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THERMODYNAMIC FUNCTIONS FOR PURE PLUTONIUM

by

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Abstract

Values for heat capacity, enthalpy and entropy increments, free energy function, vapor pressure, and heat and entropy of vaporization for solid and liquid plutonium at temperatures from 298.16 to 2500°K are tabulated. Heats of transition are also included.

Introduction

Thermodynamic functions for pure plutonium are presented here in tabular form and as analytic expressions. Generally the table values are more accurate than the analytic expressions, but the analytic expressions represent the data accurately enough for most practical thermodynamic calculations. Where measured values for properties were not available, estimates were made. The calculations are described in some detail so as to simplify the task of revising the tables should more or better measurements become available.

Transition Temperatures

Although knowledge of exact transition temperatures is of importance for many purposes, errors of a few degrees in a transition temperature make little difference in the thermodynamic quantities in the present tables.

Several values are available for each of the transition temperatures in pure plutonium.[1a] Apparently these temperatures are sensitive to small amounts of impurities, and it is believed that the variation in results reported from different laboratories is a consequence of variation in metal purity. The temperatures quoted by Jette[2] were chosen for this paper because it is thought that they were obtained with metal of higher purity than that used in other investigations.

Heats of Transition

Heats of transition are also available from several sources. Pascard[3] gives values derived from the areas under thermal analysis curves with an estimated accuracy of ± 20%. Dean, Kay and Loasby[4] have measured the heat capacities of the various allotropes and the heats of transition by a calorimetric method involving adiabatic self-heating. Loasby[5] has reported more recent data from the same laboratory. Konobeevsky[6] et al. also give heats of transition determined calorimetrically. Sandenaw and Gibney[7] and also Schonfeld[1b] give values for the $\alpha \rightarrow \beta$ heat. Schonfeld's number is computed from measurements of the pressure coefficient of the transition temperature while Sandenaw and Gibney obtained their result in an adiabatic self-heating experiment. The only way to assess the reliability of all these data is by intercomparison. Within the stated limits of accuracy of each set, Pascard, Konobeevsky and Loasby are all in quite good agreement, and the values chosen for this tabulation are the choices which give the best agreement with all three sets of data.

Bridgman[8] also gives a value for the $\alpha - \beta$ heat derived from the pressure coefficient of the transition temperature. This is far out of line with the others and was not used.

Heat Capacities

Analytic expressions for the heat capacities of the allotropes have been derived from Loasby's tabulated values[5] and used to compute the tables. Lacking any data except Loasby's for the heat capacity of liquid plutonium this has been taken to be a constant 10.0 cal/g-atom over the entire liquid range. This is a fairly important number for the present tables, but there appears to be no reasonable way to estimate it.

Low Temperature Measurements

Sandenaw et al.[9] have measured the heat capacity of plutonium between about 4°K and room temperature by an adiabatic self-heating method. Various bumps and dips were found in the heat capacity curve, and the heat capacity over certain temperature ranges was not reproducible. The effects are presently attributed to radiation damage which occurs at low temperatures and anneals out with a consequent unpredictable energy release at higher temperatures. This lack of reproducibility of the heat capacity at low temperatures casts some doubt on the $H^o_{298} - H^o_o$ and S^o_{298} values calculated from the heat capacity measurements, but as the most recent figures[9] are about what would be estimated anyway, these values were used in computing the tables.

