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THE THERMOCHEMICAL PROPERTIES OF THE SYSTEM URANIUM–OXYGEN–CHLORINE

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ABSTRACT

The thermochemical properties (i.e. standard enthalpies and entropies, heat capacities, enthalpies and entropies of fusion and evaporation) of the various compounds in the system uranium–oxygen–chlorine are consistently assessed. Where experimental evidence is lacking, educated estimates have been invoked. The results may serve for a tentative calculation of the phase relationships in the ternary system, e.g. in terms of oxygen pressure and chlorine pressure. An isotherm at 750 K is presented as an example.

INTRODUCTION

The following compilation is an attempt to evaluate comprehensively the relevant thermochemical data pertinent to the ternary system U–O–Cl, and to present them in a manner useful for identifying the conditions necessary for the stability of the various phases in this system. **

SOLID PHASES

Table 1 lists the compounds that have been considered. It also lists their standard entropies. About half of these had to be estimated, but the authors are confident that they are correct within the stated limits of accuracy. The experimental values have been derived, as is usual, from low-temperature heat capacities. Not all the original publications are available to the present authors, but Katz and Rabinowitch [1] have reported the earlier results

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** The following notation is used throughout the paper: ⟨ ⟩ solid state; [ ] solid solution (subscript denotes solvent); { } liquid state; ( ) gaseous state. 1 cal = 4.184 J.

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TABLE 1

Standard entropies (E = estimated)

Compound	S^0_{298}(e.u.)	Ref.
$\langle U\rangle\alpha$	12.00 ±0.05	[28]
$\langle UOCl\rangle$	24.5 ±2.0	E
$\langle UOCl_2\rangle$	33.06 ±0.1	[29]
$\langle U_2O_2Cl_5\rangle$	78.0 ±2.0	E
$\langle UOCl_3\rangle$	40.6 ±2.0	E
$\langle UO_2Cl\rangle$	26.9 ±2.0	E
$\langle (UO_2)_2Cl_3\rangle$	66.0 ±2.0	E
$\langle UO_2Cl_2\rangle$	36.0 ±0.1	[30]
(UO_2Cl_2)	89	E
$\langle UCl_3\rangle$	38.0 ±0.2	[1]
(UCl_3)	85.3	E[2]
$\langle UCl_4\rangle$	47.14 ±0.2	[1]
(UCl_4)	93.2 ±1.5	[3]
(U_2Cl_8)	149.1 ±6.0	E
$\langle UCl_5\rangle$	59.0 ±2.5	E
(U_2Cl_{10})	169 ±2.5	E
$\langle UCl_6\rangle$	68.3 ±0.4	[1]
(UCl_6)	103.4	[2]
$\langle$"UO_2"$\rangle$	18.41 ±0.05	[28]
$\langle U_4O_9\rangle$	79.86 ±0.15	[31]
$\langle U_3O_8\rangle$	67.53 ±0.12	[28]
(Cl_2)	53.290±0.010	[28]

obtained by U.S. authors. Other surveys [2–4] have also been perused.

The other set of data required for the actual evaluation are the heat capacities. Here again, estimates had to be invoked where experimental results are not available. Table 2 summarizes the heat capacities in the form of three-term expressions. Unless some unexplored transformations occur in these compounds, these data should also be reasonable. For the modes of estimating unknown heat capacities and entropies, reference may be made to the monograph of Kubaschewski and Alcock [5].

The individual and the selected values of the standard enthalpies of formation are listed in Table 3. Most of these have been obtained by aqueous solution calorimetry [6–12] or by direct reaction in a calorimeter [13]. Calorimetric enthalpies of reaction are always preferred to values that might be derived from equilibrium measurements. There is, however, one exception; the experimental enthalpy of formation of $\langle$"$UOCl_3$"$\rangle$ [7] indicated too high a stability in the final evaluation of the phase diagram, contradicting our experience. The selected value is an estimation, about 3.5 kcal less negative than the experimental one which was obtained from a material of which the phase purity is still in doubt.

