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Title: THERMODYNAMICS AND SUBLIMATION CHEMISTRY OF PLUTONIUM - OXYGEN - CHLORINE

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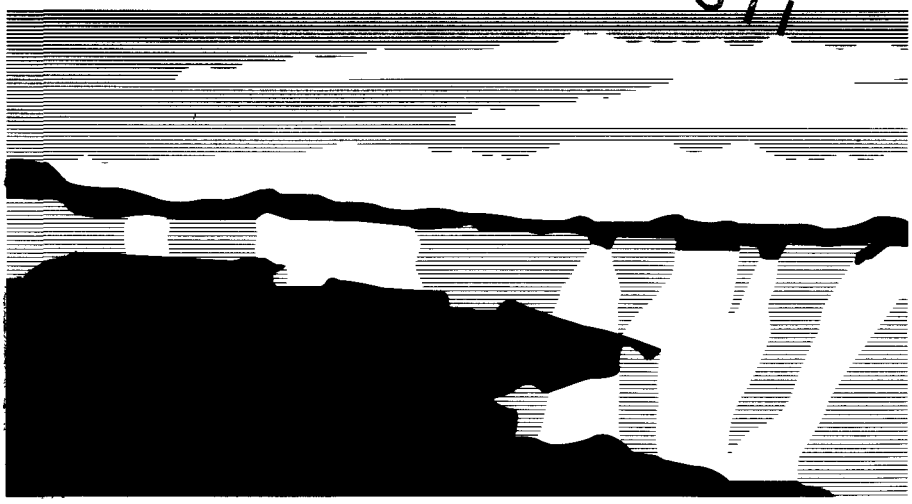

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Thermodynamics and Sublimation Chemistry of PuOCl

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Introduction

Pyrochemical processing of plutonium produces spent salts that contain plutonium bearing species. One of the species is PuOCl. The behavior of pure PuOCl at high temperatures and PuOCl in the liquid salt matrix is not well characterized. The purpose of the study is to establish the vapor pressure and vapor composition for the sublimation of PuOCl. The results