Th(IV) in acetone. Since the thorium system cannot be studied spectrophotometrically, other means had to be investigated. If it can be assumed that the thorium system behaves similarly to the uranium system and that it will be slightly displaced towards higher chloride ion concentrations, it would mean that a pure $ThCl_4$ solution would buffer on the [Cl^-] at a value of say 10^{-6} mol dm^{-3}. In such a case it can be shown that with the aid of least-squares treatment, a series of conductometric measurements on mixtures of UCl_4 and $ThCl_4$ with different Th:U ratios can yield the corresponding stepwise formation constants, K_4 and K_5, for the thorium system. This facilitates the construction of the combined distribution diagram as shown in Fig. 2. It follows that in mixtures of UCl_4 and $ThCl_4$ in acetone, where the $ThCl_4$ and UCl_4 are present in comparable amounts, the dominant ionic species are $ThCl_3^+$ and UCl_5^-. Ce(IV) and U(IV) cannot obviously be treated in the same way, but since Ce(IV) and Th(IV) can, such a study could indirectly lead to the sought after comparison of U(IV) and Ce(IV) as Lewis acids towards chloride.

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Thermodynamic Properties of Protoactinium Hydrides

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Pressure-composition isotherms of the protoactinium-hydrogen system were measured in the range of $10^{-5} \leqslant p \leqslant 100$ bar, $0 \leqslant H/Pa < 3$, $373 \leqslant K \leqslant 795$ for increasing and decreasing H/Pa-ratios. Large hysteresis was observed on hydriding and dehydriding.

The shape of the isotherms and X-ray structure analysis indicate the existence of different phases.

TABLE II. Partial molar free enthalpies and entropies obtained from dehydring isotherms.

H/Pa	550–740 K	
	$\overline{\Delta H}(H_2)$ kJ mol^{-1}	$\overline{\Delta S}(H_2)$ J K^{-1} mol^{-1}
0.1–1.3	94.2	121.7
1.6	106.0	147.3
2.0	106.2	149.7
2.9	22.0	65.5

The precision of the $\overline{\Delta H}(H_2)$ values is about ±4 kJ mol^{-1} and that of the $\overline{\Delta S}(H_2)$ values is about ±3 J K^{-1} mol^{-1} both on the 0.95 confidence level.

At $H/Pa < 0.1$ the metal is saturated with hydrogen (phase I). At $1.3 < H/Pa < 1.7$ and temperatures above 550 K a second phase (phase II) with an unique fcc-structure is observed. Another high temperature phase with β-UH_3-related structure exists in the range $2.0 \leqslant H/Pa \leqslant 3.0$. At temperatures below 500 K and $1.3 < H/Pa \leqslant 3.0$ an α-UH_3-related solid solution (phase IV) is identified. In the regions $0.1 < H/Pa < 1.3$ and $1.7 < H/Pa < 2.0$ two phases coexist [2].

For all compositions lnp-1/T-relationships are linear with a significant change in slope at about 550 K on hydriding. There are not enough data to confirm this difference in slope on dehydriding. Partial molar free enthalpies and entropies for selected compositions were calculated from the lnp-1/T-functions and are reported in Tables I and II. From these data the original hydrogen partial pressure may be obtained using the relationship

$$-RT \ln p\, H_2 = \overline{\Delta G}(H_2) = \overline{\Delta H}(H_2) - T\overline{\Delta S}(H_2)$$

Integral free energies of formation were calculated by integrating the lnp-H/Pa-isotherms. Graphs of integral free energies of formation *versus* temperature for constant compositions are linear in the regions above and below 580 K with a significant

TABLE I. Partial molar free enthalpies and entropies obtained from hydriding isotherms.

H/Pa	373–550 K		550–740 K	
	$\overline{\Delta H}(H_2)$ kJ mol^{-1}	$\overline{\Delta S}(H_2)$ J K^{-1} mol^{-1}	$\overline{\Delta H}(H_2)$ kJ mol^{-1}	$\overline{\Delta S}(H_2)$ J K^{-1} mol^{-1}
0.1–1.3	71.4	99.6	67.8	93.8
2.0	83.2	138.9	75.2	128.0
2.4	78.6	134.9	65.9	117.0
2.9	31.7	86.5	31.7	80.9

TABLE III. Integral free enthalpies and entropies of formation on hydriding.