This mode of selection left but one gap, namely the enthalpy of formation

TABLE 2

Heat capacities (E = estimated)

$C_p = a + b \times 10^{-3}T + c \times 10^{5}T^{-2}$

Compound	*a*	*b*	*c*	Temp. range (K)	Ref.
$\langle UOCl \rangle$	18.12	3.43	−1.98	298–900	E
$\langle UOCl_2 \rangle$	23.65	3.5	−1.77	298–850	[19]
$\langle U_2O_2Cl_5 \rangle$	56.0	8.5	−5.42	298–700	[19]
$\langle UOCl_3 \rangle$	29.3	5.0	−2.85	298–900	E
$\langle UO_2Cl \rangle$	21.54	5.32	−1.85	298–1000	E
$\langle (UO_2)_2Cl_3 \rangle$	54.0	8.5	−7.0	298–900	E
$\langle UO_2Cl_2 \rangle$	27.54	4.35	−2.73	298–851	[27]
$\{UO_2Cl_2\}$	38.2			851–b.p.	E
(UO_2Cl_2)	24.48	0.857	−3.16	298–1500	E
$\langle UCl_3 \rangle$	20.8	7.75	+1.05	298–1114	[32]
$\{UCl_3\}$	31.0			1114–1900	E
(UCl_3)	21.75		−2.3	298–1500	E
$\langle UCl_4 \rangle$	27.2	8.57	−0.79	298–863	[32], [33]
$\{UCl_4\}$	38.8			863–1100	[33]
(UCl_4)	27.0		−2.16	298–1500	E
(U_2Cl_8)	59.4		−4.75	298–800	E
$\langle UCl_5 \rangle$	33.47	8.47	−1.28	298–600	E
$\{UCl_5\}$	44.62			600–900	E
(UCl_5)	31.8		−3.2	298–2000	E
$\langle UCl_6 \rangle$	41.45	8.38	−1.77	298–452	E
$\{UCl_6\}$	51.14			452–800	E
(UCl_6)	37.77		−2.95	298–1200	E
$\langle \text{“}UO_2\text{”} \rangle$	19.2	1.62	−3.96	298–1500	[2]
$\langle U_4O_9 \rangle$	85.15	8.47	−15.87	298–900	[34]
$\langle U_3O_8 \rangle$	67.5	8.83	−11.94	298–900	[2]
$\langle U \rangle \alpha$	6.6	2.61	8.95	298–941	[2]
(Cl_2)	8.82	0.06	−0.68	298–3000	[5]

of $\langle \text{“}UO_2Cl\text{”} \rangle$. X-ray work at Petten has shown that UO_2Cl_2 dissociates via $(UO_2)_2Cl_3$ and UO_2Cl to UO_2 (see also ref. 8). With this knowledge, mass spectrometric results of Münstermann [14] can be evaluated leading finally to the standard enthalpy of formation of $\langle \text{“}UO_2Cl\text{”} \rangle$, namely $\Delta H^0_{f,298} = -279.9$ kcal mol^{-1}, which is slightly more negative than the additive value, -278 kcal mol^{-1}. However, in view of the uncertainties in these evaluations, a possible error of ± 2.0 kcal mol^{-1} is being assigned to the selected value, -279.5 kcal mol^{-1} (Table 3).

LIQUID STATE

With reference to the liquid phase values for the melting points, enthalpies and entropies of fusion are recorded in Table 4, where applicable. These are

TABLE 3

Standard enthalpies of formation of solid compounds

Compound	ΔH^0_{298} (kcal mol^{-1}) individual values	Ref./method		ΔH^0_{298} (kcal mol^{-1}) selected value
$\langle UOCl\rangle$	-199.3 ± 1.0	[6] [35]	soln. calorimetry	-199.3 ± 1.0
$\langle UOCl_2\rangle$	$-255.6\ \pm0.65$	[6]	soln. calorimetry	-255.6 ± 0.7
	$-260\ \ \pm2$	[2]	lit. assessment	
	-254.5	[1]	recalc. [3]	
$\langle U_2O_2Cl_5\rangle$	$-525.2\ \pm1.0$	[6]	soln. calorimetry	-525.2 ± 1.0
$\langle$"$UOCl_3$"$\rangle$	$-276.1\ \pm0.5$	[7]	re-evaluated	-272.5 ± 2.0
	-275	[7]	re-evaluated by [3]	
	> -273		from stability considerations	
$\langle$"UO_2Cl"$\rangle$	-279.9	[14]	see text	-279.5 ± 2.0
	-278		additively	
$\langle (UO_2)_2Cl_3\rangle$	$-574.7\ \pm0.4$	[8]	soln. calorimetry	-574.7 ± 0.5
	$-574.7\ \pm0.5$	[6]	soln. calorimetry	
$\langle UO_2Cl_2\rangle$	$-297.2\ \pm0.2$	[9]	soln. calorimetry	-297.2 ± 0.3
	-291.37 ± 0.81	[7]	recalc. [36]; see [9]	
	-296.7	[14]	mass spectrometry	
$\langle UCl_3\rangle$	$-206.0\ \pm0.8$	[12]	soln. calorimetry	-206.0 ± 0.8
	$-207.3\ \pm1.0$	[1]	recalc. [3]	
	$-213.5\ \pm2.0$	[2]	lit. survey	
$\langle UCl_4\rangle$	$-243.3\ \pm0.7$	[9]	soln. calorimetry	-243.5 ± 0.5
	$-243.6\ \pm0.6$	[10]	soln. calorimetry	
	$-251.4\ \pm1.0$	[11]	soln. calorimetry	
$\langle UCl_5\rangle$	$-248.9\ \pm0.5$	[12] [35]	soln. calorimetry	-248.9 ± 0.5
	$-247.7\ \pm0.5$	[13]	direct calorimetry	
	-253	[1]	soln. calorimetry recalc. [31]	
$\langle UCl_6\rangle$	$-255.3\ \pm0.5$	[12] [35]	soln. calorimetry	-255.3 ± 0.8
	-252	[13]	estimated [4]	
	$-261.7\ \pm2.0$	[3]	survey	
	-261	[31]		
$\langle U_4O_9\rangle$	-1078.0	[31]		-1078.0 ± 1.9
$\langle U_3O_8\rangle$	$-854.4\ \pm0.6$	[28]		-854.4 ± 0.6
$\langle UO_2\rangle$	-259.32 ± 0.20	[28]		-259.3 ± 0.2

taken from Medvedev's tables [3] or are estimated. In the case of $\langle UCl_4\rangle$, there seems to be a transformation just below the melting point, at 820 K to which [3] assign an Lt of 2.8 kcal mol^{-1}. This should be incorporated in any evaluation of the high-temperature data.

