol, so that ΔHf° NH_4F(c) = -111.75±0.06;

(2) Armstrong et al. (1959) obtained:

$$NF_3(g) + 4NH_3(g) \rightarrow 3NH_4F(c) + N_2(g);\ \Delta H = -259.5\pm1.0\ \text{kcal/mol}$$

which using ΔHf° NF_3(g) = -31.60±0.1 kcal/mol (evaluated from sources in JANAF (1971)) results in ΔHf° NH_4F(c) = -111.67±0.4 kcal/mol.

The decomposition pressures are described by:

$$(NH_4)_3UO_2F_5(c) \rightarrow 0.5NH_4[(UO_2)_2F_5](c) + 2.5NH_3(g) + 2.5HF(g) \qquad (3)$$

$$\log P(\text{atm}) = 8.01 - 4.468\text{x}10^3/T \ (516\text{-}538 \text{ K})$$

$$\Delta G°_3 = 102.3 - 176.4\text{x}10^{-3}T \text{ kcal/mol U}$$

and

$$0.5NH_4[(UO_2)_2F_5](c) \rightarrow UO_2F_2(c) + 0.5NH_3(g) + 0.5HF(g) \qquad (4)$$

$$\log P(\text{atm}) = 6.927 - 4.878\text{x}10^3/T \ (647\text{-}703 \text{ K})$$

$$\Delta G°_4 = 22.3 - 30.3\text{x}10^{-3}T \text{ kcal/mol U}$$

Assuming the ΔC_p's for these decompositions are negligible and with the use of:

$$NH_4F(c) \rightarrow NH_3(g) + HF(g); \ \Delta H_5 = 35.40 \pm 0.20 \text{ kcal/mol} \qquad (5)$$

we obtain $\Delta H_1 = -\Delta H_3 - \Delta H_4 + 3\Delta H_5 = -18.4 \pm 6.0$ kcal/mol and $\Delta H_2 = -2\Delta H_4 + \Delta H_5 = -9.2 \pm 2.0$ kcal/mol.

Since the temperature range for these decomposition measurements is short, these results are not unreasonable. If the measured pressures are used with the preferred values for $\Delta Hf°$, the following relations result for the decompositions:

$$\Delta G_3 = 99{,}700 - 171.6T \text{ cal/mol}$$

$$\log P(\text{atm}) = 7.80 - 4.36\text{x}10^3/T$$

and

$$\Delta G_4 = 24{,}200 - 33.1T \text{ cal/mol}$$

$$\log P(\text{atm}) = 7.53 - 5.29\text{x}10^3/T$$

Approximate S° values of 86±5 and 90±5 cal/mol·K are calculated for $NH_4(UO_2)_2F_5(c)$ and $(NH_4)_3UO_2F_5(c)$, respectively.

$NH_4[(UO_2)_2F_5]\cdot 3H_2O(c)$ and $NH_4[(UO_2)_2F_5]\cdot 4H_2O(c)$

Tsvetkov et al (1971) measured the vapor pressure of the hexagonal tetrahydrate $NH_4[(UO_2)_2F_5]\cdot 4H_2O(c)$ and the orthorhombic trihydrate. They reported the following:

$$NH_4[(UO_2)_2F_5]\cdot 3H_2O(c) \rightarrow NH_4[(UO_2)_2F_5](c) + 3H_2O(g) \qquad (1)$$

$$\log P(\text{atm}) = 7.02\pm0.54 - 2{,}684\pm181/T \quad (303\text{-}372\ K)$$

and

$$NH_4[(UO_2)_2F_5]\cdot 4H_2O(c) \rightarrow NH_4[(UO_2)_2F_5]\cdot 3H_2O(c) + H_2O(g) \qquad (2)$$

$$\log P(\text{atm}) = 6.84\pm1.10 - 2{,}533\pm350/T \quad (303\text{-}338\ K)$$

These vapor pressure equations lead to the following:

	(1)	(2)
$\Delta H°$ =	12.3±0.8 kcal/mol $H_2O(g)$	11.6±1.6 kcal/mol $H_2O(g)$
$\Delta S°$ =	32.2±2.5 cal/mol $H_2O(g)$	31.3±4.5 cal/mol $H_2O(g)$
$\Delta G°$ =	2.7±1.0 kcal/mol $H_2O(g)$	2.3±1.6 kcal/mol $H_2O(g)$

In both cases $\Delta S°$ appears low. Normally a ΔS of 35-36 cal/mol $H_2O(g)$ would be expected. The $\Delta G°$'s have been accepted and have been used with the estimated $\Delta S°$ = 35±2 cal/mol $H_2O(g)$ to obtain $\Delta H°_1$ = 13.1±1.3 kcal/mol $H_2O(g)$ and $\Delta H°_2$ = 12.7±1.7 kcal/mol $H_2O(g)$.

These lead to the following approximate formation properties:

	trihydrate	tetrahydrate
$\Delta Hf°$	-1128	-1198 kcal/mol
ΔGf	-1015	-1072 kcal/mol
S	116±10	126±10 cal/mol·K

3.300 U-X Compounds and the Alkali Metals, M (M=Li, Na, K, Rb, or Cs)

3.301 U-F-M Compounds

MUF_6(c) (M = Na(β), K, Rb, and Cs)

Kudryashov et al. (1978a) measured the enthalpy of oxidation of the alkali metal uranium (V) hexafluorides, MUF_6(c) in aqueous solutions containing 0.8% H_2O_2 (i.e. $H_2O_2(250H_2O)$), 1.72% K_2CO_3 + 2.5% KOH (i.e. $KOH(120H_2O)$), and the reaction of UCl_4(c) in the same media (ΔH_2 = -175.4±0.3 kcal/mol).

$$MUF_6(c) + [3K_2CO_3 + 4KOH + 1/2H_2O_2](aq) \rightarrow [K_4UO_2(CO_3)_3 + 6KF + MOH + 2H_2O](aq);\ \Delta H_1 \quad (1)$$

$$UCl_4(c) + [3K_2CO_3 + 2KOH + H_2O_2](aq) \rightarrow [K_4UO_2(CO_3)_3 + 4KCl + 2H_2O](aq);\ \Delta H_2 \quad (2)$$

With their measured ΔH_{soln} KCl(c) (3.96±0.01 kcal/mol) and their ΔH's of solution MF(c) tabulated below, the following composite is obtained from which the tabulated ΔHf°'s are derived:

$$UCl_4(c) + 0.5H_2O_2(aq)^* + MF(c) + 5KF(c) \rightarrow MUF_6(c) + KOH(aq)^* + 4KCl(c);\ \Delta H_3 \quad (3)$$

MUF_6	ΔH_1 kcal	ΔH_{soln} MF(c) kcal/mol	ΔH_3 kcal
Na(β)	-117.0 ± 0.3	+0.05 ± 0.01	-94.59 ± 0.6
K	-114.1 ± 0.1	-4.08 ± 0.01	-101.62 ± 0.5
Rb	-111.8 ± 0.8	-6.34 ± 0.10	-106.18 ± 0.7
Cs	-109.6 ± 0.5	-8.77 ± 0.06	-110.81 ± 0.7

---

[*] The values used for ΔHf $KOH(120H_2O)$ = -115.077 kcal/mol and ΔHf $H_2O_2(250H_2O)$ = -45.69 kcal/mol are adjusted from Wagman et al. (1973, etc.) to be compatible with CODATA selections.

$NaUF_7$(c) and Na_2UF_8(c)

Katz (1964, 1966) measured the vapor pressure of UF_6(g) (gas evolution) over $UF_6 \cdot NaF$(c) and $UF_6 \cdot 2NaF$(c) and reported (1966):

$$2(UF_6 \cdot NaF(c) \rightarrow UF_6(g) + UF_6 \cdot 2NaF(c) \qquad (1)$$

$$\log P(\text{atm}) = 8.18 - 3.4\text{x}10^3/T \quad (340 - 400\ K)$$

$$\Delta G_1 = 15{,}900 - 37.4T \text{ cal/mol}$$

and (1964):

$$UF_6 \cdot 2NaF(c) \rightarrow UF_6(g) + 2NaF(c) \qquad (2)$$

$$\log P(\text{atm}) = 6.37 - 4.18\text{x}10^3/T \quad (500 - 573\ K)$$

$$\Delta G_2 = 19{,}100 - 29.1T \text{ cal/mol}$$

Cathers et al. (1958) reported the existence of $UF_6 \cdot 3NaF$(c) and measured the UF_6(g) vapor pressure over it by the transpiration method (626 to 873 K) as did Groves (1961).

However, Katz (1964) found no evidence for $UF_6 \cdot 3NaF$ and indicated that the measurements by Cather et al. (1958) were on $UF_6 \cdot 2NaF$(c). Malm et al. (1966) prepared $UF_6 \circ NaF$ and measured the UF_6 vapor pressure at 373 K ~ 35 mm, in fair agreement with Katz's measurements.

Tentatively the measurements of Katz for the systems specified are accepted and, with an estimated $\Delta C_p \approx -11$ cal/mol·K, $\Delta H_1 = 16.6$ and $\Delta H_2 = 21.5$ kcal/mol UF_6 from which the tabulated $\Delta Hf°$'s are obtained.

3.302 U-F-O-M Compounds

$M_3UO_2F_5(c)$ (M = Na, K, Rb, Cs)

Mukhametshina et al. (1974b) measured the ΔH's of solution of $MF(c)$, $UO_2F_2(c)$, and $M_3UO_2F_5(c)$ in 2M HCl. These measurements lead to the following:

$$3MF(c) + UO_2F_2(c) \rightarrow M_3UO_2F_5(c);\ \Delta H$$

M	ΔH kcal/mol $M_3UO_2F_5(c)$
Na	-7.58±0.27
K	-28.82±0.26
Rb	-32.95±0.66
Cs	-34.86±1.38

The selected values are based on these relationships.

$M(UO_2)_2F_5(c)$ (M = Na, K, Rb, Cs)

Suponitskii et al. (1974) from a series of ΔH's of solution of these compounds in 2M HCl obtained the following enthalpies for formation from $MF(c)$ and $UO_2F_2(c)$:

$$MF(c) + 2UO_2F_2(c) \rightarrow M(UO_2)_2F_5(c);\ \Delta H$$

M	ΔH kcal/mol $M(UO_2)_2F_5$
Na	-8.15±0.22
K	-18.64±0.24
Rb	-23.28±0.62
Cs	-27.32±0.70

The selected values are based on these results.

$M_5(UO_2)_2F_9(c)$ (M = K, Rb, Cs)

Mukhametshina et al (1974a), from a series of ΔH's of solution of these compounds in HCl reported, for the enthalpies of reaction of alkali metal fluorides with $UO_2F_2(c)$:

$$5MF(c) + 2UO_2F_2(c) \rightarrow M_5(UO_2)_2F_9(c); \Delta H$$

M	ΔH kcal/mol $M_5(UO_2)_2F_9(c)$
K	-52.76±1.2
Rb	-63.38±1.5
Cs	-68.16±2.25

The selected values are based on these tabulated numbers.

3.303 U-Cl-M Compounds

$MUCl_5(c)$ (M = K, Rb, Cs)

The following summarizes the ΔH's for the formation of $MUCl_5(c)$ from the components salts ($MCl(c)$ and $UCl_4(c)$) from measurements in 2% HCl, 0.5% $FeCl_3$ solutions; they are accepted.

$$MCl(c) + UCl_4(c) \rightarrow MUCl_5(c);\ \Delta H$$

	ΔH kcal/mol $MUCl_5$		
	K	Rb	Cs
Martynova et al. (1968)	-5.5±0.5		
Vdovenko et al. (1974)	-6.8±0.6	-10.5±0.8	-13.6±0.8

$M_2UCl_6(c)$ (M = Li, Na, NaK/2, K, Rb, Cs)

The following summarizes the ΔH's for the formation of $M_2UCl_6(c)$ from the component salts ($MCl(c)$ and UCl_4)):

$$2MCl(c) + UCl_4(c) \rightarrow M_2UCl_6(c);\ \Delta H$$

	ΔH kcal/mol M_2UCl_6					
	M = Li	Na	NaK/2	K	Rb	Cs
Martynova et al. (1968) [measurements in 2%HCl, 0.5% $FeCl_3$]		-1.5±0.6	-6.0±0.6	-9.8±0.6		
Vdovenko et al. (1974) [measurements in 2%HCl, 0.5% $FeCl_3$]	1.1±0.6	-1.7±0.7		-9.4±0.5	-16.1±0.6	-24.1±0.8
Fuger and Brown (1971) [measurements in 1M HCl]						-26.7±0.3
[measurements in 6M HCl]						-25.8±0.4

The selected values were obtained from the average ΔH.

$Rb_4UCl_8(c)$

The results of Vdovenko et al. (1974), from measurements in 2% HCl, 0.5% $FeCl_3$ solutions lead to:

$4RbCl(c) + UCl_4(c) \rightarrow Rb_4UCl_8(c)$; $\Delta H = -16.5 \pm 0.8$ kcal/mol $Rb_4UCl_8(c)$

This is the basis for the selected value.

$CsU_2Cl_9(c)$

The results of Vdovenko et al. (1974) from measurements in 2% HCl, 0.5%$FeCl_3$ solutions lead to:

$CsCl(c) + 2UCl_4(c) \rightarrow CsU_2Cl_9(c)$; $\Delta H = -13.1 \pm 1.4$ kcal/mol CsU_2Cl_9

This is the basis for the selected value.

$MUCl_6$(c) (M = Na(α and β), K, Rb, and Cs)

Kudryashov et al. (1978b) measured the enthalpy of oxidation of the alkali metal uranium (V) hexachlorides, $MUCl_6$, in 2% HCl, 0.5% $FeCl_3$ aqueous solutions:

$$MUCl_6(c) + [FeCl_3 + 2H_2O](aq) \rightarrow [UO_2Cl_2 + FeCl_2 + 4HCl + MCl](aq);\ \Delta H_1 \quad (1)$$

With their measured ΔH's of solution for $FeCl_3$(c) (-32.55±0.1 kcal/mol), $FeCl_2$(c) (-18.7±0.2 kcal/mol) and MCl(c) cited below and the results of Vdovenko et al. (1973) for the reaction of UCl_4(c) in the same media:

$$UCl_4(c) + [2FeCl_3 + 2H_2O](aq) \rightarrow [UO_2Cl_2 + 2FeCl_2 + 4HCl](aq); \quad (2)$$
$$\Delta H_2 = -45.3 \pm 0.1 \text{ kcal/mol}$$

the following summary reaction is obtained:

$$UCl_4(c) + FeCl_3(c) + MCl(c) \rightarrow FeCl_2(c) + MUCl_6(c);\ \Delta H_3 \quad (3)$$

$MUCl_6$(c)	ΔH_1	ΔH MCl(c) kcal/mol	ΔH_3
Na(α)	-61.6 ± 0.5	1.19 ± 0.02	3.6 ± 0.6
Na(β)	-61.4 ± 0.4	1.19 ± 0.02	3.4 ± 0.5
K	-51.7 ± 0.3	4.37 ± 0.02	-3.0 ± 0.5
Rb	-45.0 ± 0.2	4.08 ± 0.02	-10.1 ± 0.4
Cs	-41.9 ± 0.2	4.01 ± 0.02	-13.2 ± 0.4

The ΔHf°'s are obtained from ΔH_3.

3.304 U-Br-M Compounds

$M_2UBr_6(c)$ (M = Rb, Cs)

The results of Vdovenko et al. (1973), from the ΔH's of solution of the components in 0.5% $FeCl_3$, 2% HCl lead to:

$$2RbBr(c) + UBr_4(c) \rightarrow Rb_2UBr_6(c); \Delta H_1 = -14.86 \pm 0.15 \text{ kcal/mol } Rb_2UBr_6 \quad (1)$$

$$2CsBr(c) + UBr_4(c) \rightarrow Cs_2UBr_6(c); \Delta H_2 = -23.02 \pm 0.15 \text{ kcal/mol } Cs_2UBr_6 \quad (2)$$

These are accepted.

III. Tables of Values for $\Delta Hf°$, $\Delta Gf°$, $S°$, $C_p°$, and $H-H_0$ at 298.15 K and $\Delta Hf°$ at 0 K for the Uranium-Halogen Containing Compounds

The values are consistent with the CODATA key values for thermodynamics and the IAEA series, "The Chemical Thermodynamics of Actinide Elements and Compounds".

Included in the tabular summary are values for the non-halogen containing uranium compounds which were necessary for this evaluation.

The compounds covered are listed in the standard order of arrangement except for those containing the alkali metals which are arranged by compound class of the uranium-halogen compound with the alkali metal.

See Section I - 2.5 and Section I - 2.4 for the conventions used for the Table headings, the chemical formulae and physical states.

Note Added in Proof

There are significant new results that necessitate modification of the values selected for certain uranium fluorides. These adjusted values are included in the tabulation.

The calorimetric measurements of Cordfunke, (private communication, June 1980) result in:

ΔHf° $UF_3(c) = -360.6 \pm 1.0$ kcal/mol

ΔHf° $UF_4(c) = -459.1 \pm 1.0$ kcal/mol

These values are based on two different measurement paths. The paths are:

1. The direct fluorinations of $UF_3(c)$ and $UF_4(c)$ to $UF_6(c)$.
2. Solution measurements of $UF_3(c)$, $UF_4(c)$, and $UO_3(c,\gamma)$ and and $U_3O_8(c)$ in a H_2SO_4, $Ce(SO_4)_2$, H_3BO_3 aqueous medium.

The above values are accepted and result in the adjustment of the values for $UF(g)$, $UF_2(g)$, $UF_3(g)$, $UF_4(g)$ and $UF_4 \cdot 2.5H_2O(c)$ as well, since they are all dependent upon the ΔHf° $UF_4(c)$.

The values for $UF_{4.25}(c)$, $UF_{4.5}(c)$, $UF_5(,\alpha)$ and $UF_5(c,\beta)$ and $UF_5(g)$ are also dependent upon $UF_4(c)$; however, there are indications from solution calorimetric measurements in progress by O'Hare (private communication, June 1980) on $UF_5(c,\alpha)$ and $UF_5(c,\beta)$ that their ΔHf°'s should be more positive, rather than more negative as required by the above cited ΔHf° $UF_4(c)$ and the Agron (1958) data.

Until the situation regarding $UF_5(c,\alpha)$ and (c,β) is clarified, the values for these two compounds and for $UF_{4.25}$, $UF_{4.5}(c)$, and $UF_5(g)$ are maintained as in Section II, but with larger uncertainties.

In addition, Westrum (private communication, June 1980) measured the low temperature heat capacity for UF_3(c) resulting in S° = 29.50±0.10 and C_p° = 22.73±0.10 cal/mol·K which replace the estimated S° = 30.0±1.0 and C_p° = 23.4±1.0 cal/mol·K.

NBS THERMO PROP OF U-HALOGEN CONTG CMPDS ON CODATA BASE IN KCAL/MOL & CAL/MOL.K

	FORMULA WT	DHO	DH298	DG298	H298 - H0	S298	CP298
1 U(CS')	238.0290	0	0	0	1.521 +-0.005	12.00 +-0.05	6.612 +-[0.010]
2 U(G)	238.0290	126.97 +-2.00	127.0 +-2.0	116.4 +-2.0	1.554 +-[0.010]	47.725 +-0.020	5.663 +-[0.010]
3 U+3(A)	238.0290		-116.9 +-0.9	-114.9 +-1.1		-41.8 +-2.0	
4 U+4(A)	238.0290		-141.3 +-0.8	-126.9 +-0.5		-99. +-3.	
5 UO2(C)	270.0278	-258.40 +-0.20	-259.3 +-0.2	-246.6 +-0.2	2.696 +-[0.010]	18.41 +-0.05	15.20 +-[0.10]
6 UO2+2(A)	270.0278		-243.5 +-0.4	-227.7 +-0.5		-23.2 +-0.9	
7 UO3(C:GA') ORTHORHOMBIC ASSUMED	286.0272	-291.35 +-0.30	-292.5 +-0.3	-273.9 +-0.3	3.486 +-[0.010]	22.97 +-0.05	19.52 +-[0.10]
8 U3O8(C:AL') ORTHORHOMBIC	842.0822	-851.75 +-0.60	-854.4 +-0.6	-805.4 +-0.6	10.216 +-[0.010]	67.54 +-0.15	56.97 +-[0.10]
9 UF(G)	257.0274	-5.7 +-5.0	-6. +-5.	-13. +-5.	2.28 +-[0.10]	60. +-4.	9.04 +-[0.10]
10 UF2(G)	276.0258	-132.6 +-7.0	-133. +-7.	-136. +-7.	3.28 +-[0.10]	71. +-4.	16.0 +-[1.0]
11 UF3(C)	295.0242	-360.31 +-1.00	-360.6 +-1.0	-344.2 +-1.0	4.392 +-0.010	29.50 +-0.10	22.73 +-0.10
12 UF3(G)	295.0242	-251.4 +-5.0	-252. +-5.	-250. +-5.	4.04 +-[0.10]	79. +-4.	17.8 +-[1.0]
13 UF4(C) MONOCLINIC	314.0226	-458.75 +-1.00	-459.1 +-1.0	-437.4 +-1.0	5.390 +-[0.010]	36.25 +-0.05	27.73 +-[0.10]
14 UF4(G)	314.0226	-382.72 +-1.20	-383.7 +-1.2	-377.5 +-1.7	4.76 +-[0.10]	88. +-4.	21.8 +-[1.0]
15 UF4:2.5H2O(C) ORTHORHOMBIC	359.0611		-640.1 +-1.2	-584.0 +-1.3		60.0 +-2.0	
16 UF4.25(C)	318.7722		-466. +-4.	-443. +-4.		37.7 +-1.5	
17 UF4.5(C)	323.5218		-477. +-4.	-453. +-4.		39.4 +-1.5	
18 UF5(C:AL')	333.0210		-494. +-4.	-469. +-4.		47.7 +-2.0	
19 UF5(C:BE')	333.0210		-496. +-4.	-469. +-4.		42.9 +-1.5	
20 UF5(G)	333.0210	-460.8 +-5.0	-462. +-5.	-450. +-5.	5.6 +-[1.0]	93. +-5.	26.2 +-[1.0]
21 UF6(C)	352.0194	-524.80 +-0.40	-525.1 +-0.4	-494.4 +-0.4	7.545 +-[0.010]	54.4 +-0.3	39.86 +-[0.10]
22 UF6(G)	352.0194	-511.79 +-0.40	-513.25 +-0.40	-493.26 +-0.40	6.384 +-[0.010]	90.3 +-0.5	30.98 +-[0.10]