of the sublimation study and the thermodynamic properties associated with the sublimation process will be presented.

Experimental

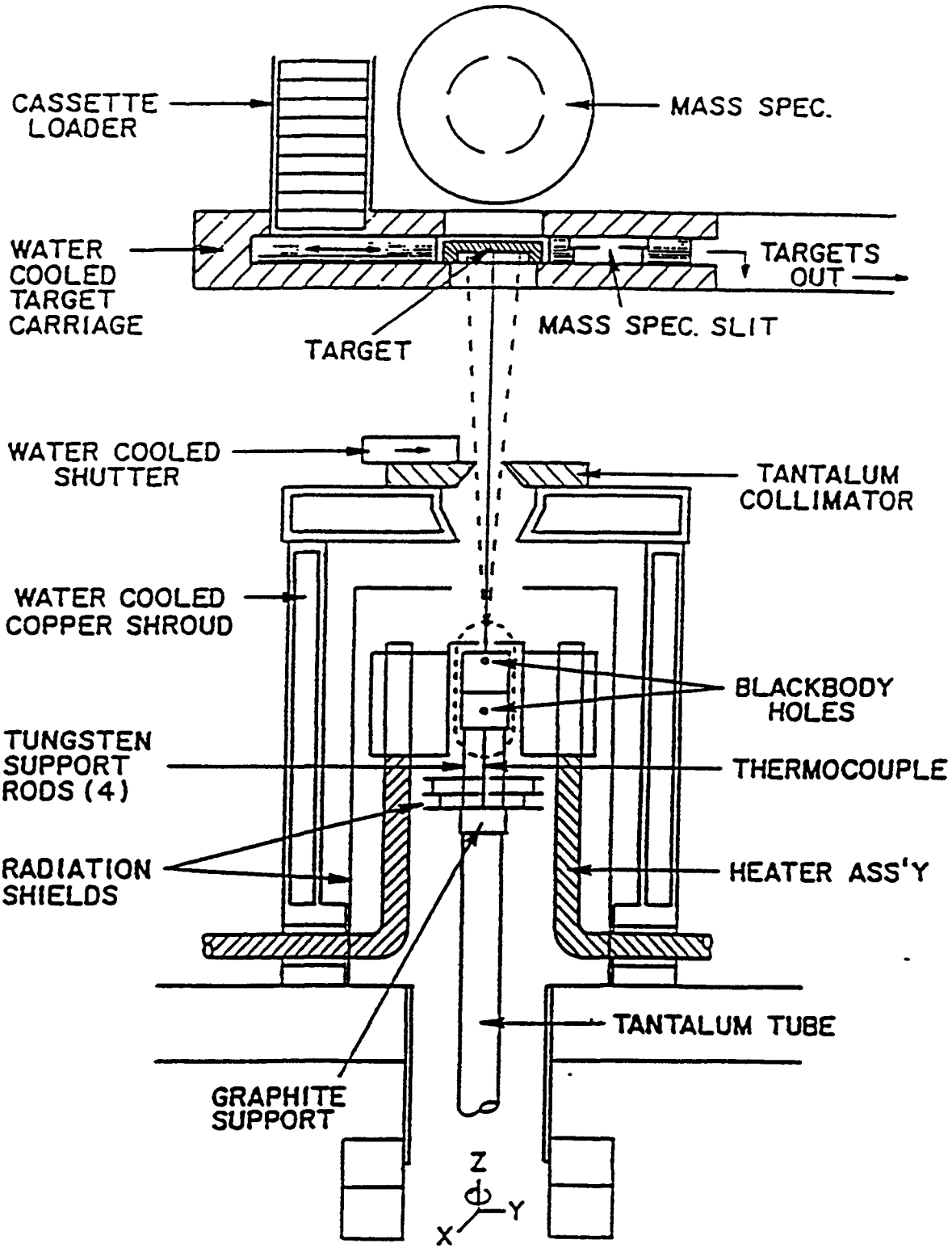
The sublimation of PuOCl was studied by Knudsen effusion mass spectrometry. A diagram of the apparatus is given in Figure 1. The PuOCl sample was contained in a platinum cup inside a platinum effusion cell which was contained inside a molybdenum effusion cell. The temperature of the sample was measured with a chromal-alumel thermocouple. The vapor species that were monitored included; $PuCl_4$, $PuCl_3$, PuOCl, PuO, and Pu. The vapor pressure of PuOCl was measured in the temperature range 1095 - 1270 K. The mass spectrometer was calibrated by studying the sublimation of UF_4.

The PuOCl was prepared by the following reaction;

$3PuCl_3\ (s) + Sb_2O_3\ (s) = 3PuOCl\ (s) + 2SbCl_3\ (g)$.

The $PuCl_3$ was prepared by the chlorination of liquid plutonium metal.

COSS SECTIONAL VIEW OF UHV TARGET/MASS-SPECTROMETER KNUDSEN EFFUSION APPARATUS



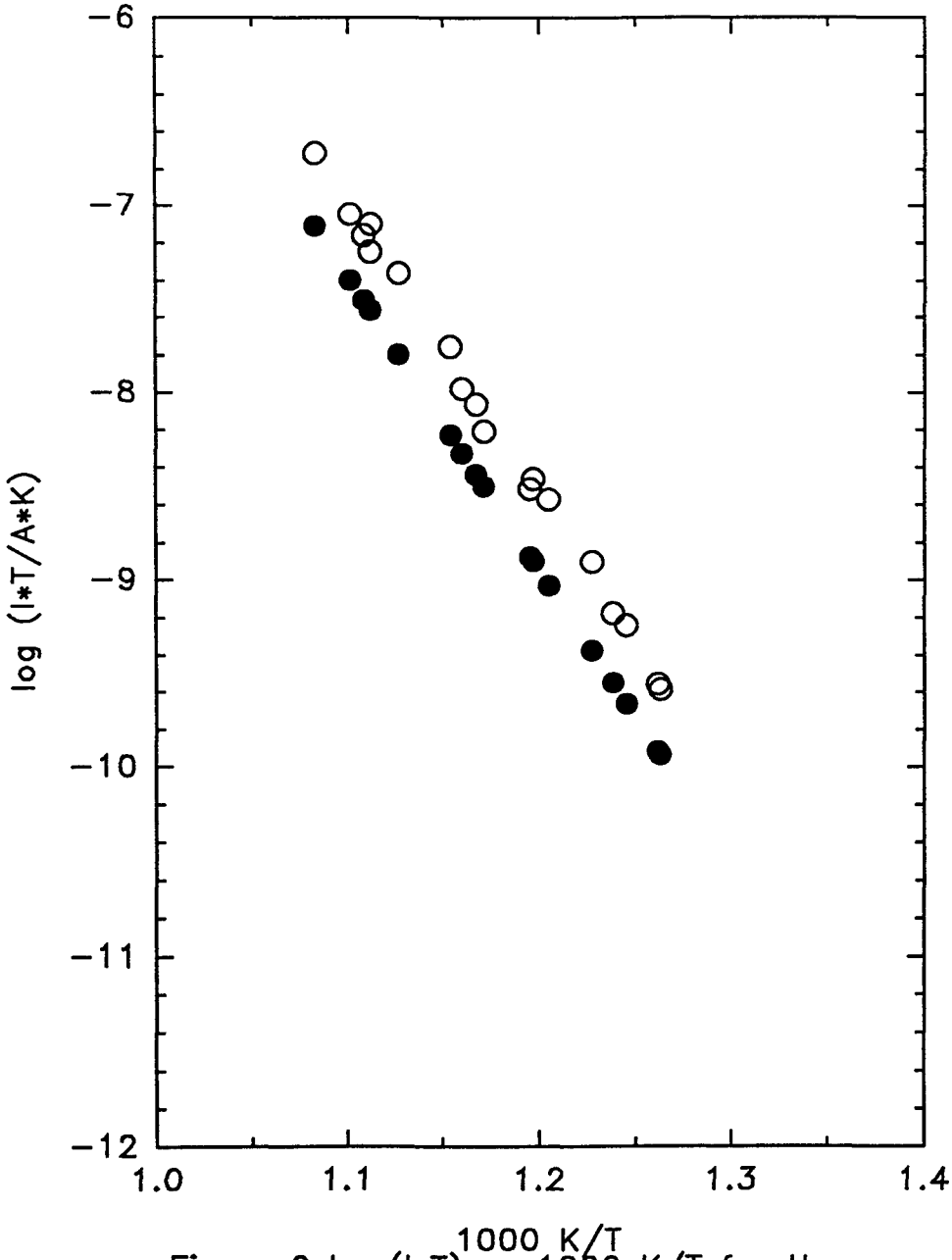


Figure 2. Log(I*T) vs 1000 K/T for the sublimationof UF_4(s); open circles– log(I*T) data, closed circles– Hildenbrand's log(P/atm) data.

Calibration

UF_4 (s) = UF_4 (g)

The intensity of UF_3^+/UF_4 at 45 eV was monitored as a function of temperature.

T (K)	I*T (A*K)	P (atm)[a]	C (atm/A*K)[b]
791.8	2.601e-10	1.156e-10	0.445
792.6	2.778e-10	1.211e-10	0.436
866.7	1.765e-08	5.966e-09	0.338
835.6	3.475e-09	1.264e-09	0.364
902.5	6.920e-08	3.118e-08	0.451
853.7	6.235e-09	3.162e-09	0.508
803.0	5.762e-10	2.185e-10	0.379
887.7	4.362e-08	1.600e-08	0.367
836.6	3.060e-09	1.331e-09	0.435
807.6	6.689e-10	2.824e-10	0.422
829.9	2.698e-09	9.395e-10	0.348
923.5	1.936e-07	7.748e-08	0.400
908.1	8.955e-08	3.991e-08	0.446
899.6	7.943e-08	2.740e-08	0.345
814.9	1.250e-09	4.216e-10	0.337
862.1	1.048e-08	4.776e-09	0.456
856.7	8.698e-09	3.668e-09	0.422
899.8	5.655e-08	2.765e-08	0.489
		average	0.410

$\log (I*T) = -(15606 \pm 238)/T + (10.17 \pm 0.28)$

$\Delta H°(298\ K) = 312.5 \pm 4.6$ kJ/mol

[a] Hildenbrand's Data[1]