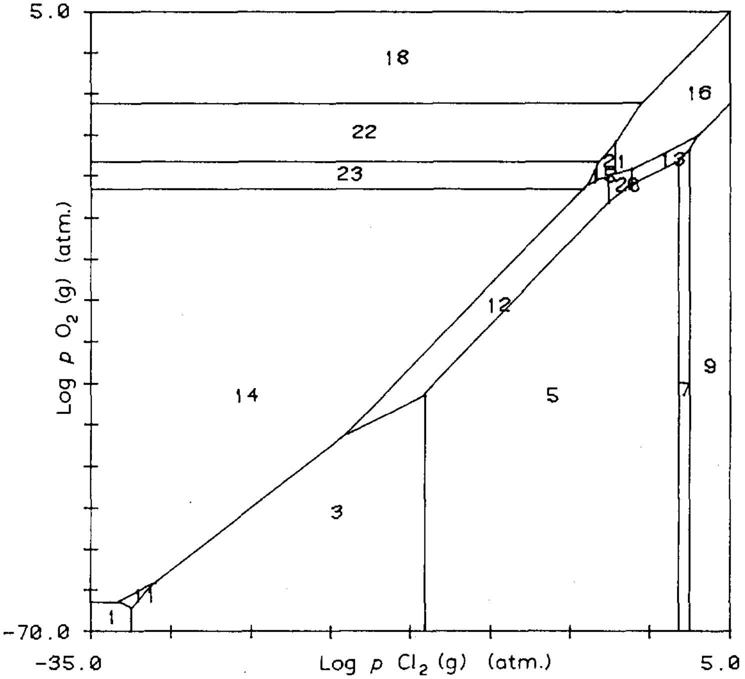

Fig. 1. Phase relationships, log p_{Cl_2}, vs. p_{O_2}, in the system U–O–Cl at one temperature (750 K). 1 = U, 3 = UCl_3, 5 = UCl_4, 7 = UCl_5, 9 = UCl_6, 11 = UOCl, 12 = $UOCl_2$, 13 = $UOCl_3$, 14 = UO_2, 15 = UO_2Cl, 16 = UO_2Cl_2, 18 = UO_3, 20 = $U_2O_2Cl_5$, 21 = $U_2O_4Cl_3$, 22 = U_3O_8, 23 = U_4O_9.

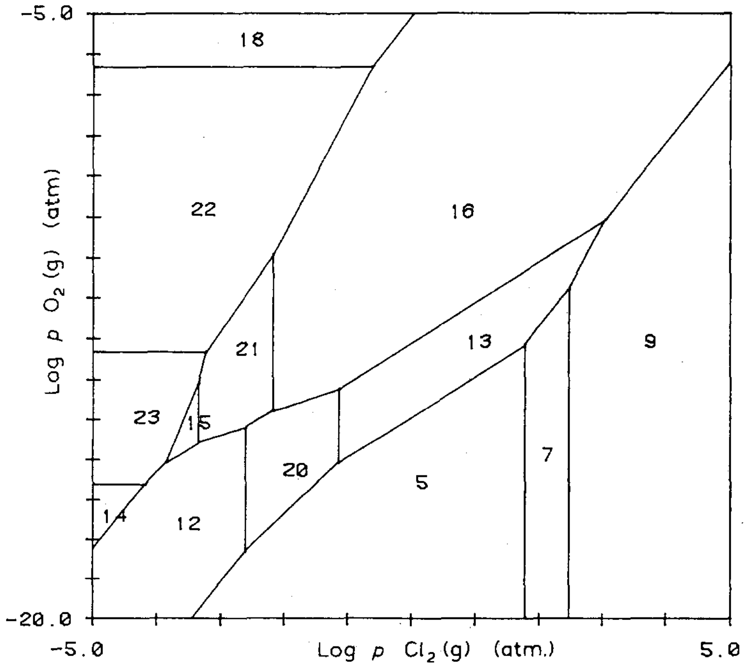

Fig. 2. Detail of the U–O–Cl phase diagram at 750 K; notation as in Fig. 1.

TABLE 4

Melting points, heats and entropies of fusion (E = estimated)

Compound	m.p. (K)	Ref.	L_f (kcal mol^{-1})	σ_f (e.u. mol^{-1})	Ref.
UO_2Cl_2	851	[3]	10.53	12.37	E
UCl_3	1114	[3]	11.1	9.97	E
UCl_4	863	[3]	11.94	13.84	[3]
UCl_5	600	E	8.5	14.17	E
UCl_6	451	[3]	5.0	11.1	E
"UO_2"	3123	[3]	18.0	5.76	[3]

GASEOUS STATE

For the assessment of the enthalpies of formation of the gaseous species, one must now turn to the results of equilibrium measurements to be combined with the accepted entropies and heat capacities. Starting with (UCl_3), reference may be made to Katz and Rabinowitch [1] who record the sublimation pressures of two independent U.S. sources, UCRL-2 and UCRL-3, which may be repeated here: "The upper limit of the volatility of UCl_3 is in the vicinity of 10^{-2} mm Hg at 820°C and 3.5 10^{-3} mm at 750°C (UCRL-2). An empirical equation has been devised which fits the vapour pressure data at 600–1000°C (UCRL-3):

$\log p_{\mathrm{mm}} = -12\,000\ T^{-1} + 10.0$"

Using $\Delta C_p = -4.5$, an average from the present tabulation, Table 2, and an entropy of sublimation estimated by Rand [2], $\Delta S^0_{298} = 47.3$, one finds for ΔH_{298}(sblm), in kcal

1023 K	1093 K	
70.5	72.6	UCRL-2
67.0	67.8	UCRL-3

of which $\Delta H^0_{298} = 70.5 \pm 2.8$ kcal mol^{-1} is selected. This leads, for the reaction $\langle UCl_3\rangle \rightarrow (UCl_3)$, to the Gibbs free energy

$$\Delta G^0_T = 72\,300 - 77.4T + 10.35\ T \log T \qquad (1)$$

(A mistake has obviously occurred in the corresponding evaluation by [2]). This, finally, leads to a standard enthalpy of formation of (UCl_3) of -136.0 ± 3.6 kcal mol^{-1}, Table 5. With $\Delta C_p = -9.5$ for $\{UCl_3\} = (UCl_3)$, one obtains for this equilibrium

$$\Delta G^0_T = 66\,730 - 107.4T + 21.85\ T \log T$$

corresponding to a hypothetical boiling point of ca. 1850 K and an entropy of evaporation at this temperature of $\sigma_e = 26.6$ e.u. which is reasonable.

TABLE 5

Standard enthalpies of formation of the gaseous species and normal boiling points

Compound	ΔH^0_{298} (kcal mol^{-1})	boiling point (K)	entropy of evaporation (cal K^{-1} mol^{-1})
UO_2Cl_2	-232.5	1475	32.6
UCl_3	-136.0 ± 4.0	ca. 1850	26.6
UCl_4	-198.0 ± 1.5	1057	25.4
U_2Cl_8	-425.1 ± 6.0		
U_2Cl_{10}	-468.5		
UCl_6	-236.1 ± 2.0		

Turning now to (UCl_4), one may revert to the equilibrium

$$2\langle UOCl_2\rangle = \langle UO_2\rangle + (UCl_4) \tag{2}$$

which has been studied in three independent investigations with the following results in terms of Gibbs free energy (kcal)

(i) $\Delta G^0 = 54\,200 - 46.47T$ (698–893 K) [15]

(ii) $\Delta G^0 = 53\,600 - 45.44T$ (698–823 K) [16]

(iii) $\Delta G^0 = 55\,630 - 48.29T$ (723–813 K) [17]

The agreement is excellent as may be seen from the comparison at 750 K

$\Delta G^0_{\mathrm{i}} = 19\,350$, $\Delta G^0_{\mathrm{ii}} = 19\,520$ and $\Delta G^0_{\mathrm{iii}} = 19\,410$ (cal)

Taking $\Delta G^0_{750} = 19\,450$ cal and simplifying ΔC_p to a constant value of -5.3 cal K^{-1}, one obtains

$$\Delta G^0_{(2)} = 45\,100 - 81.18T + 12.2\,T\log T \text{ (298–863 K)}$$

This leads to a standard enthalpy of formation of gaseous UCl_4 of $\Delta H^0_{298} = -199\,200$ cal mol^{-1}.

Prasad et al. [18] measured the vapour pressure of solid and liquid tetrachloride. For the equilibrium

$$\langle UCl_4\rangle \rightarrow (UCl_4) \tag{3}$$

they obtained: $\log p(\mathrm{atm}) = -10\,443\ T^{-1} + 10.46$, which converted into calories gives

$$\Delta G^0_{(3)} = 47\,783 - 47.86\,T \text{ (763–862 K)}$$

whereas [19] at ECN, employing a transportation method, found

$$\Delta G^0_{(3)} = 46\,680 - 45.89\,T \text{ (699–828 K)}$$

Using ΔC_p from Table 2 and the standard entropies of $\langle UCl_4\rangle$ and (UCl_4) from Table 1, ΔH^0_{298} for reaction (3) works out at 44795 (according to [18]) and 45600 (according to [19]) cal mol^{-1} to give for (UCl_4): $\Delta H^0_{f,298} = -198.5$ and -197.7 kcal mol^{-1}, respectively (Table 6). Earlier

TABLE 6

Enthalpy of sublimation and standard enthalpy of formation of gaseous tetrachloride (kcal mol^{-1})

