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THE DENSITY OF LIQUID PLUTONIUM METAL

by

C. E. Olsen, T. A. Sandenaw, and C. C. Herrick

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#### ABSTRACT

Measurements were made of the product of surface tension ( $\gamma$ ) and the contact angle ( $\theta$ ) of liquid plutonium vs solid tantalum and of the density of liquid plutonium ( $\rho$ ) as functions of temperature between 655 and 960°C. The following values were obtained:  $\gamma \cos \theta = 1030 - (0.967)T$  d/cm and  $\rho = \left[ 17.56_7 - (1.45_1 \times 10^{-3})T \right] \pm 0.021$  g/cm<sup>3</sup>.

A single determination was also made of the liquid density of a plutonium-7.93 atomic percent iron alloy and the following value obtained:  $\rho = \left[ 16.88 - (1.36_9)T \right] \pm 0.012$  g/cm<sup>3</sup>.

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## INTRODUCTION

Because of the potential use of plutonium in liquid metal reactors, it is important to know its liquid density. In addition, because of the large number of allotropic modifications which exist in solid plutonium, knowledge of this value is also of theoretical interest.

The first determination of the liquid density of plutonium was made by Comstock and Gibney and reported by Jette.<sup>1</sup> In their determination, the plutonium was melted in a quartz container of known geometry. The liquid level was determined by x-ray shadow-graphic techniques. Meniscus corrections were made. The results of their determinations gave a value of  $16.50 \pm 0.08 \text{ g/cm}^3$  at  $665^\circ\text{C}$  and a volume coefficient of expansion of  $50 \times 10^{-6} \text{ cm}^3/\text{cm}^3\text{-}^\circ\text{C}$ .

## APPARATUS

### Furnace

Because of its intense chemical activity, plutonium must be melted either in a good vacuum or in an inert atmosphere such as helium or argon. A vacuum furnace designed and built by A. Comstock was modified for the purpose of this determination. The arrangement