$\log (P/atm) = -(15691 \pm 109)/T + (9.90 \pm 0.11)$

$\Delta H°(298\ K) = 313.8 \pm 2.1$ kJ/mol

[b] C=P/I*T

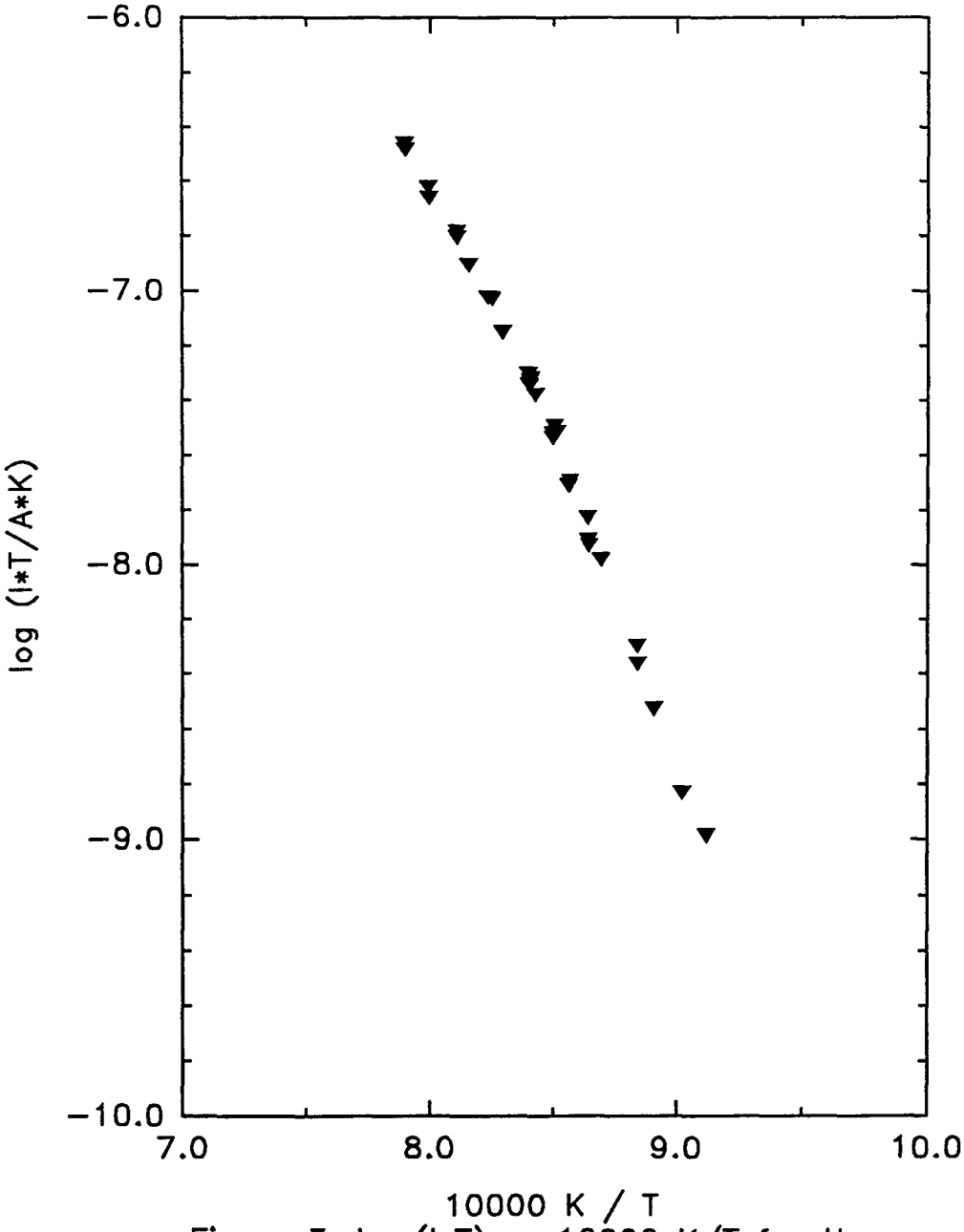


Figure 3. Log(I*T) vs 10000 K/T for the sublimation of PuOCl.

PuOCl Sublimation

$3\ PuOCl\ (s) = Pu_2O_3\ (s) + PuCl_3\ (g) \quad T < 1190\ K$

The intensity of $PuCl_2^+/PuCl_3$ at 45 eV was monitored as a function of temperature.

Point	T (K)	I*T (A*K)	log (I*T/A*K)
3	1150.6	1.065e-08	-7.973
8	1189.7	4.911e-08	-7.309
11	1190.9	5.103e-08	-7.292
12	1096.8	1.049e-09	-8.979
15	1176.9	3.063e-08	-7.514
18	1177.0	2.951e-08	-7.530
19	1131.1	4.394e-09	-8.357
21	1131.4	5.083e-09	-8.294
29	1157.7	1.251e-08	-7.903
32	1157.2	1.197e-08	-7.922
33	1190.1	4.786e-08	-7.320
36	1157.9	1.507e-08	-7.822
37	1176.1	3.257e-08	-7.487
38	1174.9	3.098e-08	-7.509
56	1190.8	4.650e-08	-7.332
62	1190.3	4.629e-08	-7.334
63	1186.8	4.256e-08	-7.371
64	1167.4	2.064e-08	-7.685
68	1168.2	1.983e-08	-7.703
73	1108.5	1.499e-09	-8.824

$\log (I*T/A*K) = -(23668 \pm 371)/T + (12.58 \pm 0.32)$

$\log (P/atm) = -(23668 \pm 371)/T + (12.13 \pm 0.32)$

$\Delta H°\ (298\ K) = 459.13 \pm .71\ kJ/mol$

$\Delta S°\ (298\ K) = 244.0 \pm 6.1\ J/mol\ K$

PuOCl Sublimation

$PuCl_3$ (l, in L_1) = $PuCl_3$ (g) T > 1190 K

$L_1 \equiv [1-x\ PuCl_3 \bullet x\ Pu_2O_3]$ (l)

The intensity of $PuCl_2^+/PuCl_3$ at 45 eV was monitored as a function of temperature.

Point	T (K)	I*T (A*K)	log (I*T/A*K)
2	1205.9	7.202e-08	-7.142
4	1233.2	1.589e-07	-6.799
5	1233.6	1.663e-07	-6.779
22	1214.7	9.623e-08	-7.017
24	1226.1	1.263e-07	-6.899
26	1266.2	3.534e-07	-6.452
28	1266.0	3.351e-07	-6.475
42	1212.3	9.515e-08	-7.022
49	1251.1	2.414e-07	-6.617
55	1250.7	2.208e-07	-6.656

$\log (I*T/A*K) = -(16503 \pm 488)/T + (6.57 \pm 0.39)$

$\log (P/atm) = -(16503 \pm 488)/T + (6.12 \pm 0.39)$

PuOCl Sublimation

Vapor Species

The vapor species that were observed were $PuCl_3^+$, $PuOCl^+$ and their fragments.

Intensity-temperature products were converted to pressures with the UF_4 calibration constant, C=0.410 atm/A*K, and the fragmentation corrected cross section, 0.870.

Vaporization Reactions

T < 1190 K

$$3\ PuOCl\ (s) = Pu_2O_3\ (s) + PuCl_3\ (g) \quad [1]$$

T > 1190 K

$$PuCl_3\ (l,\ in\ L_1) = PuCl_3\ (g) \quad [2]$$

$$L_1 \equiv [1\text{-}x\ PuCl_3 \bullet x\ Pu_2O_3]\ (l)$$

$$L_1\ (l) = PuOCl\ (g) \quad [3]$$

PuOCl Sublimation

Thermodynamics

$3\ PuOCl\ (s) = Pu_2O_3\ (s) + PuCl_3\ (g)$ [1]

$\Delta H°\ (298\ K) = 459.13 \pm .71\ kJ/mol$

$\Delta S°\ (298\ K) = 244.0 \pm 6.1\ J/mol\ K$

What is the heat of formation of Pu_2O_3 (s) ?

$\Delta H°\ (298\ K) = -1682.2\ kJ/mol$

$\Delta H°\ (298\ K) = -1656\ kJ/mol$ estimated by Bessman et al.[2]

What is the entropy of $PuCl_3$ (g) ?

$S°\ (298\ K) = 382.8\ J/mol\ K$

$S°\ (298\ K) = 367.4\ J/mol\ K$ Fuger et al.[3]

The entropy of $PuCl_3$ (g) derived in this study is more in line with the value calculated by statistical methods, 380.2 J/mol K.

PuOCl Sublimation

Thermodynamics

What is the free energy of formation of PuOCl calculated from the vaporization data assuming the peritectic decomposition of PuOCl occurs at 1190 K?

