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**The Behavior of Oxygen Partial
Pressure Over Slightly
Substoichiometric Plutonia at 1410 K**

Ernest W. Johnson

MASTER

August 31, 1982

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Abstract

Monsanto Research Corporation is charged with processing encapsulated plutonium dioxide heat sources into radioisotopic thermoelectric generators (RTGs) to support deep-space missions. One of the problems associated with the sometimes protracted ground storage of these devices is the ingrowth of carbon dioxide and carbon monoxide in the gas phase due to the cyclical reaction established between the fuel ($^{238}\text{PuO}_2$) and the carbon impact body. This ingrowth proceeds according to the two equations:

To reduce this effect, a gas management system was instituted that enabled periodic removal of the generated CO and CO_2 with replacement by argon. The removal of these components was monitored and permitted an assessment of the degree of substoichiometry as well as its effect on the chemical activity of the CO and CO_2 . This in turn was used to estimate the oxygen activity and to calculate $\Delta\bar{G}(\text{O}_2)$ as a function of stoichiometry.

1. Introduction

Monsanto Research Corporation is charged with processing encapsulated plutonium dioxide heat sources into radioisotopic thermoelectric generators (RTGs) to support deep-space missions. One of the problems associated with the sometimes protracted ground storage of these devices is the ingrowth of carbon dioxide and carbon monoxide in the gas phase due to the cyclical reaction established between the fuel ($^{238}\text{PuO}_2$) and the carbon impact body. This ingrowth proceeds according to the two equations:

This reaction stops after launch because the two solid-phase reactants are physically separated when the inside of the RTG is evacuated to space for performance reasons. When the RTG is stored on the ground, however, the product gases become established and can cause degradation of the solid-state thermoelectric elements. Controlling the reduction of the plutonia to such an extent that Equation 1 becomes thermodynamically unfavorable minimizes the continued generation of CO and CO_2 .

To minimize this effect, the General Purpose Heat Source (GPHS) modules, after

assembly, are welded into stainless steel containers and attached to a manifold which permits controlled analyses, gas exchanges, and evacuations of the cover gas. Two 250-W modules are placed in each MRMF* container. The insulation properties of the carbon parts both used as physical barriers between the container and the module itself result in a fuel temperature calculated to be 1410 K. A schematic of the GPHS module is shown in Figure 1.

2. Individual Gas Tap Analyses

During the gas tapping operations, a sample of the cover gas is withdrawn. Evacuation of the canister containing the fuel modules is continued until the pressure is <0.1 Pa, whereupon the canister is filled with purified argon. After a week or two, the gas tap, evacuation, and the backfill process is repeated.

From PVT data taken during a gas tap, one can then calculate the quantity of oxygen removed from the fuel at each gas exchange. The total quantity of plutonia in two GPHS modules is 4.63 mole, so the fuel stoichiometry at each exchange can be calculated. As the initial composition is O/Pu = 2.00, the stoichiometry as a function of number of gas exchanges is as shown in the last column of Table 1.

One can calculate the free energy by considering the reaction

$$-\Delta G_T^O = 67,500 - 20.75^*$$

$$= 2.3 RT \log \frac{P(CO)_2}{P(CO) P(O_2)^{1/2}}$$

or

$$\log P(O_2) = 2 \left[\frac{(20.75 T - 57,500)}{2.3 RT} + \log P(CO_2) - \log P(CO) \right].$$

At the calculated temperature of 1410 K,

$$\log P(O_2) = 2 \left[-5.93 + \log P(CO_2) - \log P(CO) \right].$$

These values are provided in Table 2.

The "experimental" system suffers from nonisothermal conditions, however. The effective temperature of the carbon, by utilizing Reaction (2), can be estimated by the following:

$$\Delta G_T^O = -2.3RT \log \frac{P(CO)^2}{P(CO_2)} = 40,800 - 41.7T.*$$

Then

$$T = \frac{40,800}{41.7 - 2.3R \log \left[P(CO)^2 / P(CO_2) \right]}.$$

From this expression, calculated carbon temperatures are given in Table 2. The recommended value is 875 K, as it is known that the first value was low as the result of a large quantity of helium which increased markedly the thermal conductivity. The last value has a large amount of error as the result of the small values of the pressures. Therefore, the actual effective carbon temperature is taken as 875 K.

*Module Reduction and Monitoring Facility.