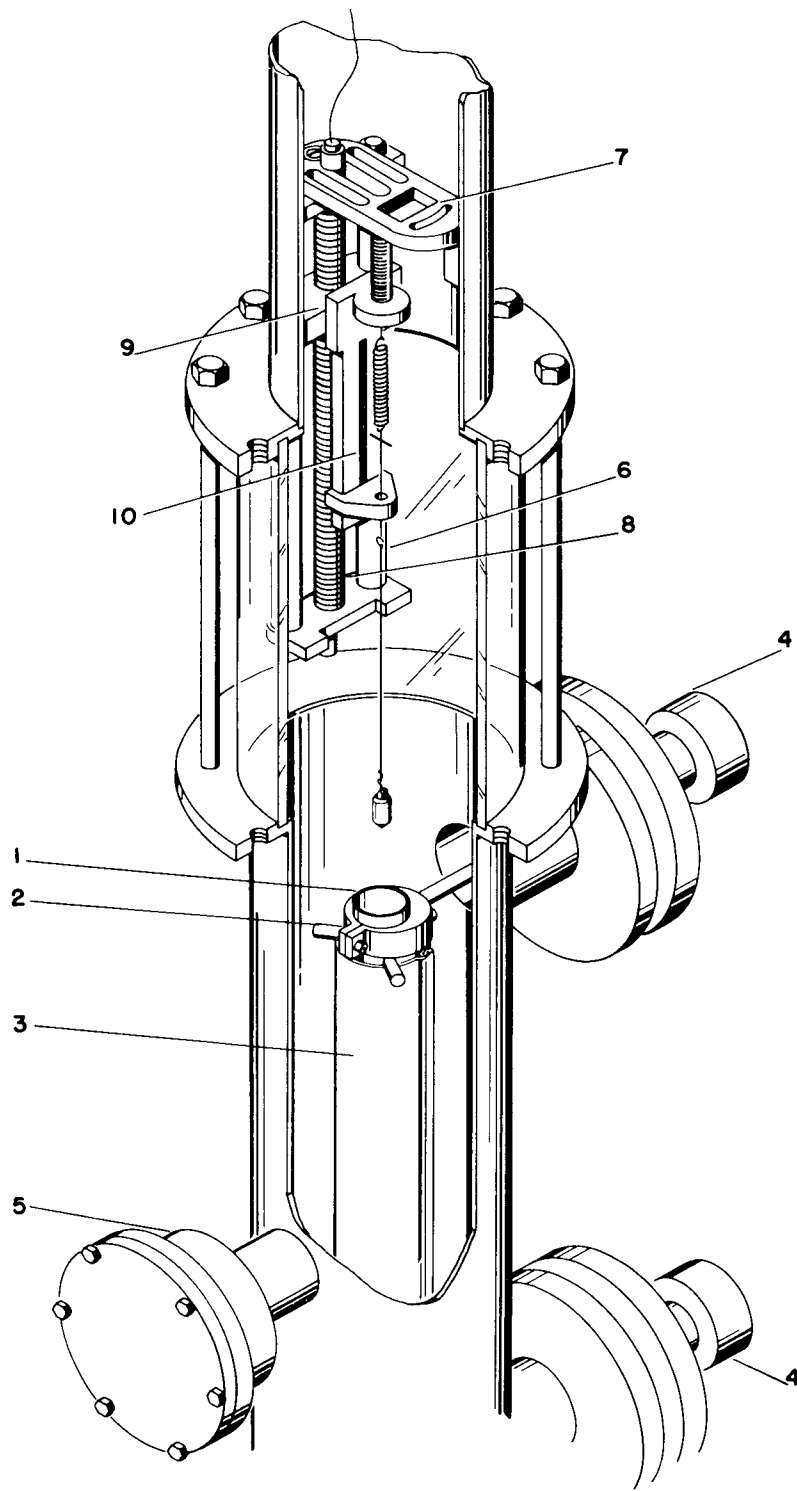


Fig. 1. Top of furnace and measuring apparatus.

of the top portion of the furnace and of the measuring apparatus is shown in Figure 1. The furnace assembly consists of an axially mounted oil diffusion pump, cold trap, and furnace casing. The furnace proper consists of an Inconel tube (1), supported by two stainless steel end grips (2), which screw into two vacuum-tight, water-cooled, electrically-insulated, terminal blocks (4). The end grips also support nickel-foil radiation shields (3). Inside the heater tube, at a lower end, are mounted radiation shields which support a chromel-alumel thermocouple extending to the bottom of the crucible support. The crucible, which is inserted inside the tube furnace, is held away from the sides of the furnace by fired Lavite spacing blocks. Also fastened to the crucible are two chromel-alumel thermocouples which are led out of the top of the furnace tube to Kovar thermocouple feed-through seals at (5).

#### Weighing Mechanism

The top of the furnace housing terminates in a flange plate which is drilled and tapped for stay bolts and is grooved for an "O" ring and a pyrex glass cylinder. A housing having a flange plate similar to the one on the furnace housing is placed over the glass cylinder. During operation the entire assembly is rigidly held together by means of stay bolts. The upper end of the housing (not shown) terminates in a plate with a centrally located viewing port into the crucible, and a Sylphon bellows rotary seal. Inside the housing is mounted a track (6) which can be positioned on the support

(7). The track screw (8) and the rotary seal are linked together by a flexible shaft. The track carries a block (9) which can be moved vertically by means of the track screw. Fastened to this block is a quartz spring support (10) which has a solenoid at the top and an adjustable stop at the bottom. On the armature of the solenoid is a hook to which the top of a quartz spring is fastened. A cross having loops at each end of the longer member is used to connect the spring to the bob wire and as a stop to prevent the elongation of the quartz spring beyond its designed limit.

#### Electrical Controls

Power for the tube furnace is provided by a 220 volt primary and a 5 volt, 400 amp secondary transformer. The primary voltage is adjusted by means of a 2.4 KVA powerstat. Inserted in one lead to the primary is a 5 ohm, 50 watt rheostat which can be short-circuted by a relay. This relay is controlled by a Brown temperature controller operated from the furnace thermocouple. With the relay closed, the primary voltage is adjusted to give a temperature slightly higher than is desired. The rheostat is then adjusted during operation to give the desired temperature. The crucible thermocouples go to a strip recorder and a potentiometer. Safety controls on the water flow and vacuum system are incorporated to turn off the diffusion pump and furnace in the event of either water or vacuum failure.

## Crucible and Bob

Plutonium is an extremely active material owing to its chemical properties and to its surface tension and creeping properties. Although ceramic materials<sup>2</sup> can be used for containers of melts and alloys, they cannot be employed with plutonium because this material will creep through the crucible walls or react with the crucible or both. However, investigations<sup>3</sup> have revealed that no intermetallic compounds are formed with vanadium, chromium, niobium, molybdenum, tantalum, or tungsten and that these elements have sufficiently low solubilities in molten plutonium so that they can serve as containers. Because of density, availability, and solubility considerations, tungsten was chosen for the bob and tantalum for the crucible and support wire.

## PROCEDURE

The bob with its support wire is adjusted so that it is above the specimen position and centered with respect to the crucible.

The furnace, crucible, and bob are degassed at 850°C until the pressure in the system is below  $1 \times 10^{-5}$  mm. The system is then cooled and the vacuum broken with either helium or argon gas. The plutonium, in the form of a freshly machined rod of smaller than crucible diameter, is added to the crucible. The system is evacuated and heated slowly through the melting point to permit the degassing of the melt. Then the bob is lowered into the molten metal and the depth

adjusted so that the bob is completely immersed but so that it will not strike the bottom of the crucible during operation of the solenoid. Experience has shown that, even with freshly machined material, an oxide skin is formed on the molten metal so strong that it will completely support the bob. At temperatures between 825 and 850°C this film breaks, permitting wetting of the bob, crucible, and wire. To ensure that the bob is not sticking, it is oscillated at each temperature by operating the solenoid. Then the elongation of the spring is measured with a cathetometer until at least three consistent readings are obtained. From the oscillation periods, evidence of the changes in melt viscosity can be obtained.

The quartz springs were calibrated directly by measuring their elongations as a function of the weight suspended from them. The volumes of the bobs were determined by weighing them in and out of bromobenzene, the density of the bromobenzene being determined at the same time by means of a Westphal balance. The equation used for calculation of the density of the liquid plutonium, applying a surface tension correction is:

$$\rho = (m - K\delta l)/v + 2\pi r \cos \theta \gamma/vg \quad (1)$$

where  $m$  is mass of bob,  $K\delta l$  is the mass corresponding to spring elongation  $\delta l$ ,  $v$  is volume of bob,  $r$  is radius of wire,  $\theta$  is contact angle of liquid with wire,  $\gamma$  is the surface tension and  $g$  is gravitational constant at the location. Corrections were made for thermal

expansion of the bob by means of the following equation:

$$V = V_0 \left[ 1 + 3\alpha (T - T_0) \right] \quad (2)$$

where  $\alpha$  is the coefficient of linear expansion,  $T_0$  is the temperature of calibration,  $T$  is the temperature of measurement, and  $V_0$  is the volume at  $T_0$ . If different bob volumes and wires are used, it is possible to solve for both the density and  $\gamma \cos \theta$ .

## EXPERIMENTAL RESULTS

### Pure Plutonium

Two density determinations were made on pure plutonium. From the observed spring elongation at various temperatures and the mass of the bob, the bouyant force was calculated using the equation:

$$F = m - K\delta l = \rho v + 2\pi r \cos \theta \gamma / g \quad (3)$$

where the symbols have the meanings given in equation (1). Next the observed forces were least-squared to linear and quadratic equations. From the size of the quadratic term and the experimental error, it appeared that the data would best fit the linear equation. A value for  $\gamma \cos \theta$  was obtained by solving the two least-squared force equations simultaneously and correcting for thermal expansion of the tungsten bob. Observed densities were then calculated using surface tension and expansion corrections and these values least-squared to a linear equation to obtain the final density equation. A tabulation of the data follows and they are also shown in Figure 2.

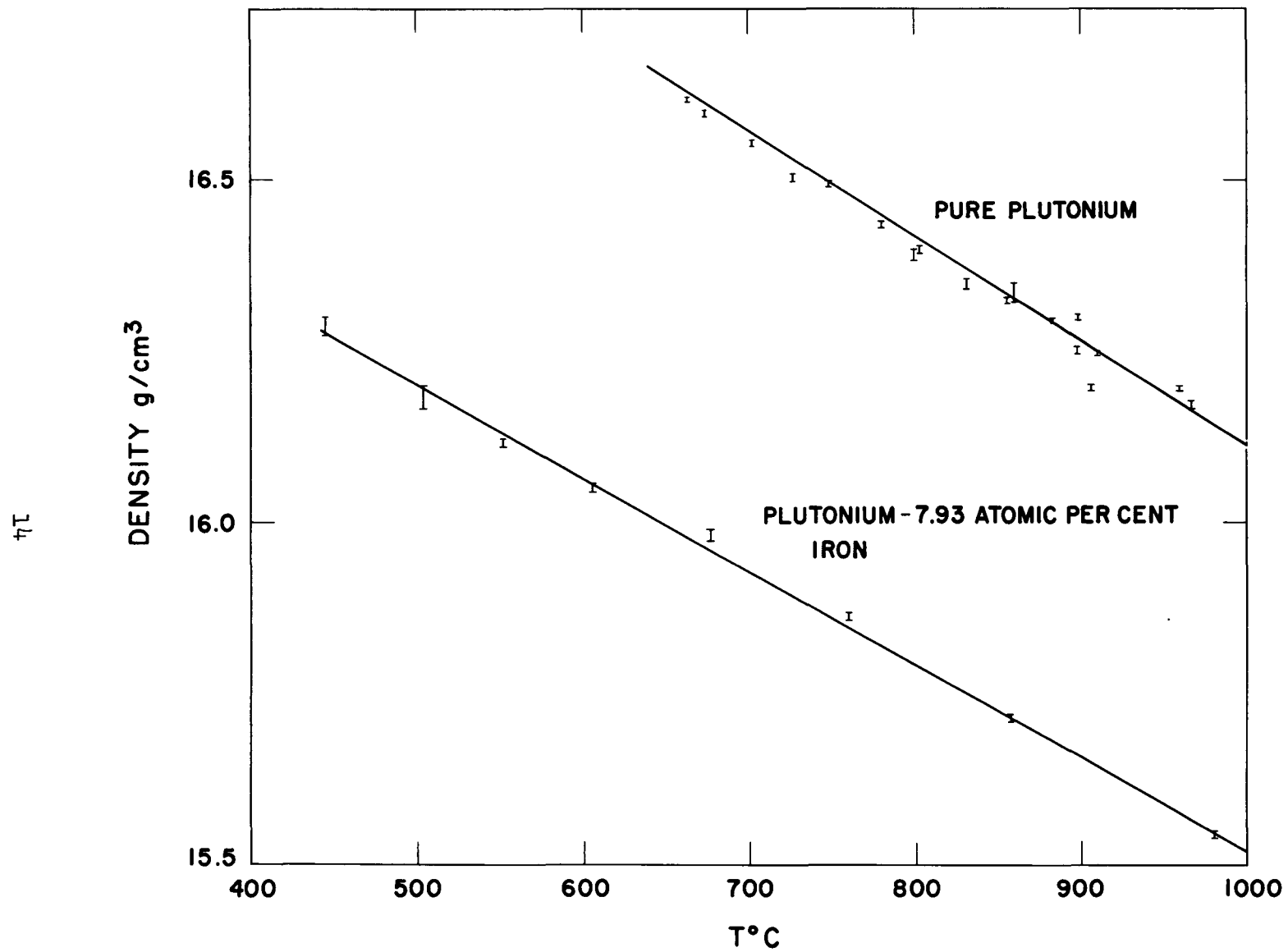


Fig. 2. Density vs temperature of plutonium-iron alloy.



	Determination 1	Determination 2
Temperature (°C)	674 - 960	655 - 960
Mass of bob (g)	20.8603	16.7440
Volume of bob at 23°C (cm <sup>3</sup> )	1.0839	0.8701
Radius of wire (cm)	0.0125	0.00625
Gravity acceleration (cm/sec)	979.13	979.13
Thermal expansion of Tungsten <sup>4</sup> (cm/cm - °C)	$4.4 \times 10^{-6}$ (20 - 630°C)	$5.1 \times 10^{-6}$ (630 - 1340°C)

Linear least-squared forces

$$F_1 = \left[ 18.95_1 - \left( 1.25_1 \times 10^{-3} \right) T \right] \pm 0.027 \text{ g}$$

$$F_2 = \left[ 15.23_8 - \left( 1.02_7 \times 10^{-3} \right) T \right] \pm 0.008 \text{ g}$$

Quadratic least-squared forces

$$F_1 = \left[ 18.94_6 - \left( 1.23_1 \times 10^{-3} \right) T - \left( 8.3 \times 10^{-9} \right) T^2 \right] \pm 0.029 \text{ g}$$

$$F_2 = \left[ 15.46_4 - \left( 1.59_6 \times 10^{-3} \right) T - \left( 3.5 \times 10^{-7} \right) T^2 \right] \pm 0.005 \text{ g}$$

Surface tension (plutonium against tantalum in vacuo)

$$\gamma \cos \theta = 1030 - (0.967) T \text{ d/cm}$$

Least-squared density (corrected for thermal expansion of bob and surface tension)

$$\rho = \left[ 17.56_7 - \left( 1.45_1 \times 10^{-3} \right) T \right] \pm 0.021 \text{ g/cm}^3$$

where T is °C.

## Plutonium-Iron Alloy

A single determination was made of the liquid density of a plutonium-7.93 atomic percent iron alloy. In this determination a tungsten support wire was used. Since the surface tension correction is a small one, it was assumed that  $\gamma \cos \theta$  would not be significantly different in this case than for tantalum and unalloyed plutonium. A correction for thermal expansion of the bob was made. The data were least-squared to a linear equation and the following values obtained (see also Figure 2):

$$m = 20.7647 \text{ g}$$

$$v = 1.0783 \text{ cm}^3 \text{ at } 23^\circ\text{C}$$

$$r = 0.0113 \text{ cm}$$

$$F = \left[ 18.12_7 - (1.17_0 \times 10^{-3}) T \right] \pm 0.014 \text{ g}$$

$$\rho = \left[ 16.88_8 - (1.36_9 \times 10^{-3}) T \right] \pm 0.012 \text{ g/cm}^3$$

## DISCUSSION OF RESULTS

Plutonium, like bismuth, is an element whose density as a liquid is greater than that of the solid at the melting point. Although the oscillation period of the spring provided no quantitative data on the viscosity, it did show that the viscosity of liquid plutonium decreases with increasing temperature. Measurements of the contact angles on solidified melts gave values of between 20 and 30° on tantalum. The values of  $\gamma \cos \theta$  may be slightly in error due to the solution of the wire.

The plutonium-iron alloy showed a greater than calculated decrease in the liquid density when compared with unalloyed plutonium. Calculations of the volume of mixing give a positive volume of mixing of 1 to 2 percent at 600°C, depending on the molar volume assumed for iron. This is consistent with the plutonium-iron phase diagram. The thermal expansion coefficient of the liquid alloy is also significantly less than that of pure plutonium.

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