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LOS ALAMOS SCIENTIFIC LABORATORY
LOS ALAMOS of the NEW MEXICO
University of California

THE SOLUBILITIES OF SELECTED ELEMENTS IN LIQUID PLUTONIUM
III. TUNGSTEN

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THE SOLUBILITIES OF SELECTED ELEMENTS IN LIQUID PLUTONIUM

III. TUNGSTEN

by

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ABSTRACT

The solubility of tungsten in liquid plutonium has been measured over the temperature range 700° to 1000°C. The solubility increased from 29 ppm (by weight) W at 700°C to 291 ppm W at 950°C. The data fit the empirical equation

$$\log N_W = 0.3518 - 4.639 \times 10^3 T^{-1},$$

where N_W is the solubility expressed as the mole fraction of W, and T is the temperature in degrees Kelvin.

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INTRODUCTION

Studies of the solubilities of selected elements in liquid Pu have been undertaken in this Laboratory. The solubilities of C(1) and Ta(2) over the temperature range 700° to 1000°C have been reported as the initial elements to be studied in the series. The investigation of the solubility of W in Pu is discussed in this paper.

EXPERIMENTAL

Materials

Electrorefined Pu(3) and high purity W were used throughout this investigation. The analyses of these materials prior to this study are shown in Table 1.

Equipment

The gas-tight solubility equipment is shown in Figure 1. It was possible to obtain repeated samples at high temperatures with this apparatus without apparent alteration in the system.

Ta tubes were used to collect filtered samples at temperature. Porous CaF_2 discs were press-fitted into the end of each tube to form a filter. Each filter was checked for leakage prior to use.

The melt temperatures were measured to ± 2.0°C with Pt-Pt, Rh thermocouples.

Table 1

Analyses of Pu and W

Element	ppm in Pu[a]	ppm in W	Element	ppm in Pu	ppm in W
Li	< 0.2	< 1	Am	15	--
Be	< 0.1	< 1	O_2	5 - 20	--
Na	< 10	30	Mo	< 1	< 1000
Mg	< 5	< 1	W	15 ± 5	--
Ca	< 5	20	Th	< 15	--
Al	< 5	10	Ta	< 30	< 0.1
La	< 10	--	Zr	< 10	< 30
Si	< 10	50	H_2	5 ± 5	--
Pb	< 2	< 1	C	< 10	--
Cu	< 2	20	F	< 2	--
Ni	< 10	3	U	< 30	--
Cr	< 5	< 10	Fe	< 20	3
B	< 0.5	< 3	Pu	100.00%	
Mn	< 2	< 1			
Sn	< 1	< 3			
Bi	< 1	< 1			
Co	< 10	< 10			
Zn	< 10	<100			

[a] Parts per million parts Pu, by weight.