Refs.	Method	ΔH_{298} (sblm.)	$\Delta H^0_{f,298}$
[15], [16], [17]	equil. decompos. pressure		-199.2
[2]	assessment	50.1	-193.2
[3]	assessment	47.6	-195.5
[18]	sblm. pressure	44.8	-198.5
[19]	sblm. pressure	45.6	-197.7
		selected value:	-198.0 ± 1.5

work on the sublimation of UCl_4 has been assessed by Rand [2] and by Glushko et al. [3]. The former obtained $\Delta H_{298} = 50100$, the latter 47600 cal mol^{-1}, leading to ΔH^0_{298} for (UCl_4) of -193.3 and -195.8 kcal mol^{-1}, respectively. The standard enthalpies of formation of (UCl_4) and their sources are listed in Table 6. The value $\Delta H^0_{298} = -(198.0 \pm 1.5)$ kcal mol^{-1} is selected.

For the evaporation

$$\{UCl_4\} \rightarrow (UCl_4) \tag{4}$$

one can now derive a Gibbs free energy equation with the accepted data, namely

$$\Delta G^0_{(4)} = 36\,730 + 26.64\, T \log T - 113.22\, T$$

corresponding to a normal boiling point of 887°C with $\sigma_e = 25.4$ cal K^{-1} mol^{-1}. Prasad et al. [18] measured equilibrium (4), and obtained

$$\Delta G^0_{(4)} = 34\,898 - 33.036\, T\ (868\text{–}1008\ \text{K})$$

They found for the boiling point the value 1057 K.

For the association

$$2(UCl_4) = (U_2Cl_8) \tag{5}$$

a Gibbs free energy of

$$\Delta G^0_{(5)} = -24\,400 + 32\, T$$

at approximately 745 K has been derived from two independent equilibrium measurements by Binnewies and Schäfer [20]. Entropy and heat capacity of (U_2Cl_8) are estimated according to Kubaschewski [21] who uses an empirical relationship between these quantities of single and double molecules (for values see Tables 1 and 2). The change of entropy at 745 K for equilibrium (5) is calculated to be $\Delta S^0_{(5)} = -32.5$ cal K^{-1} mol^{-1} which agrees well with Binnewies and Schäfer's estimated 32 cal K^{-1} mol^{-1}.

The enthalpy of reaction (5) at 298 K is then obtained: $\Delta H^0_{(5)} = -27.1$ kcal leading to a standard enthalpy of formation of (U_2Cl_8) of $\Delta H^0_{298} = -425.1 \pm 5$ kcal mol^{-1}. Glushko et al. [3] list $\Delta H^0_{298} = -415.3$ kcal mol^{-1} on the basis of [20]. The difference stems mainly from the enthalpy of formation accepted here and by [3], respectively.

$\langle UCl_5 \rangle$ is not very stable; some thermal decomposition into $\langle UCl_4 \rangle$ and (Cl_2) occurs already at 350 K at atmospheric pressure [22]. When $\langle UCl_4 \rangle$ and (Cl_2) are heated in a sealed tube at 450–650 K gaseous uranium pentachloride is readily formed solely as a dimer. Gruen and McBeth [23] obtained for the reaction

$$2\langle UCl_4 \rangle + Cl_2 \rightarrow (U_2Cl_{10}) \qquad (6)$$

$$\Delta G^0_{11} = 15\,130 - 15.4\,T\,(450\text{–}650\text{ K})$$

with $\Delta G^0_f / \langle UCl_4 \rangle = -241\,227 + 66.357T$ (500–863 K) one finds for (U_2Cl_{10})

$$\Delta G^0_f = -467\,324 + 117.314\,T$$

From this $\Delta S^0_{500} = -117.3$ e.u. and $S^0_{500} = 202.1$ e.u. Now, at 298 K, $S^0(U_2Cl_{10})$ is estimated to be 169 e.u., by comparison with W_2Cl_{10} [24], and $\Delta H^0_f = -468.5$ kcal mol^{-1}. From $\Delta G^0_f(U_2Cl_{10})$, and $\Delta G^0_f\langle UCl_5 \rangle = -248\,900 + 86.225\,T$, one finds for

$$2\langle UCl_5 \rangle \rightarrow (U_2Cl_{10}) \qquad (7)$$

$$\Delta G^0_{12} = 30\,476 - 55.136\,T\,(298\text{–}650\text{ K})$$

from which $\Delta H^0_{298}(\text{sblm}) = 15.24$ kcal mol^{-1}.