*Data taken from Reference 1.

Department of Energy

GENERAL PURPOSE HEAT SOURCE

FIGURE 1 - General purpose heat source.

Table 1 - GAS TAP DATA FROM THE ORIGINAL MRMF TWO-MODULE CONTAINER

Gas Tap Number	Pressure (atm)		Log (atm)		O/Pu
	CO	CO ₂	CO	CO ₂	
1	0.0326	0.0310	-1.49	-1.51	1.99973
2	0.0396	0.0159	-1.40	-1.80	1.99953
3	0.0197	0.0037	-1.70	-2.43	1.99945
4	0.0075	0.0008	-2.12	-3.05	1.99942
5	0.0016	0.0001	-2.80	-4.00	1.99941

The value for effective carbon temperature is not unreasonable. The stainless steel container surface is steady at slightly under 570 K. Although container interference has been noted at higher temperatures, it is evident from the wide range of CO and CO₂ pressures that the stainless steel participation is not a factor here.

From these observations one may calculate the partial molal free energy of oxygen in slightly substoichiometric plutonia, $\bar{G}(\text{O}_2)$, by the following:

$$(\text{O}_2)_{\text{ref}} = [\text{O}_2]_{\text{PuO}_x}; \quad (4)$$

$$\bar{G}(\text{O}_2) = 2.3 \text{ RT } \log P(\text{O}_2).$$

These values are shown in Table 2 for the five gas taps performed.

Figure 2 shows the values from this analysis plotted as triangles. The location of this work's curve infers that the actual fuel temperature is lower than the calculated values, or that the initial stoichiometry is lower than the assumed 2.000.

The technique employed in this evaluation is quite different from others. Usually a flowing gas (H₂/H₂O or CO/CO₂) is employed to control the oxygen activity over the fuel. Weights can be a problem also. The advertized accuracies in O/M are ± 0.001 (Swanson) and ± 0.002 (Woodly). Because of the large quantity of plutonia (4.63 mole), accuracy of the gas phase analyses ($\sim \pm 0.5\%$), and the fact that all oxygen is originating from the fuel itself, the O/M value is probably accurate to ± 0.00002 O/M units.

The problems in this study concern temperature: gradients and unmeasurability. The 500 W exiting the 15 cm long by 15 cm diameter stainless steel container results

Table 2 - DATA MEASURED IN TABLE 1 CAN BE EMPLOYED TO DETERMINE SOME THERMODYNAMIC PROPERTIES OF THE TWO-MODULE CONTAINER

Tap Number	O/Pu	Effective Carbon T, K	Log P(O ₂)	$\Delta \bar{G}(\text{O}_2)$
			atm	cal/mole
1	1.99973	843	-11.90	-76,770
2	1.99953	881	-12.66	-81,670
3	1.99945	883	-13.32	-85,930
4	1.99942	869	-13.72	-88,510
5	1.99941	833	-14.26	-91,990

FIGURE 2 - Data from Reference 2 for plutonia (dots) with MRC data (triangles) for the oxygen potential as a function of stoichiometry. The diamonds are calculated from multiple storage can data.

in rather severe gradients. As this heat source is a "prime" or flight-type unit, one cannot measure the actual fuel temperature, although earlier measurements on an electrically heated mock-up were used to estimate the fuel temperature. A positive consideration is the steadiness of the heat flux. The 87+ yr half-life of the plutonium-238 results in an essentially nonvarying temperature plagued only by the time-dependent increase in gas thermal conductivity between each gas tap that results from the small accretion of helium generated by the alpha decay of the plutonium-238.

In general, the method could be employed to measure accurately O/M values very close to 2. The study shows that one decreases the CO activity by a decade every four or so gas exchanges, and that the actual temperature is probably lower than the calculated value as there is an extremely steep rise in $-\Delta\bar{G}(O_2)$ over relatively small stoichiometry changes.

3. Open-Manifold Analyses

The foregoing analysis was of the initial closed container test phase. After that test, three additional cans were attached

to the manifold. The interim mode was changed to permit the reduction scheme to occur in a large volume (cans plus manifold) between gas exchanges/evacuations/analyses. The four cans contained a total of 18.52 moles of plutonia.

The techniques elaborated on earlier were used to obtain the data in Table 3.

The five $\Delta\bar{G}(O_2)$ values for this analysis are shown in Figure 2 as diamonds. Although scatter is evident, the first point (N = 1) suffers from a large helium inventory (16.5%), which no doubt lowered the plutonia temperature by 30 to 50 K or so. Whatever the case, these values appear much more in line with other measurements at the calculated 1410 K (1137°C) temperature.

[Note: A calculation of effective carbon temperature yielded a value of 976 $\pm$ 16 K, or about 100 K hotter than the single closed-can experiment. The room temperature had increased by about 10 K (spring-time vs. winter, more cans dumping heat into the room), and a small standoff insulation pad is now being used to insulate each can from the support cradle. This should not cause a 100 K difference, however.]

Table 3 - OPEN MANIFOLD ANALYSES FOR FOUR MRMF CANS

N	O/Pu	Log P(CO) atm	Log P(CO ₂) atm	Log P(O ₂) atm	$\Delta\bar{G}(O_2)$ Kcal/mole
1	1.99776	-0.707	-1.559	-13.56	-87.5
2	1.99603	-1.103	(-2.167) ^a	-13.99	-90.3
3	1.99430	-1.474	(-2.775) ^a	-14.46	-93.3
4	1.99393	-1.591	(-3.382) ^a	-15.44	-99.6
5	1.99348	-1.734	-3.103	-14.60	-94.2

^a Parentheses indicate CO₂ pressures were calculated assuming that the first point has a slope of -0.588 on a semilog plot of P as a function of N.

4. Oxygen/Plutonium

If one sums all the oxygen that has appeared through open manifold Tap 12 (as of June 11, 1982), the following tabulation results:

Gas Taps 1-5 (on V-1)	5.4 mmole [0]
V-1 Storage Can	(8.0) mmole [0]
V-5 Storage Can	(2.4) mmole [0]
V-1/V-5/V-7/V-9 (open)	38.1 mmole [0]
Manifold (open)	<u>73.5 mmole [0]</u>
	127.4 mmole [0]

As the total plutonia is 18.48 mole, the resultant stoichiometry, O/Pu ratio, is 1.9931. Table 4 provides that information on an individual measurement format. Comparison of these data with Table 2 values for an isolated can shows that the added ballast volume permits a much-enhanced reduction of the fuel (essentially another order of magnitude).

Table 4 - GAS ANALYSES FOR CO AFTER V-1 AND V-5 MRMF CANS WERE RECANNED

Number	Date	Can Number	CO			Manifold
			(%)	P(kPa)	(mmole)	CO (mmole)
1	02/03/82	V-1	---	---	---	---
		V-5	3.97	4.5	1.38	
2	02/15/82	V-1	1.3	1.6	0.5	(2.1)
		V-5	6.7	8.1	2.4	
3	02/24/82	V-5	4.4	5.4	1.6	---
4	03/03/82	V-1	4.1	5.0	1.5	9.8
		V-5	1.3	1.6	0.5	
5	03/18/82	V-1	0.3	0.4	0.1	3.6
		V-5	0.6	0.7	0.2	
6	03/26/82	V-1 + V-5	2.5	3.2	1.9	17.4
		V-7 + V-9	15.5	19.9	12.8	
7	04/07/82	V-1 + V-5	1.5	1.3	1.1	5.8
		V-7 + V-9	6.7	8.0	4.8	
8	04/16/82	V-1 + V-5	1.7	1.4	1.2	17.1
		V-7 + V-9	2.9	3.4	2.1	
9	04/30/82	V-1 + V-5	1.2	1.4	0.8	6.2
		V-7 + V-9	2.2	2.6	1.6	
10	05/14/82	V-1 + V-5	1.1	1.3	0.8	4.6
		V-7 + V-9	1.6	1.9	1.1	
11	05/28/82	V-1 + V-5	0.7	0.6	0.5	3.1
		V-7 + V-9	0.8	0.7	0.6	
12	06/11/82	V-1 + V-5	0.4	0.5	0.3	4.6
		V-7 + V-9	0.5	0.6	0.4	
Total mmoles [0]				38.1		73.5

Note: In general, CO₂ pressures were undetected and, thus, their contribution to oxygen depletion from the fuel is ignored.

5. Conclusions

The open manifold-ballast volume system permits the in situ reduction of plutonia in assembled GPHS modules to the extent that the partial pressure of carbon monoxide can be reduced to levels which can be accommodated in subsequent processing and ground storage of the GPHS RTG.

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