LA-3303

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UNITED STATES
ATOMIC ENERGY COMMISSION
CONTRACT W-7405-ENG. 36

Printed in USA. Price $1.00. Available from the
Clearinghouse for Federal Scientific
and Technical Information,
National Bureau of Standards,
U. S. Department of Commerce,
Springfield. Virginia

LA-3303
UC-4, CHEMISTRY
TID-4500 (41st Ed.)

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Report written: March 22, 1965
Report distributed: June 25, 1965

The Solubility of Selected Elements in Liquid Plutonium

IV. Evaluation of Sampling Techniques

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ABSTRACT

Quench cast, filtered, and unfiltered thief samples were taken from liquid Pu saturated with W over the temperature range 700° to 925°C., and the results were evaluated. The three methods were in agreement when saturation was approached from a lower temperature. Only the filtered samples were reliable when saturation was approached from a higher temperature.

INTRODUCTION

The solubilities of selected elements in liquid Pu are being studied in this Laboratory.(1,2,3) In this, as in similar investigations, the reliability of the data is limited mainly by the accuracy of the sampling methods.

Several conditions must apply before the apparent solubility can be interpreted as a true equilibrium solubility. Obviously, the solubility value must be independent of the sampling method. It is a necessary condition that the true solubility be invariant with time at temperature. However this is not sufficient, as many examples are known where insignificant rates of solution produce no significant change in apparent solubility over a reasonably long period of time. It is also a necessary condition that the true solubility be independent of the direction of approach to saturation. This normally is done by temperature variation. However, it is at least theoretically possible to obtain the same erroneous solubility value by approaching equilibrium from both directions. For example, one can visualize a system where very slow rates of solution could produce such an erroneous result. Therefore in determining solubility, it is necessary to evaluate both the rate of saturation and the constancy of the solubility regardless of direction of approach to equilibrium.

Obviously the solubility study should involve a known equilibrium; i.e., the solid phase should be known. In this work the equilibrium reaction was

W (s) + Pu (l) = W (sat'd sol'n in liq Pu).

In the experiments reported here the following sampling methods have been intercompared for both directions of approach to equilibrium:

1. Sampling by pipetting from the settled liquid phase.
2. Bottom-pouring and quenching the liquid phase.
3. Filtration of the liquid phase.

EXPERIMENTAL

Materials

Electrorefined Pu(4) and high purity W were used throughout this investigation. The analyses of these prior to this study are shown in Table 1.

Equipment

A gas-tight furnace tube, previously described,(3) was used to dissolve the W in liquid Pu. Tantalum tubes were used for collecting filtered samples. These tubes were press-fitted with CaF$_2$ discs to form a filter. Each CaF$_2$ disc had been formed by pressing at 10,000 p.s.i and sintering at 1000°C. to produce a 1/8-in.-thick cylinder. Pore diameter was 10μ.* Each filter was checked for leakage prior to use.

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

Table 1
Analyses of Pu and W

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

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

[b] Parts per million parts W, by weight.

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*The CaF$_2$ discs were prepared by S. Stoddard.

Procedure

Experiments were conducted in degassed CaF_2 crucibles. Approximately 50 *g.* of Pu and 5 to 10 *g.* of W sheet were placed in a crucible. The crucible was centered in the furnace tube, and the apparatus was assembled and sealed. The apparatus was evacuated to a pressure less than 4×10^{-5} Torr and then heated to a selected temperature. A W rod, which entered the furnace tube from above, was then lowered into the melt. The rod was shaken by an external vibrator. The apparatus was maintained at the selected temperature for the desired time interval.

Filtered samples were obtained under Ar. A Ta sampling tube was lowered into the furnace tube through a Wilson seal. The tube was kept approximately 2 cm. above the melt for 30 min. to reach temperature. It was then lowered into the melt, and suction was applied to the open end of the tube. This forced liquid through the filter and up approximately 5 to 10 cm. into the tube. The tube was raised to a cooler section of the furnace tube where the sample was frozen and then withdrawn. There was no Ta contamination of the metal sample in this procedure.

Unfiltered thief samples were obtained in quartz tubes by the same method.

Chill cast, that is, quenched, samples were obtained by casting methods.(5) The bottom of the reaction crucible was pierced with the W stirring rod after a selected time at temperature. The melt drained rapidly and was chill cast into a cooled Cu casting mold.

Portions of each sample were taken from several positions in each casting or tube in an attempt to eliminate sample bias.(6,7) Duplicate analyses of the samples were made spectrophotometrically to a precision of ± 3 percent.(8) Normally at least four samples were taken at each temperature after saturation.

RESULTS AND CONCLUSIONS

Two methods of approach were studied for each sampling method. In the first, the approach was from undersaturation (a lower temperature). In this case the three sampling methods were equivalent, as shown in Table 2. Previous work had shown that a 24 hr. equilibration time was sufficient to establish a constant solubility for W.

Table 2

Effect of Sampling Method on the Apparent Solubility of W (Approached 24 hr. equilibration time from undersaturation)

Temperature, °C	Apparent Solubility, p.p.m. Filtered	Cast	Unfiltered Thief
750	55	57	—
800	80	75	—
825	—	102	103
850	122	123	125
875	160	165	160
900	205	200	205
925	232	230	235

In the second method, the approach was from oversaturation (a higher temperature), in which excess solute precipitated from an oversaturated solution. Excess precipitate did cause high results for all but the filtered samples as shown in Table 3. Moreover, the unfiltered samples were badly segregated, so that no average apparent solubility could be calculated reliably.

Table 3

Effect of Sampling Method on the Apparent Solubility of W (Approach from Oversaturation, 24 hr. equilibration time)

Temperature, °C	Apparent Solubility, p.p.m. W Filtered	Cast	Unfiltered Thief
750	55	85-135	50- 70
800	85	100-125	105-140
850	126	145-420	175-225
900	205	—	200-250

Additional studies on the solubility of Ta in liquid Pu have shown that all unfiltered samples were subject to similar errors when a solubility measurement was approached from oversaturation. Filtered samples, on the other hand, were homogeneous and independent of the direction of approach, as shown in Table 4.

Table 4

Effect of Sampling Method on the Apparent Solubility of Ta at 900°C. (90 hr. equilibration)

Sampling Method	Approach from:	p.p.m. Ta Under-saturation	Over-saturation
Filtered		1940	2100
Cast		2050	2300-2600
Unfiltered Thief		1830	2500-2700

It is apparent that the filtration method should be preferred for the solubility measurements in these systems. The use of two directional approach, that is, both from undersaturation and oversaturation, should eliminate non-equilibrium data for solubility measurements that are independent of time and approach.

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