$\langle UCl_6 \rangle$ also has a low thermal stability with respect to $\langle UCl_4 \rangle$ at temperatures around 100°C; at room temperature, however, loss of chlorine is hardly detectable [22]. Earlier work on the sublimation of $\langle UCl_6 \rangle$ has been assessed by Rand and Kubaschewski [2]; they obtained for

$$\langle UCl_6 \rangle \rightarrow (UCl_6) \qquad (8)$$

$\Delta H^0_{298} = 18.8$ kcal mol^{-1}, leading to $\Delta H^0_{f,298}\ (UCl_6) = -236.1$ kcal mol^{-1}. Cordfunke and Prins [25] determined the equilibrium

$$\langle U_3O_8 \rangle + 3(Cl_2) \rightarrow 3(UO_2Cl_2) + O_2 \qquad (9)$$

for which they obtained

$$\Delta G^0_9 = 142\,300 - 67.8\,T\,(1133\text{–}1328\text{ K})$$

When we take for $\langle U_3O_8 \rangle$ [26]

$$\Delta G^0_f = 844\,800 + 149.9\,T\,(843\text{–}1445\text{ K})$$

We obtain for (UO_2Cl_2)

$$\Delta G^0_f = -234\,167 + 27.37\,T$$

with $S^0(UO_2Cl_2) = 89$ e.u., and C_p from Table 2, we derive from $\Delta G^0_{1200} = -201.30$ kcal mol^{-1} the value: $\Delta H^0_{1200} = -235.5$ kcal mol^{-1}, and from this

$\Delta H^0_{298} = -232.5$ kcal mol^{-1} (Table 5). For the sublimation

$$\langle UO_2Cl_2\rangle \rightarrow (UO_2Cl_2) \tag{10}$$

$\Delta H^0_{298} = 65.7$ kcal mol^{-1}. From the free energy of formation of solid UO_2Cl_2 [27]

$$\Delta G^0_f = -296\,341 + 75.765\,T\,(298\text{–}800\text{ K})$$

and $\Delta G^0_f(UO_2Cl_2)$, we derive

$$\Delta G^0_{10} = +62\,174 - 48.395\,T$$

Now, with the estimated enthalpy and entropy of fusion (Table 4), and $\Delta C_p = +8.5$ cal K^{-1} mol^{-1}, we find for

$$\langle UO_2Cl_2\rangle \rightarrow \{UO_2Cl_2\} \tag{11}$$

taking the melting point of UO_2Cl_2 to be 851 K

$$\Delta G^0_{11} = 3297 + 53.47\,T - 19.572\,T\log T$$

and for

$$\{UO_2Cl_2\} \rightarrow (UO_2Cl_2) \tag{12}$$

$$\Delta G^0_{12} = 58\,878 + 19.572\,T\log T - 101.865\,T$$

implying a normal boiling point of 1475 K, and $\sigma_e = 32.60$ e.u.

CONCLUSIONS

Thus, a complete set of thermochemical standard values for the solid, liquid, and gaseous compounds in the system uranium–oxygen–chlorine is presented. As an example of application, the phase relationships in terms of oxygen and chlorine pressures have tentatively been calculated. The isotherm at 750 K is presented in Figs. 1 and 2. One word of warning, however, although the thermochemical data in Tables 1–4 are consistent and believed to be fairly accurate (that is, of the order of ±1 kcal mol^{-1} for every individual compound), the phase boundaries plotted in Figs. 1 and 2 are so sensitive to small errors that there is still room for adjustments. For instance, the phase boundary $U_2O_2Cl_5/UOCl_3$ may move more to the right on the basis of new experimental work. In particular, further evidence for the stability of the compounds denoted ⟨"$UOCl_3$"⟩ and ⟨"UO_2Cl"⟩ is desirable. For this, independent experimental methods should be employed—mass spectrometric analysis, for example. However, the present assessment may serve as a reliable basis for further experimental work.

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