	FORMULA WT	DH0	DH298	DG298	H298 - H0	S298	CP298
23 UOF2(C)	292.0252		-359.6 +-1.5	-342.8 +-1.5		28.5 +-1.0	
24 UOF2:H2O(C)	310.0405		-430.7 +-0.8	-400.3 +-1.1		38.5 +-2.0	
25 UO2F2(C)	308.0246	-394.21 +-0.30	-395.2 +-0.3	-372.2 +-0.3	4.710 +-[0.010]	32.40 +-0.10	24.67 +-[0.10]
26 UO2F2(A)	308.0246		-403.8 +-0.5	-362.4 +-0.6		-29.5 +-1.0	
27 UO2F2(570H2O)	308.0246		-402.32 +-0.35				
28 UO2F2(4HF+1600H2O)	308.0246		-403.05 +-0.40				
29 UO2F2(47HF+12970H2O)	308.0246		-403.40 +-0.40				
30 UO2F2(25HF+3110H2O)	308.0246		-403.55 +-0.40				
31 UO2F2(17HF+380.8H2O)	308.0246		-403.78 +-0.40				
32 UO2F2:3H2O(C)	362.0708		-605.8 +-1.0				
33 UOF(OH)(C)	290.0342		-341. +-3.				
34 UOF(OH):0.5H2O(C)	299.0419		-376.7 +-1.5				
35 UO2(OH)F:H2O(C)	324.0493		-452.8 +-2.0	-411.5 +-2.0		43. +-3.	
36 UO2(OH)F:2H2O(C)	342.0646		-524. +-3.	-468.7 +-2.0		53. +-4.	
37 UCL'3(C)	344.3880	-207.51 +-1.00	-207.0 +-1.0	-190.9 +-1.0	5.318 +-[0.010]	38.0 +-0.3	24.5 +-[1.0]
38 UCL'4(C)	379.8413	-243.87 +-0.60	-243.5 +-0.6	-222.2 +-0.6	6.28 +-[0.10]	47.1 +-0.3	29.16 +-[0.10]
39 UCL'4(G)	379.8413		-193.4 +-1.0	-187.9 +-1.1		100. +-3.	
40 UCL'4(A)	379.8413		-301.0 +-0.8	-252.4 +-0.6		-45. +-3.	
41 UCL'4(HCL'+7.93H2O:AQ')	379.8413		-282.7 +-0.8				
42 UCL'4(HCL'+9.25H2O:AQ')	379.8413		-284.8 +-0.8				
43 UCL'4(HCL'+11.10H2O:AQ')	379.8413		-287.2 +-0.8				
44 UCL'4(HCL'+13.88H2O:AQ')	379.8413		-289.7 +-0.8				

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NBS THERMC PROP OF U-HALOGEN CONTG CMPDS ON CODATA BASE IN KCAL/MOL & CAL/MOL.K
                                         FORMULA WT   DH0        DH298      DG298      H298 - H0    S298       CP298

  45 UCL'4(HCL'+18.50H2O;AU')            379.8410                -292.3
                                                                   +-0.8
  46 UCL'4(HCL'+27.75H2O;AU')            379.8410                -295.0
                                                                   +-0.8
  47 UCL'4(HCL'+55.5H2O;AU')             379.8410                -298.1
                                                                   +-0.8

  48 UCL'4(HCL'O4+27.75H2O;AU')          379.8410                -297.1
                                                                   +-0.8
  49 UCL'4(HCL'O4+55.5H2O;AU')           379.8410                -298.6
                                                                   +-0.8
  50 UCL'4(HCL'O4+111H2O;AU')            379.8410                -299.2
                                                                   +-1.0

  51 UCL'4(HCL'O4+555H2O;AU')            379.8410                -296.2
                                                                   +-1.0
  52 UCL'4(HCL'O4+00H2O;AU')             379.8410                -288.5
                                                                   +-2.0
  53 UCL'5(C)                            415.2940                -253.      -227.                   58.
                                                                   +-3.       +-3.                   +-2.

  54 UCL'6(C)                            450.7470   -261.8       -261.      -230.      8.90         68.3       42.0
                                                      +-3.0        +-3.       +-3.     +-[0.10]      +-0.4      +-[1.0]
  55 UCL'6(G)                            450.7470                -242.2     -221.8                 103.
                                                                   +-3.4      +-3.6                  +-4.
  56 UOCL'2(C)                           324.9344   -254.83      -255.0     -238.1     4.586        33.06      22.72
                                                      +-0.60       +-0.6      +-0.6    +-[0.010]     +-0.05     +-[0.10]

  57 UO2CL'2(C)                          340.9338   -296.57      -297.2     -273.9     5.157        35.98      25.78
                                                      +-0.30       +-0.3      +-0.3    +-0.008       +-0.05     +-0.04
  58 UO2CL'2(G)                          340.9338                -234.
                                                                   +-3.
  59 UO2CL'2(A)                          340.9338                -323.4     -290.5                  3.9
                                                                   +-0.4      +-0.5                  +-1.0

  60 UO2CL'2:H2O(C)                      358.9492                -372.8     -335.8                 46.
                                                                   +-0.5      +-0.8                  +-2.
  61 UO2CL'2:3H2O(C)                     394.9800                -517.4     -453.0                 65.
                                                                   +-0.4      +-0.8                  +-2.
  62 UO2CL'2(0.901HCL'+50H2O)            340.9338                -321.0
                                                                   +-0.6

  63 UO2CL'2(1.802HCL'+50H2O)            340.9338                -319.3
                                                                   +-0.6
  64 UO2CL'2(2.703HCL'+50H2O)            340.9338                -317.6
                                                                   +-0.6
  65 UO2CL'2(3.604HCL'+50H2O)            340.9338                -316.0
                                                                   +-0.6

  66 UO2CL'2(4.505HCL'+50H2O)            340.9338                -314.5
                                                                   +-0.6
```

NBS THERMC PROP OF U-HALOGEN CONTG CMPDS IN CODATA BASE IN KCAL/MOL & CAL/MOL.K

	FORMULA WT	DH0	DH298	DG298	H298 - H0	S298	CP298
67 UO2CL'2(5.405HCL'+50H2O)	340.9338		-313.1 +-0.6				
68 UO2CL'2(HCL'+7.93H2O:AQ')	340.9338		-312.3 +-0.4				
69 UO2CL'2(HCL'+9.25H2O:AQ')	340.9338		-313.6 +-0.4				
70 UO2CL'2(HCL'+11.10H2O:AQ')	340.9338		-315.0 +-0.4				
71 UO2CL'2(HCL'+13.88H2O:AQ')	340.9338		-316.5 +-0.4				
72 UO2CL'2(HCL'+18.50H2O:AQ')	340.9338		-318.1 +-0.4				
73 UO2CL'2(HCL'+27.75H2O:AQ')	340.9338		-319.8 +-0.4				
74 UO2CL'2(HCL'+55.5H2O:AQ')	340.9338		-321.5 +-0.4				
75 UO2CL'2(HCL'+111.0H2O:AQ')	340.9338		-322.4 +-0.4				
76 UO2CL'2(HCL'+50000H2O:AQ')	340.9338		-323.2 +-0.4				
77 UOCL'3(C)	360.3874		-278. +-5.	-256. +-5.		41. +-2.	
78 (UO2)2CL'3(C)	646.4165		-574.7 +-0.4				
79 UO2(OH)CL':2H2O(C)	358.5190		-480.5 +-0.4				
80 UF3CL'(C)	330.4772				5.64 +-[0.10]	38.9 +-1.0	28.4 +-[1.0]
81 UF2CL'2(C)	346.9318				5.85 +-[0.10]	41.6 +-2.0	28.6 +-[1.0]
82 UFCL'3(C)	363.3864				6.07 +-[0.10]	44.3 +-1.0	28.9 +-[1.0]
83 UBR'3(C)	477.7410		-167.0 +-1.0	-160.9 +-1.2		46. +-2.	26.0 +-0.5
84 UBR'3(G)	477.7410		-93.6 +-1.5	-102.9 +-1.7		98. +-3.	
85 UBR'4(C)	557.6453		-191.7 +-0.6	-183.4 +-0.9		57. +-2.	30.6 +-[1.0]
86 UBR'4(G)	557.6453		-144.1 +-2.0	-151.5 +-2.2		110. +-3.	
87 UBR'5(C)	637.5493		-193.7 +-2.0	-183.9 +-2.2		70. +-3.	38.4 +-[1.0]
88 UOBR'2(C)	413.8364	-229.27 +-2.00	-232.7 +-2.0	-222.2 +-2.0	4.989 +-[0.010]	37.66 +-0.06	23.42 +-[0.10]

NBS THERMO PROP OF U-HALOGEN CONTG CMPDS ON CODATA BASE IN KCAL/MOL & CAL/MOL.K

	FORMULA WT	DH0	DH298	DG298	H298 - H0	S298	CP298
89 UO2BR'2(C)	429.8350		-271.84 +-0.32	-264.9 +-0.4		40.5 +-1.0	
90 UO2BR'2:H2O(C)	447.8512		-347.97 +-0.34	-317.2 +-0.7		50. +-2.	
91 UO2BR'2:3H2O(C)	483.8824		-491.88 +-0.36	-433.6 +-1.4		69. +-4.	
92 UOBR'3(C)	493.7404		-228. +-5.	-215. +-5.		49. +-3.	
93 UO2(OH)BR':2H2O(C)	402.9703		-468.03 +-0.30				
94 UCL'2BR'(C)	388.8390		-194.1 +-2.0	-181.7 +-2.5		42. +-4.	
95 UCL'3BR'(C)	424.2923		-231.2 +-2.0	-213.6 +-2.2		51. +-3.	
96 UCL'BR'2(C)	433.2903		-179.4 +-2.0	-170.8 +-2.5		46. +-4.	
97 UCL'2BR'2(C)	468.7430		-217.0 +-2.0	-203.4 +-2.5		56. +-4.	
98 UCL'BR'3(C)	513.1940		-203.7 +-2.0	-192.9 +-2.5		57. +-4.	
99 UI3(C)	618.7425		-111.7 +-1.0	-111.5 +-1.2		53. +-2.	26.8 +-(1.0)
100 UI4(C)	745.6470		-124.0 +-0.7	-122.7 +-0.9		63. +-2.	32.1 +-(1.0)
101 UI4(G)	745.6470		-73.7 +-2.2	-88.8 +-2.4		118. +-3.	
102 UCL'3I(C)	471.2925		-214.7 +-2.0	-198.4 +-2.0		51. +-2.	
103 UBR'3I(C)	604.6455		-173.9 +-2.0				
104 (NH4)3UO2F5(C)	419.1353		-748.0 +-0.7	-644.3 +-2.0		90. +-5.	
105 NH4[(UO2)2F5](C)	653.0863		-915.1 +-0.8	-842.8 +-2.0		86. +-5.	
106 NH4[(UO2)2F5]:3H2O(C)	707.1323		-1128. +-5.	-1015. +-3.		116. +-10.	
107 NH4[(UO2)2F5]:4H2O(C)	725.1477		-1198. +-6.	-1072. +-4.		126. +-10.	
108 NA'UF6(C;UE!)	375.0092		-647.3 +-1.3				
109 KUF6(C)	391.1211		-652.7 +-1.2				
110 RB'UF6(C)	437.4872		-655.0 +-1.4				

NBS THERMO PROP OF U-HALOGEN CONTG CMPDS ON CODATA BASE IN KCAL/MOL & CAL/MOL.K

	FORMULA WT	DH0	DH298	DG298	H298 - H0	S298	CP298
111 CS'UF6(C)	484.9240		-658.7 +-1.3				
112 NA'UF7(C)	394.0076		-670. +-2.	-631.5 +-2.0		65. +-3.	
113 NA'2UF8(C)	435.9953		-810. +-3.	-764.7 +-2.0		79. +-4.	
114 NA'3UO2F5(C)	433.9892		-816.2 +-0.6				
115 K3UO2F5(C)	482.3258		-832.6 +-0.6				
116 RB'3UO2F5(C)	621.4232		-829.9 +-0.8				
117 CS'3UO2F5(C)	763.7363		-829.1 +-1.6				
118 NA'(UO2)2F5(C)	658.0371		-936.4 +-0.7				
119 K(UO2)2F5(C)	674.1496		-945.2 +-0.7				
120 RB'(UO2)2F5(C)	720.5154		-947.6 +-0.9				
121 CS'(UO2)2F5(C)	767.9531		-950.7 +-0.9				
122 K5(UO2)2F9(C)	906.5512		-1524.1 +-1.5				
123 RB'5(UO2)2F9(C)	1138.3802		-1523.4 +-1.8				
124 CS'5(UO2)2F9(C)	1375.5687		-1523.7 +-2.5				
125 KUCL'5(C)	454.3960		-354.0 +-0.8				
126 RB'UCL'5(C)	500.7618		-358.0 +-1.0				
127 CS'UCL'5(C)	548.1995		-362.9 +-1.0				
128 LI'2UCL'6(C)	464.6290		-437.7 +-0.9				
129 NA'2UCL'6(C)	496.7266		-441.7 +-0.5				