H/Pa	373–550 K		550–740 K	
	ΔH_f° kJ mol^{-1}	ΔS_f° J K mol^{-1}	ΔH_f° KJ mol^{-1}	ΔS_f° J K mol^{-1}
1.3	–46.5 ± 0.7	–65.0 ± 1.3	–42.4 ± 2.0	–58.5 ± 2.8
1.7	–62.1 ± 0.7	–88.5 ± 1.5	–52.1 ± 2.3	–72.9 ± 3.4
2.0	–74.9 ± 0.8	–109.7 ± 1.5	–59.7 ± 3.6	–86.4 ± 5.0
2.2	–82.5 ± 0.7	–122.2 ± 1.5	–69.3 ± 2.7	–102.1 ± 4.0
2.4	–91.8 ± 0.9	–138.9 ± 1.9	–72.3 ± 3.9	–108.7 ± 5.5
3.0	–110.9 ± 1.1	–176.4 ± 2.2	–90.1 ± 5.3	–143.1 ± 7.9

TABLE IV. Integral free enthalpies and entropies of formation on dehydriding.

H/Pa	550–740 K	
	ΔH_f° KJ mol^{-1}	ΔS_f° J K^{-1} mol^{-1}
1.3	–62.2 ± 2.0	–80.3 ± 2.9
1.7	–83.6 ± 0.8	–109.5 ± 1.3
2.0	–99.6 ± 1.2	–131.9 ± 1.9
2.4	–117.0 ± 1.0	–157.3 ± 1.5
3.0	–128.6 ± 6.9	–180.8 ± 9.9

All precisions are on the 0.95 confidence level.

change in slope at this temperature. Here again not enough data were available to proof this difference in slope on dehydriding. Enthalpies and entropies of formation derived from those graphs for selected compositions are presented in Tables III and IV.

The magnitude of hysteresis, expressed as the ratio of hydriding and dehydriding pressure, reaches a maximum of 45 in the II + III diphasic region near H/Pa = 2 at a temperature of 573 K. It decreases regularly to 11 as the temperature increases to 741 K. Cycling experiments were conducted to identify the origin of hysteresis and the true equilibrium conditions. Samples partially dehydrided at constant temperature and rehydrided reached their original hydriding hydrogen pressure. On the other hand during heating and cooling at constant composition the pressure of samples prepared on hydriding reversibly followed the lnp-1/T-lines for hydriding for that composition. In the same way the pressures of samples prepared on dehydriding reversibly follow the lnp-1/T-lines for dehydriding. This means that hysteresis is a matter of changes in compositions and not in gas pressure. At constant composition both, hydriding and dehydriding samples are in perfect equilibrium with the gas phase. Since the gas pressures are different, something must be different in the hydrides. This is confirmed by X-ray diffraction data for phases II and III; products formed on hydriding have larger lattice parameters than those observed for the same composition on dehydriding. Also the higher partial free entropy values indicate, that products, obtained on dehydriding must be in a more ordered state. Probably hysteresis is due to difficulties in the rearrangement of protoactinium atoms after phase changes or the ordering of hydrogen atoms or both. Calorimetric measurements and neutron diffraction studies should give a better insight in this problem. Since free energies of formation are more negative on dehydring the hydriding products are considered as metastable. The enthalpy and entropy of formation of β-PaH_3 on dehydriding is in excellent agreement with the values for its β-UH_3 analog: ΔH_f° (UH_3, β, 29.8 K) = –127.0 KJ mol^{-1} and ΔS_f° (UH_3, β, 298 K) = –184.2 J K^{-1} mol^{-1} [1].

1 H. E. Flotow, J. M. Haschke and S. Yamauchi, 'Chem. Thermod. of Actinide Elements and Comp'., IAEA, Vienna, part 9 (in press) (1983).

2 J. M. Haschke, W. Bartscher, J. Rebizant and J. W. Ward, *separate contribution to this conference.*

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The Thermal Oxidation of Tetrachlorobis(N,N,N',N'-tetramethylurea)uranium(IV)

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The thermal oxidation of $UCl_4 \cdot 2tmu$ (tmu ≡ N,N,N',N'-tetramethylurea) was studied in an oxygen atmosphere by using thermogravimetry and differential scanning calorimetry.

Thermogravimetric results indicated that the oxidation reaction can be described as: