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LOS ALAMOS SCIENTIFIC LABORATORY
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THE SOLUBILITY OF SELECTED ELEMENTS IN LIQUID PLUTONIUM

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THE SOLUBILITY OF SELECTED ELEMENTS IN LIQUID PLUTONIUM

I. CARBON

by

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ABSTRACT

The solubility of carbon in liquid plutonium has been measured over the temperature range 700°-950°C. The solubility increases from 690 ppm (by weight) C at 700° to 2350 ppm C at 950°C. The data fit the emperical equation

$$\log N_C = 0.50-2.30 \times 10^3\ T^{-1},$$

where N_C is the mole fraction of C and T is the temperature in degrees Kelvin.

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INTRODUCTION

The solubilities of sparingly-soluble elements in liquid plutonium generally have not been measured. In order to make meaningful measurements, the liquid plutonium must be free from impurities that interact in solution with the impurity element. Now that high purity plutonium has become available in quantity, such measurements are possible.

Experiments are programmed to determine the solubilities of selected solid elements and compounds in liquid plutonium over the temperature range of 650 to approximately 1000°C. This report summarizes the results obtained with carbon.

EXPERIMENTAL

Materials

Electrorefined Pu was used in all experiments. The procedure for preparing this material has been described.(1) Analysis of the Pu is shown in Table 1. Type AUC graphite was used for the crucible and the stopper rod. Plutonium monocarbide was prepared by direct combination of the elements in an arc furnace.(2)

Table 1

Analysis of Electrorefined Pu

Spectrochemical		Chemical	
Element	ppm	Element	ppm
Li	< 0.2	Am	15
Be	< 0.1	Fe	< 20
Na	< 10	Pu	99.91%
Mg	< 5		
Ca	< 10	B	< 0.5
Al	< 5	Ni	< 20
La	< 10	U	< 30
Si	< 10	Th	< 15
Pb	< 2	Cl^-	< 10
Cu	< 10	Ta	< 30
Cr	< 10		
Mn	< 2	W	15 ± 5
Sn	< 1	Mo	< 5
Bi	< 1	C(1)	< 10
Co	< 10	N(1)	5 ± 3
Y	< 5	H(1)	5 ± 5
		O(1)	20-50

(1) Typical analysis of electrorefined Pu. This sample was not analyzed for these elements.

Procedure

The reaction vessel and equipment utilized in this study are similar to others used in quenching experiments.(3) This apparatus was designed so that Pu could be contacted with C in a graphite crucible for a selected time and then quenched by pouring the melt into a cold casting block under vacuum or in an inert atmosphere. Typical experiments were made by the following procedure: the apparatus, with no Pu in it, was outgassed for 1 hr under vacuum at 500°C and cooled to room temperature. The tapered end of the graphite stopper rod was then inserted in the casting hole in the graphite reaction crucible and 50 g of Pu were placed in the crucible. The apparatus was re-assembled and evacuated to less than 0.2μ pressure. The tube was heated to the selected temperature and maintained at temperature for the desired time. The tube was shaken at 10-15 min intervals at temperature to agitate the liquid.

Argon gas was then introduced and the stopper rod was raised. Liquid Pu poured rapidly through the casting hole into the magnesia pour crucible and into the cold Cu casting mold. The vessel was cooled to room temperature under vacuum and then disassembled.

In most cases castings were formed both in the Cu mold and in the pour crucible. The compositions of these castings were identical and homogeneous. Samples were broken from the centers of both of the castings under a He atmosphere and submitted for C analysis. Solubility measurements were based on results of analysis of two samples from each quenching experiment. The agreement was well within the limits of error of the method of analysis.

The castings, after sampling, were re-used in the next equilibration.

The estimated standard deviation of the C analysis is ± 10 relative percent.(4) In this study variations were, in general, small. Errors due to temperature deviations during quenching were estimated as less than 2 percent in the solubility determination. There was no evidence of inclusion of C particles in the castings after 1 hr of equilibration.

RESULTS

Several series of tests were made to demonstrate that equilibrium conditions were met between the liquid and solid phases. Time-dependence tests were made at each temperature. Those at 800° and 850°C, which were typical, are summarized in Table 2. As shown, the solubility of C in Pu was independent of time after 1.5 hr at 800°C and after 1.0 hr at 850°C.

Table 2

The Solubility of C in Pu as a Function of Time

Temperature, °C	Time at Temperature, hr	Solubility, ppm C
800	0.5	Segregated
	1.0	965
	1.5	1100
	2.0	1150
	2.5	1100
	3.0	1150
850	1.0	1400
	2.5	1300
	3.5	1400
	4.0	1400

Equilibrium conditions were approached from both higher and lower temperatures, and no significant change in solubility was indicated. For example, equilibrations were made at 700°C by approaching this temperature from lower temperatures. In addition, equilibrations were made by first equilibrating for 2.0 hr at 800°C, then cooling to 700°C and re-equilibrating for 3.0 hr prior to quenching. In both experiments the solubility value was well within the experimental error; the difference was 0.7%.

Another approach to equilibrium that was employed was to contact an excess of C as solid PuC with liquid Pu in a MgO crucible and with a MgO stopper rod. At 800°C after a 2.5 hr period of contact prior to quenching, the C content was the same as when liquid Pu was contacted with graphite. There was no reaction between the PuC-Pu and the MgO crucibles after 2.5 hr at 800°C.

Solubility Measurements

The results of the solubility experiments are shown in Table 3. These measurements were made after equilibrating from 1.5 to 4.0 hr at temperature prior to quenching. Measurements at 640°C, in which equilibrium conditions might not be met (m. pt. Pu is 639°C) averaged 385 ppm, which is in agreement with the other data.

A solid phase formed upon the inside walls of the graphite crucible during these Pu contacts. Samples of this phase contained 94 ± 1% Pu and 3.1-4.3% C by chemical analysis. From the Pu-C binary phase diagram,(5) this solid probably was hypostoichiometric PuC.

Table 3

The Solubility of C in Pu as a Function of Temperature

Temperature, °C	Experiment No.	Solubility, ppm(1)	Carbon Mole Fraction $N_C \times 10^3$
700	1	690	13.6
	2	715	14.0
	3	665	13.1
	Ave.	690	13.6
750	1	835	16.4
	2	795	15.6
	3	830	16.3
	Ave.	820	16.1
800	1	1100	21.4
	2	1300	25.2
	3	1150	22.4
	4	1100	21.4
	5	1150	22.4
	Ave.	1160	22.6
850	1	1400	27.1
	2	1300	25.2
	3	1400	27.1
	4	1400	27.1
	Ave.	1375	26.7
900	1	1900	36.5
	2	1750	33.7
	3	1900	36.5
	Ave.	1850	35.7
950	1	2200	42.0
	2	2500	47.4
	Ave.	2350	44.7

(1) Parts per million parts Pu, by weight.

DISCUSSION

From the phase diagram,(5) the solubility of C in liquid Pu throughout this temperature range probably corresponds to the equilibrium:

$$\text{PuC (solid)} = \text{PuC (saturated solution in Pu)}. \qquad (1)$$

At constant pressure it can be shown that, by thermodynamic considerations, a plot of log N_C vs $1/T$ should be linear if ΔH is constant over this temperature range. The average solubility data from Table 3 are plotted as a function of $1/T$ in Fig. 1. The data fit the empirical equation

$$\log N_C = B + AT^{-1}, \qquad (2)$$

where N_C is the solubility of hypostoichiometric PuC expressed as the mole fraction in solution and T is in degrees Kelvin. From least squares fit, this equation is

$$\log N_C = 0.50 - 2.30 \times 10^3\ T^{-1}. \qquad (3)$$

The standard error of estimate is 0.1

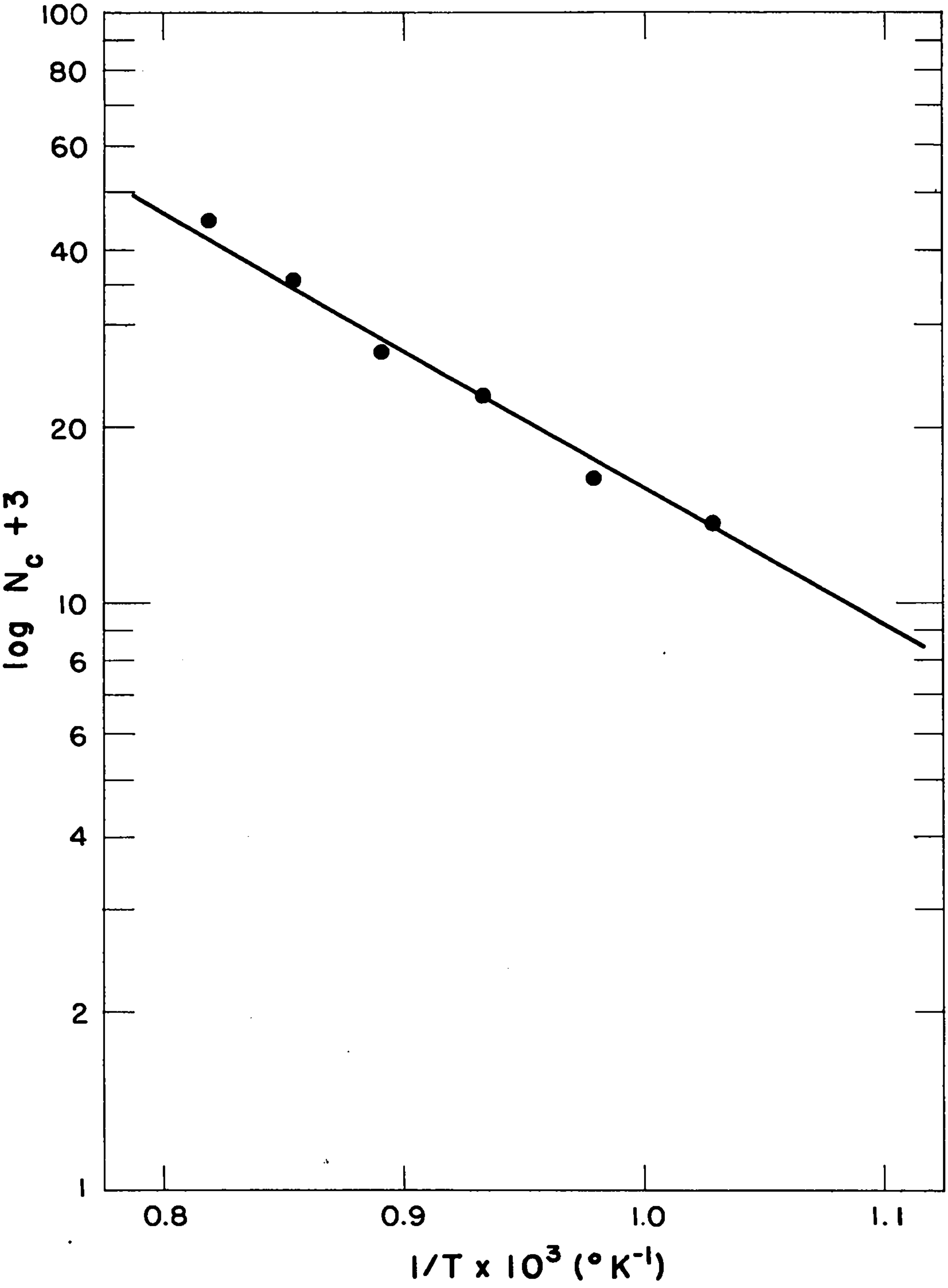

Fig. 1. Plot of log N_C vs 1/T

REFERENCES

1. L. J. Mullins, J. A. Leary, A. N. Morgan, and W. J. Maraman, "Plutonium Electrorefining," LA-2666 (1962).

2. A. E. Ogard, C. C. Land, and J. A. Leary, "The Thermal Expansion of PuC and PuC-UC Solid Solution," LA-2768 (October 1962).

3. L. J. Mullins, J. A. Leary, and K.W.R. Johnson, "Removal of Fission Product Elements from Plutonium by Liquation" from Extractive and Physical Metallurgy of Plutonium and its Alloys, W. D. Wilkinson, ed., Interscience, N.Y. (1960) p. 101.

4. W. G. Smiley, "A New Micro Combustion Method for Carbon in Plutonium," LA-1128 (1950).

5. R.N.R. Mulford, F. H. Ellinger, G. S. Hendrix, and E. D. Albrecht, "The Plutonium-Carbon System," from Plutonium 1960, E. Grison, W.H.B. Lord and R. D. Fowler, editors, Cleaver-Hume Press Ltd., London (1960) p. 301.