A - 1/4" Wilson seals for sampler tubes and stirring rod

B - Upper flange

C - Thermocouple well

D - Cooling coils

E - Cu cooling block

F - CaF_2 reaction crucible

G - CaF_2 furnace tube liner

H - Furnace

I - Cu casting block

J - Ni plate

K - Furnace support stand

L - Stainless steel furnace tube

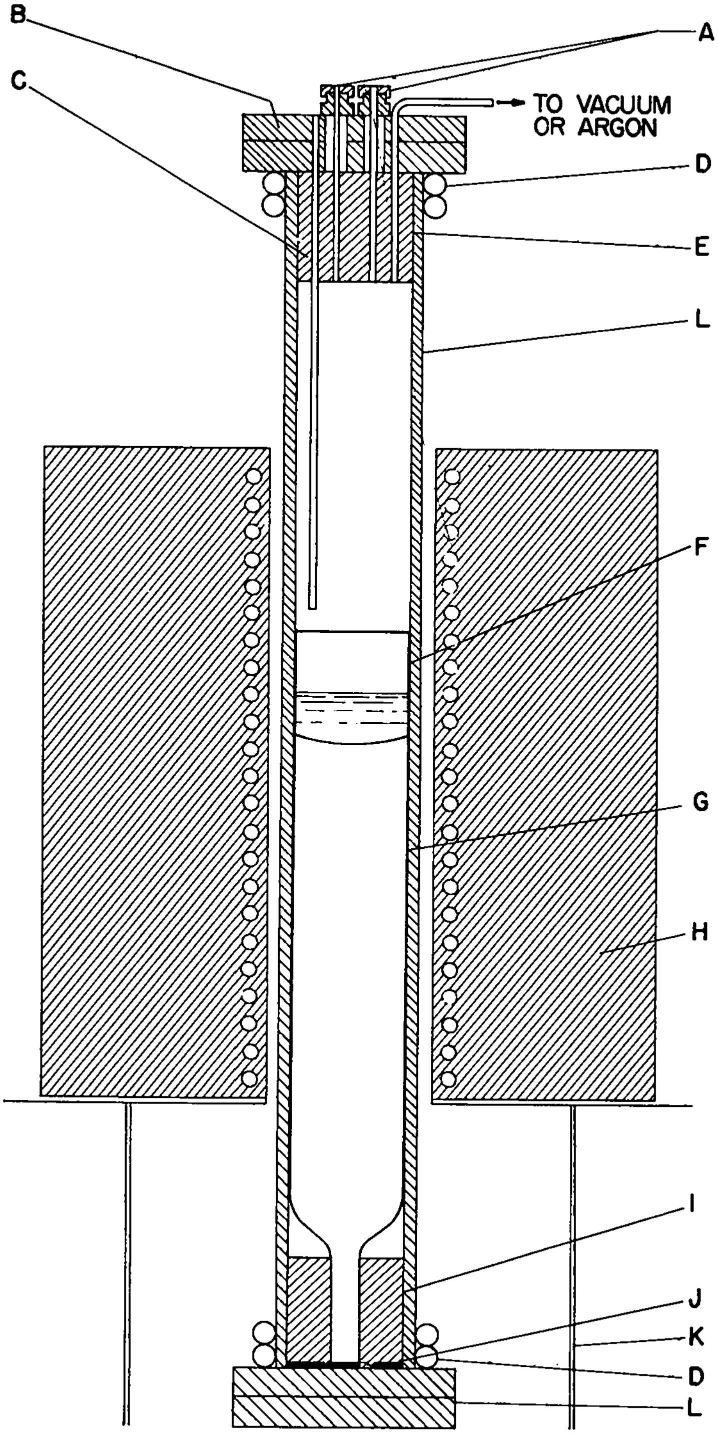

Fig. 1. Solubility apparatus.

Procedure

Experiments were carried out in degassed CaF_2 crucibles. Approximately 50 *g.* of Pu and 5 to 10 *g.* of W were placed in a crucible. The crucible was centered in the furnace tube, and the apparatus was assembled and sealed. The W rod entering the tube from above was positioned so that it would be in the crucible. The apparatus, with the pressure less than 4×10^{-5} Torr, was heated to the selected temperature and maintained by controller at temperature for a given time interval. The W rod was lowered into the molten Pu and was shaken by means of an external vibrator.

Two procedures to obtain samples were commonly employed. In the preferred method, Ar was added to the system and a Ta sampling tube was lowered into the furnace tube through the center Wilson seal. The tube was kept approximately 2 cm. above the melt for 30 min. to reach temperature and then lowered into the melt. Suction on the open end of the tube forced melt through the CaF_2 frit and into the tube. The tube was raised to a cooler section of the furnace tube where the sample was frozen and then withdrawn.

In the second method, the bottom of the reaction crucible was pierced with the W stirring rod after a selected time at temperature. The melt drained through a tube liner and was chill cast into the cooled Cu casting mold.(4) After sampling, this casting was reused in further experiments. The solubility results were in agreement for these two sampling methods in these experiments.