$\Delta\bar{G}_{PuCl3} = (-8.231*T) - 74920 \quad T=1190-1275\ K$

$\Delta\bar{G}_{PuCl3} = -84.72\ kJ \quad T=1190\ K$

$1/2PuCl_3\ (l) + 1/2Pu_2O_3\ (s) = 3/2PuOCl\ (s)\ [4]$

$\Delta G^\circ_{[4]} = -42.36\ kJ/g\text{-}atom$

$1/3\ PuCl_3\ (l) + 1/3\ Pu_2O_3\ (s) = PuOCl\ (s)\ [5]$

$\Delta G^\circ_{[5]} = -28.24\ kJ/mol$

$\Delta G^\circ_{f,PuOCl} = -28.24 + 1/3(-708) + 1/3(-1396.3)$

$\Delta G^\circ_{f,PuOCl} = -729.6\ kJ/mol$

$\Delta G^\circ_{f,PuOCl} = -742.8\ kJ/mol$ Weigel et al.[4]

A phase diagram has been proposed for the $PuCl_3$-Pu_2O_3 system, Figure 4, based on the $PuCl_3$-PuOCl phase diagram, Figure 5, and the sublimation data obtained in this study.

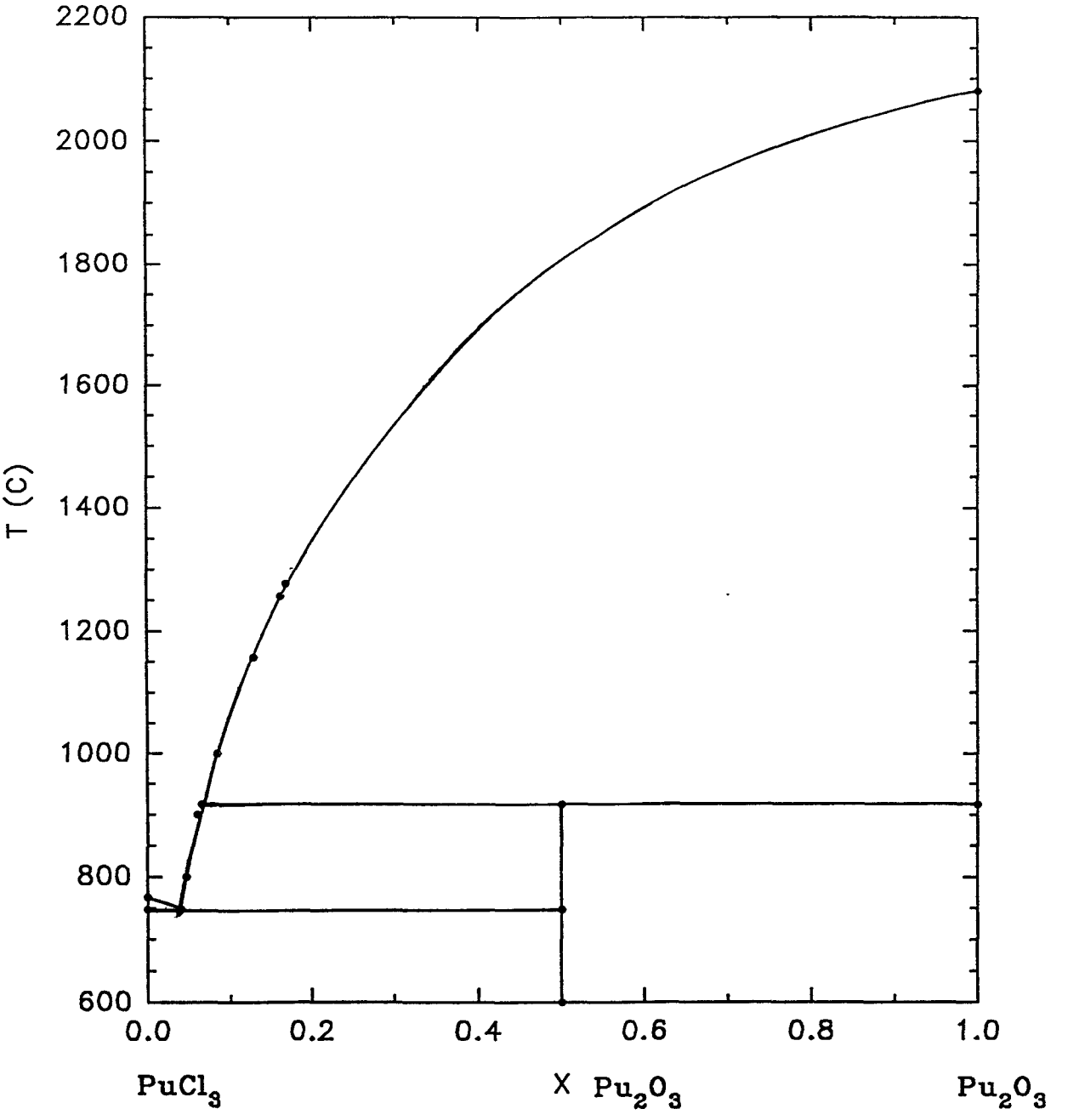


Figure 4. Proposed $PuCl_3$ – Pu_2O_3 phase diagram.

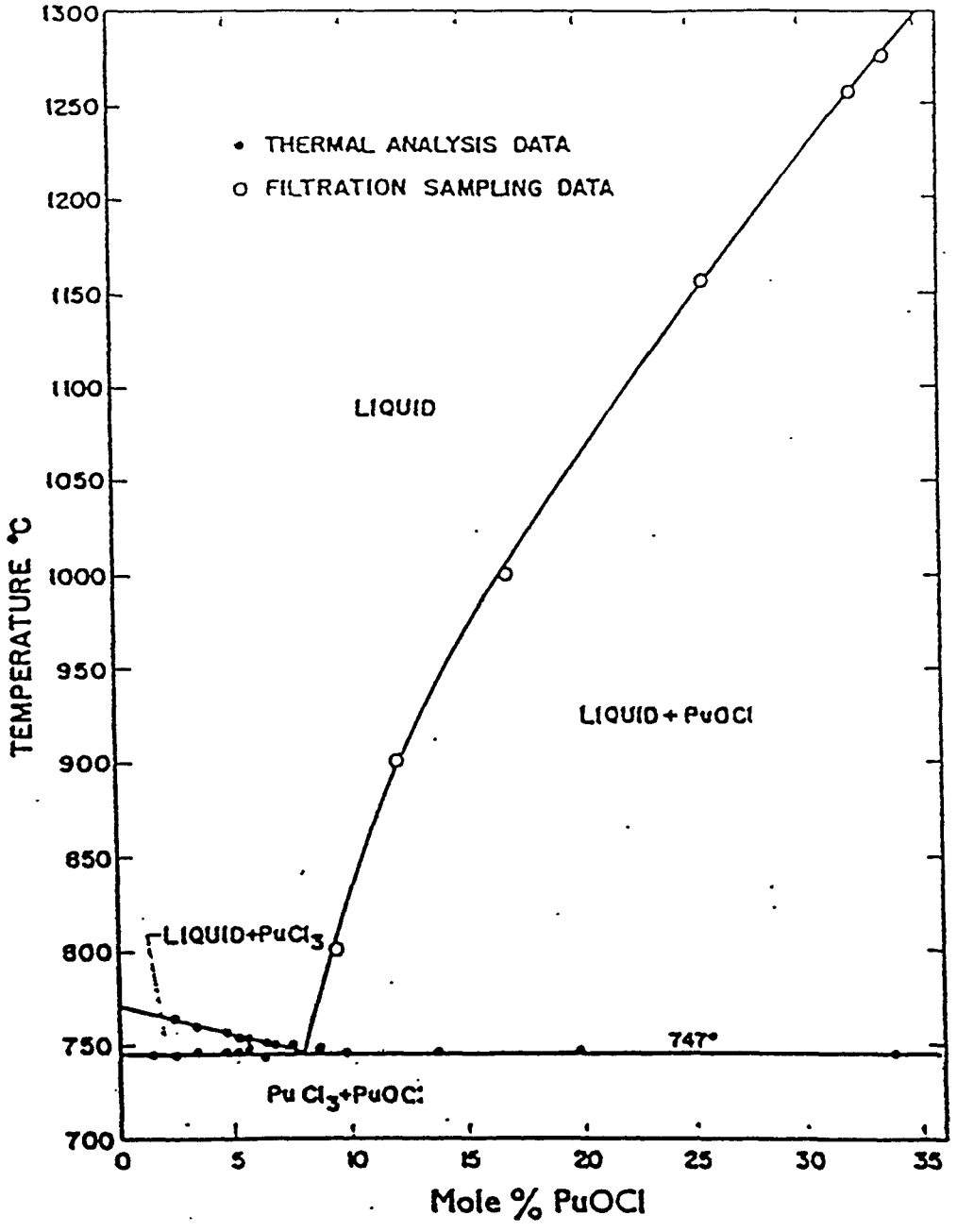


FIG. 5 —Partial phase diagram of the $PuCl_3$–PuOCl system.[5]