130 K2UCL'6(C)	528.9510		-461.7 +-0.5				
131 NA'KUCL'6(C)	512.8383		-452.2 +-0.9				
132 RB'2UCL'6(C)	621.6825		-467.5 +-0.9				

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NBS THERMO PROP OF U-HALOGEN CONTG CMPDS ON CODATA BASE IN KCAL/MOL & CAL/MOL.K
                                          FORMULA WT    DH0      DH298      DG298      H298 - H0     S298        CP298

 133 CS'2UCL'6(C)                         716.5583                -480.7
                                                                    +-1.0
 134 RB'4UCL'8(C)                         863.5242                -675.9
                                                                    +-1.0
 135 CS'U2CL'9(C)                         928.0405                -605.9
                                                                    +-2.0

 136 NA'UCL'6(C;AL')                      473.7368                -351.9
                                                                    +-0.8
 137 NA'UCL'6(C;BE')                      473.7368                -352.1
                                                                    +-0.7
 138 KUCL'6(C)                            489.8493                -364.6
                                                                    +-0.7

 139 RB'UCL'6(C)                          536.2148                -371.3
                                                                    +-0.6
 140 CS'UCL'6(C)                          583.6525                -376.3
                                                                    +-0.6
 141 RB'2UBR'6(C)                         888.3886                -395.1
                                                                    +-0.8

 142 CS'2UBR'6(C)                         983.2640                -408.7
                                                                    +-0.8
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V. Appendix: Thermal Functions for Some Uranium-Halogen Containing Compounds

T K	Cp cal/mol·K	UF(g) $H-H_0$ cal/mol	S° cal/mol·K	$-(G-H_{298})/T$ cal/mol·K
100	7.01	696	51.83	67.65
200	7.99	1439	56.94	61.14
298.15	9.04	2278	60.34	60.34
300	9.05	2294	60.39	60.34
500	10.11	4229	65.31	61.41
1000	10.76	9492	72.58	65.37
1500	10.93	14919	76.98	68.55
2000	11.01	20405	80.14	71.07
		UF_2(g)		
100	9.48	858	58.48	82.69
200	11.93	1908	65.66	72.52
298.15	16.00	3279	71.18	71.18
300	16.06	3309	71.28	71.18
500	18.33	6887	80.37	73.16
1000	16.83	15552	92.45	80.18
1500	17.35	24060	99.34	85.49
2000	18.10	32937	104.44	89.62
		UF_3(g)		
100	12.61	1009	63.11	93.46
200	15.41	2411	72.72	80.89
298.15	17.76	4044	79.33	79.33
300	17.79	4077	79.44	79.33
500	20.27	7929	89.23	81.46
1000	21.49	18457	103.78	89.36
1500	22.05	29348	112.60	95.74
2000	22.58	40504	119.02	100.78

$UF_3(c)$

T K	Cp cal/mol·K	$H-H_{298}$ cal/mol	S° cal/mol·K	$-(G-H_{298})/T$ cal/mol·K
298.15	23.38	0	30	30
300	23.39	43.	30.145	30.
400	24.12	2419.	36.974	30.927
500	24.85	4867.	42.434	32.700
600	25.58	7389.	47.029	34.715
700	26.31	9983.	51.027	36.766
800	27.04	12651.	54.588	38.775
900	27.77	15391.	57.815	40.714
1000	28.5	18205.	60.779	42.574

$UF_4(g)$

T K	Cp cal/mol·K	$H-H_0$ cal/mol	S°[a] cal/mol·K	$-(G-H_{298})/T$[a] cal/mol·K
298.15	21.815	4764	80.176 + 8.2	80.176 + 8.2
300	21.852	4804	80.311 + 8.2	80.177 + 8.2
400	23.304	7070	86.818 + 8.2	81.054 + 8.2
500	24.114	9434	92.113 + 8.2	82.753 + 8.2
600	24.598	11882	96.556 + 8.2	84.693 + 8.2
700	24.906	14358	100.373 + 8.2	86.667 + 8.2
800	25.114	16860	103.713 + 8.2	88.593 + 8.2
900	25.259	19379	106.680 + 8.2	90.441 + 8.2
1000	25.365	21910	109.347 + 8.2	92.201 + 8.2
1100	25.444	24451	111.768 + 8.2	93.871 + 8.2
1200	25.505	26998	113.985 + 8.2	95.456 + 8.2
1300	25.553	29551	116.028 + 8.2	96.961 + 8.2
1400	25.591	32109	117.923 + 8.2	98.392 + 8.2
1500	25.622	34669	119.690 + 8.2	99.753 + 8.2

$UF_5(g)$

298.15	26.222	5597	90.055 + 3.0	90.055 + 3.0
300	26.270	5646	90.218 + 3.0	90.056 + 3.0
400	28.222	8380	98.069 + 3.0	91.113 + 3.0
500	29.342	11263	104.498 + 3.0	93.167 + 3.0
600	30.022	14233	109.913 + 3.0	95.519 + 3.0
700	30.460	17259	114.576 + 3.0	97.916 + 3.0