Analysis

Samples were obtained from several positions of each casting and from at least two positions in each sampling tube in an attempt to eliminate bias.(5, 6) Duplicate analyses of the samples were made spectrophotometrically to a precision of ± 7 percent.(7)

RESULTS AND CONCLUSIONS

Two types of tests were used to determine whether the solubility measurements represented true equilibria. In the first tests, the apparent solubility was measured as a function of time at constant temperature to eliminate kinetic errors and to gain some insight into the rate of approach to saturation. In the second type, saturation was approached from both a higher and a lower temperature.

Apparent Solubility as a Function of Time

Experiments at constant temperature were made in which filtered samples were withdrawn at selected time intervals. The tests at 850° C., which are typical of those at each temperature, are summarized in Table 2. No significant changes in solubility occurred after 6 hr. at temperature. Therefore, all the data cited in this study were from solutions maintained at temperature for more than 6 hr., and usually the times ranged from 24 to 72 hr. at temperature.

Table 2

The Solubility of W in Liquid Pu at 850° C

Total Time, hr.	Solubility, ppm W
6.0	125
22.0	119
48.0	124
94.0	120
117.0	120
Average	122

Approach by Temperature

Two methods of approach to saturation were adopted. These were the approach from undersaturation (a lower temperature) in which additional solute went into solution and the approach from supersaturation (a higher temperature) in which excess solute precipitated from supersaturated solution. Filtered samples demonstrated that the two methods of approach were equivalent.

Solubility Measurements

The data from the solubility measurement experiments are summarized in Table 3.

Table 3

The Solubility of W in Liquid Pu

Temperature, °C	Number of Determinations Used for Average	Average Solubility	
		ppm	$N_W \times 10^5$
700	4	29 ± 1	3.77 ± 0.13
750	5	55 ± 3	7.20 ± 0.36
800	11	82 ± 2	10.46 ± 0.23
825	6	103 ± 1	13.39 ± 0.11
850	18	122 ± 4	15.85 ± 0.49
875	10	164 ± 3	21.31 ± 0.39
900	10	202 ± 4	25.52 ± 1.09
925	8	235 ± 6	30.44 ± 0.81
950	4	291 ± 2	37.89 ± 0.20
990	4	348 ± 12	45.17 ± 1.63

Discussion

In Figure 2 the average solubility data are plotted on a logarithmic scale against the inverse of the absolute temperature. The data form a straight line, thus indicating the linear relationship

$$\log N_W = A + BT^{-1} \tag{1}$$

where N_W is the mole fraction of W, and T is the temperature in degrees Kelvin.

The data from these experiments were placed in two computer programs to compare Equation 1 and the empirical equation frequently employed(8, 9) in solubility studies:

$$\log N_W = C + DT^{-1} + ET^{-2}. \tag{2}$$

The constants were then used to calculate solubilities at each selected temperature. Both standard deviations and the calculated values indicated that the best fit was to the equation

$$\log N_W = 0.3518 - 4.639 \times 10^3 T^{-1}. \tag{3}$$

In Table 4 the values calculated by Equation 3 are compared with those shown in Table 3; that is, the average of the experimental values. The agreement is quite good except at 750°C. At this temperature an error of 3 to 5 ppm in analysis would cause this much difference in the measured result. In other cases the differences are within the precision of the measurements.

