3 E. Brücher, R. Király and I. Nagypál, *J. Inorg. Nucl. Chem., 37,* 1009 (1975).
4 H. Otts, *Acta Chem. Scand., 27,* 2344 (1973).
5 G. Geier, U. Karlen and A. v. Zelewsky, *Helv. Chim. Acta, 52,* 1967 (1969).
6 N. A. Kostromina, T. V. Ternovaya and K. B. Yatsimirsky, *Zhur. Neorg. Khim., 14,* 154 (1969).
7 R. W. Southwood-Jones, *Doctoral Thesis,* University of Lausanne (1977).
8 B. M. Alsaadi, F. J. C. Rossotti and R. J. P. Williams, *J. Chem. Soc. Dalton,* 2153 (1980).
9 F. J. Millero, *Chem. Rev., 71,* 147 (1971).
10 G. Schwarzenbach and J. Heller, *Helv. Chim. Acta, 34,* 576 (1951).

A19

The Relative Acidity of Th(IV) and U(IV) towards Chloride in Acetone

H. E. ROHWER*

University of Port Elizabeth, South Africa

A measure of Lewis acidity of a metal ion towards an anion like chloride, for instance, could be given in terms of the chloride ion concentrations at which the various metal–chloride complexes dominate. Since some analogies and differences between U(IV), Th(IV) and Ce(IV) have been studied in our laboratories, it was of interest to see whether such a strategy could be used in acetone to confirm the notion that their relative Lewis acidity towards chloride in acetone follows the order Ce(IV) > U(IV) > Th(IV).

In order to see whether different complexes can be distinguished, the uranium system was studied spectrophotometrically by titrating UCl_4 with But_4NCl. The results could not be satisfactorily explained in terms of the species UCl_4, UCl_5^- and UCl_6^{2-} unless UCl_3^+ is considered as well. The corresponding stepwise formation constants and distribution of the species are given in Fig. 1.

From this it follows that when UCl_4 is dissolved in acetone the $[Cl^-]$ is buffered at about 10^{-8} mol dm^{-3} which is small compared to the concentration of the other species. ($\pm 0.5 \times 10^{-3}$ mol dm^{-3}). Similarly the species UCl_6^{2-} can be ignored provided the $[Cl^-]$ is not increased beyond say 10^{-6} mol dm^{-3}. This justifies the description of the system in terms of three species which are in equilibrium as depicted below by the autoionization-equilibrium and constant.

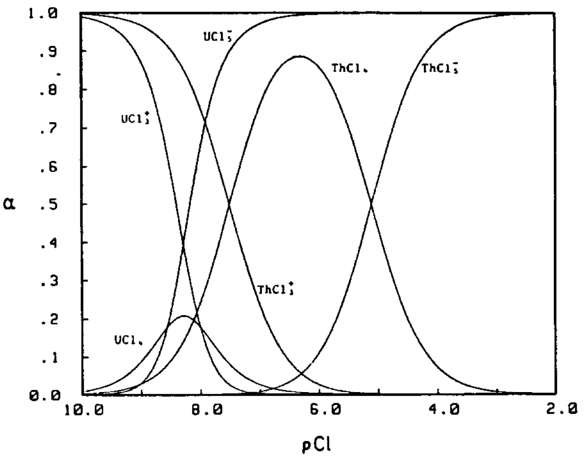

Fig. 1. Distribution diagram for the UCl_4–Chloride–System in acetone.

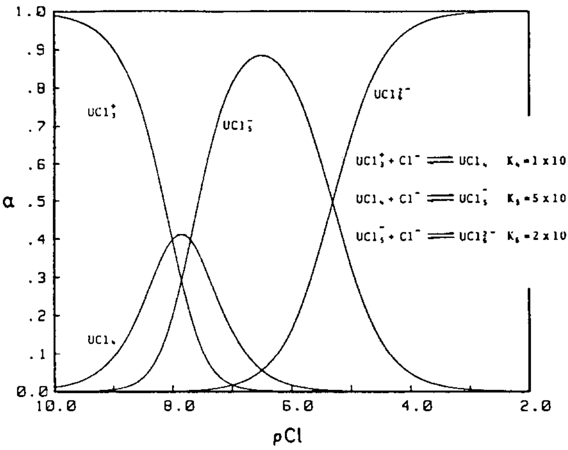

Fig. 2. Distribution diagram for the combined $ThCl_4$ and UCl_4 system in acetone.

Extent of autoionization:

$$2UCl_4 \rightleftharpoons UCl_3^+ + UCl_5^-$$

$$K_n = \frac{[UCl^+][UCl_5^-]}{[UCl_4]^2} = \frac{K_5}{K_4} = 0.5$$

Location of system on pCl Scale:

$$[Cl^-] = \frac{1}{\sqrt{K_5 K_4}} = 1.4 \times 10^{-8}$$

If the same information could be got from the corresponding thorium system, it would similarly enable one to see where the system lies on the $[Cl^-]$-scale. From this one could then give a measure for the difference in Lewis acidity between U(IV) and

---

*Currently at Albert-Ludwig-Universität, Freiburg, F.R.G.

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.

A20

Thermodynamic Properties of Protoactinium Hydrides

WILHELM BARTSCHER*, JOHN M. HASCHKE and JOHN W. WARD

Commission of the European Communities, Joint Research Centre, Karlsruhe Establishment, European Institute for Transuranium Elements, Postfach 2266, D-7500 Karlsruhe, F.R.G.

Pressure-composition isotherms of the protoactinium-hydrogen system were measured in the range of $10^{-5} \leq p \leq 100$ bar, $0 \leq H/Pa < 3$, $373 \leq K \leq 795$ 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. 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 $2.0 \leq H/Pa \leq 3.0$. At temperatures below 500 K and $1.3 < H/Pa \leq 3.0$ 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].

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.

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