800	30.756	20321	118.664 + 3.0	100.259 + 3.0
900	30.965	23407	122.298 + 3.0	102.510 + 3.0
1000	31.117	26512	125.570 + 3.0	104.655 + 3.0
1100	31.231	29629	128.541 + 3.0	106.693 + 3.0
1200	31.319	32757	131.262 + 3.0	108.629 + 3.0
1300	31.388	35892	133.772 + 3.0	110.468 + 3.0
1400	31.443	39034	136.100 + 3.0	112.217 + 3.0
1500	31.487	42181	138.271 + 3.0	113.882 + 3.0

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[a] S and $-(G-H_{298})/T$ values for $UF_4(g)$ are increased by 8.2 cal/mol·K to be consistent with equilibrium data; similarly 3.0 cal/mol·K are added for $UF_5(g)$.

$UF_6(g)$

T K	Cp cal/mol·K	$H-H_0$ cal/mol	S° cal/mol·K	$-(G-H_{298})/T$ cal/mol·K
298.15	30.985	6384.4	90.233	90.233
300	31.044	6441.7	90.425	90.233
400	33.436	9677.4	99.717	91.484
500	34.797	13095.1	107.337	93.916
600	35.620	16619.1	113.760	96.702
700	36.149	20209.4	119.293	99.543
800	36.506	23843.2	124.145	102.322
900	36.757	27507.0	128.460	104.991
1000	36.941	31192.4	132.343	107.535
1100	37.078	34893.7	135.871	109.953
1200	37.184	38607.0	139.102	112.249
1300	37.267	42329.8	142.081	114.431
1400	37.333	46059.9	144.846	116.506
1500	37.387	49796.0	147.423	118.482
1600	37.431	53537.0	149.838	120.367
1700	37.468	57282.0	152.108	122.168
1800	37.499	61030.3	154.251	123.892
1900	37.525	64781.5	156.279	125.543
2000	37.547	68535.1	158.204	127.129

$UBr_3(c)$

T K	Cp cal/mol·K	$H-H_{298}$ cal/mol	S° cal/mol·K	$-(G-H_{298})/T$ cal/mol·K
298.15	25.98	0.	46.00	46.00
300	25.99	48.	46.16	46.00
400	26.62	2679.	53.72	47.03
500	27.25	5372.	59.73	48.99
600	27.88	8129.	64.76	51.21
700	28.51	10948.	69.10	53.46
800	29.14	13831.	72.95	55.66
900	29.77	16776.	76.42	57.78
1000	30.40	19785.	79.59	59.80

$UBr_4(c,l)$

T K	Cp cal/mol·K	$H-H_{298}$ cal/mol	S° cal/mol·K	$-(G-H_{298})/T$ cal/mol·K
298.15	30.62	0.	57.00	57.00
300	30.63	57.	57.19	57.00
400	31.34	3155.	66.10	58.21
500	32.05	6325.	73.17	60.52
600	32.76	9565.	79.07	63.13
700	33.47	12877.	84.18	65.78
792	34.12	15986.	88.35	68.17
792	41.00	27586.	103.00	68.17
800	41.00	27914.	103.41	68.52
900	41.00	32014.	108.24	72.67
1000	41.00	36114.	112.56	76.44
1040	41.00	37754.	114.17	77.86

$UI_3(c)$

T K	Cp cal/mol·K	$H-H_{298}$ cal/mol	S° cal/mol·K	$-(G-H_{298})/T$ cal/mol·K
298.15	26.83	0.	53.00	53.00
300	26.84	50.	53.17	53.00
400	27.42	2763.	60.97	54.06
500	28.00	5534.	67.15	56.08
600	28.58	8363.	72.30	58.37
700	29.16	11250.	76.75	60.68
800	29.74	14195.	80.68	62.94

$UI_4(c,l)$

T K	Cp cal/mol·K	$H-H_{298}$ cal/mol	S° cal/mol·K	$-(G-H_{298})/T$ cal/mol·K
298.15	30.20	0.	63.00	63.00
300	30.27	56.	63.19	63.00
400	32.80	3226.	72.29	64.22
500	34.10	6577.	79.76	66.61
600	34.92	10031.	86.06	69.34
700	35.50	13553.	91.48	72.12
779	35.88	16373.	95.30	74.28
779	39.60	25573.	107.11	74.28
800	39.60	26404.	108.16	75.16
870	39.60	29176.	111.49	77.95

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16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)

A detailed analysis and evaluation of the thermochemistry of the uranium-halogen containing compounds is presented, with a tabular summary of the thermochemical properties given. The properties given, where data are available, are in the enthalpy of formation, ΔHf°, Gibbs energy of formation, ΔGf°, entropy, S°, heat capacity, C_p°, all at temperature 298.15 K, and the enthalpy of formation at 0 K, ΔHf°_0, and the enthalpy difference, $H^\circ(298)-H^\circ(0)$. The values are consistent with the CODATA Key Values for thermodynamics.

The analysis of the uranium-halogen containing compounds includes some vapor pressure equations and C_p equations. Some thermal functions which are not readily available in the accessible open literature are presented in the Appendix for compounds that required their use.

The tabular summary of ΔHf°, ΔGf°, includes the values for those uranium compounds which were necessary for this evaluation.

17. KEY WORDS (six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)

Data evaluation; enthalpy; entropy; Gibbs energy; heat capacity; thermochemical tables; uranium-halogen containing compounds

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