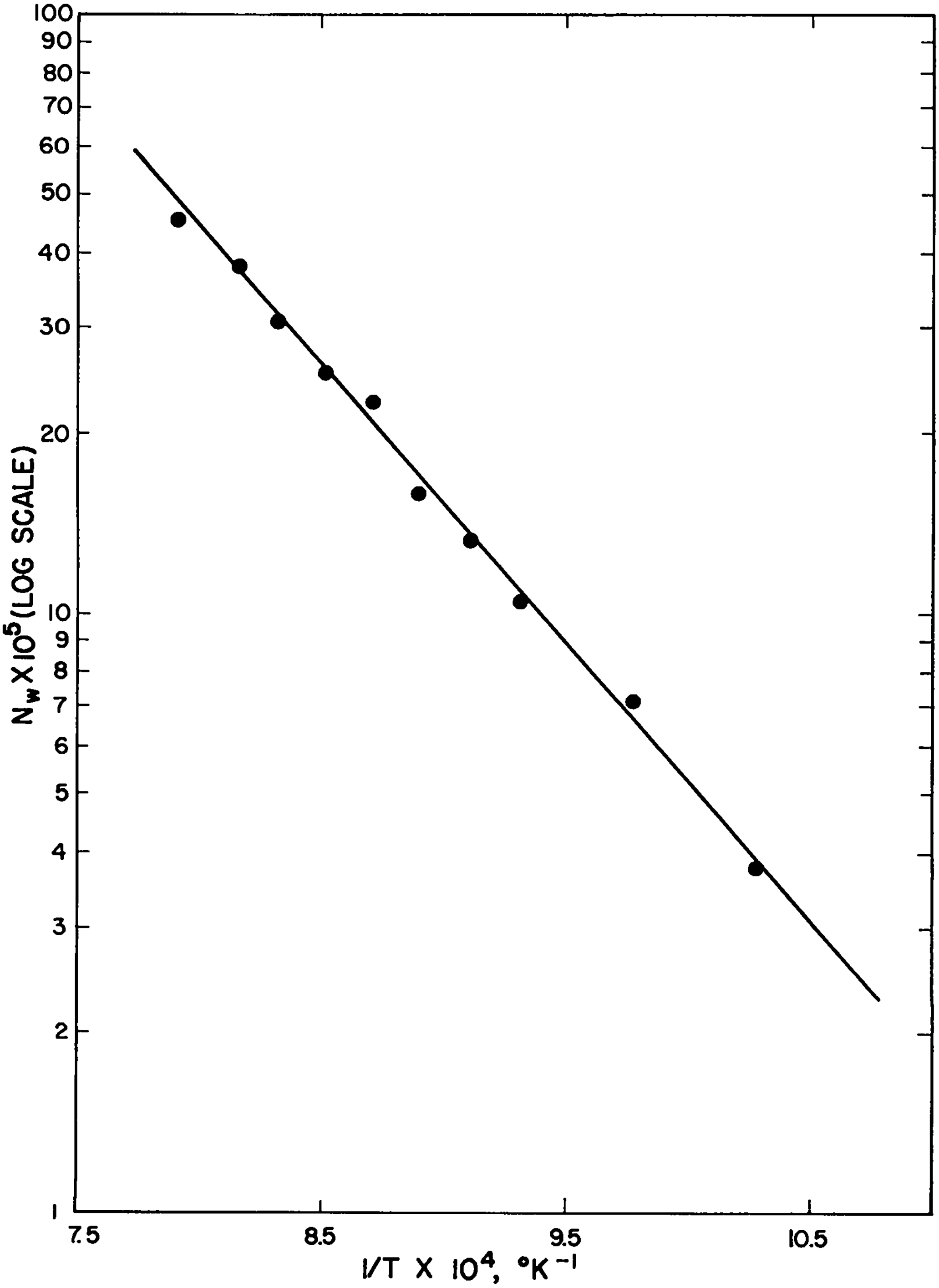

Fig 2. Log N_W vs $1/T$.

Table 4

Calculated vs. Measured Solubilities of W in Liquid Pu

Temperature, °C	$N_W \times 10^5$	
	Calculated[a]	Measured
700	3.84	3.77 ± 0.13
750	6.57	7.20 ± 0.36
800	10.69	10.46 ± 0.23
825	13.41	13.39 ± 0.11
850	16.65	15.85 ± 0.49
875	20.48	21.31 ± 0.39
900	24.97	25.52 ± 1.09
925	30.20	30.44 ± 0.81
950	36.24	37.89 ± 0.20
990	47.78	45.17 ± 1.63

[a] Calculated from Equation 3.

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