Vaporization Data

Phipps et al.[10] have measured the vapor pressure of liquid plutonium in the range 1392 to 1793°K by the Knudsen effusion technique. This is the only vapor pressure information presently available. Their equation is $\log p_{mm} = (-17587 \pm 73)/T + (7.895 \pm 0.047)$. The heat of vaporization in the measured temperature range is given as 80.46 ± 0.34 Kcal/g-atom, and the entropy of vaporization as 22.94 ± 0.22 cal/deg/g-atom. Although these data appear to be quite acceptable, some reservations are attendant on their use. The first is that a tantalum container was used, and some tantalum was undoubtedly dissolved in the liquid plutonium. This alone probably leads to a small correction for the lowering of the plutonium activity. However, Rauh and Thorn[11] have measured the vapor pressure of liquid uranium in a tantalum cell and have found a large decrease of the vapor pressure apparently somehow caused by oxygen. The effect is not completely understood but may be connected with the liquid uranium-tantalum alloy dissolving more oxygen than does pure uranium. Whatever the explanation, similar effects are expected on the vapor pressure of plutonium, and the influences of oxygen and tantalum should be investigated to insure that the vapor pressure measurement is correct.

As no spectroscopic information for the gaseous plutonium atom is available, the free energy function for plutonium monatomic gas was estimated as explained below.

The heats of vaporization of plutonium were obtained by a Third Law treatment of the data of Phipps et al. as follows: The absolute entropy of Pu(g) at 298.16°K was estimated to be the same as that of U(g), 47.73 cal/deg/g-atom.[12] This with the S^o_{298} for solid plutonium gives $\Delta S^o_{298} = 35.43$ cal/deg/g-atom for the vaporization process. The average heat capacity changes for vaporization were estimated to be the same as those for the corresponding uranium processes. Thus $\Delta C_p = -3.1$ for s → g and $\Delta C_p = -2.6$ for ℓ → g. The quantities in Table II were calculated by using the estimated ΔC_p's and ΔS_{298} and assuming that the vapor pressure of Phipps et al. at 1600°K was correct. In the range of Phipps' measurements, the vapor pressures so calculated agree well with his experimental data.

The analytic expression for the vapor pressure was calculated from the tabulated values at 1000°K and the estimated ΔC_p. The normal boiling point was obtained from the analytic expression. If it is assumed that $H_{298.16} - H_o$ for monatomic plutonium gas is the same as for uranium, 1553 cal/g-atom,[12] then $\Delta H_o^o = 91800$ cal/g-atom for the heat of vaporization of solid plutonium at 0°K.

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TABLE I. HEATS OF TRANSITION

	T, °K	ΔH, cal/g-atom	ΔS, cal/deg/g-atom
α - β	395	900 ± 20	2.28
β - γ	479	160 ± 10	0.33
γ - δ	592	148 ± 15	0.25
δ - δ'	724	10 ± 10	0.01
δ' - ϵ	753	444 ± 10	0.59
ϵ - liquid	913	676 ± 10	0.74

$H^o_{298} - H^o_o (s, \alpha) = 1500 \pm 100$ cal/g-atom

$S^o_{298} (s, \alpha) = 12.30 \pm 0.50$ cal/deg/g-atom

Average C_p for Pu(s) from 298 to 913°K is 8.9 cal/deg/g-atom

TABLE II. CONDENSED PHASES

T, °K	C_p	$H_T - H_{298}$	$S_T - S_{298}$	$-\left(\frac{F_T - H_{298}}{T}\right)_{s,\ell}$
298	8.50	0	0	12.30
395 (α)	9.10	854	2.48	12.62
395 (β)	8.35	1754	4.76	12.62
400	8.35	1796	4.87	12.68
479 (β)	8.35	2456	6.38	13.55
479 (γ)	8.35	2616	6.71	13.55
500	8.70	2805	7.09	13.78
592 (γ)	9.65	3633	8.62	14.78
592 (δ)	9.00	3781	8.87	14.78
600	9.0	3853	8.99	14.87
700	9.0	4753	10.38	15.89
724 (δ)	9.0	4969	10.68	16.12
724 (δ')	(12.0)	4979	10.69	16.12
753 (δ')	(12.0)	5327	11.15	16.38
753 (ϵ)	8.4	5771	11.74	16.38
800	8.4	6166	12.25	16.84
900	8.4	7006	13.24	17.76
913 (ϵ)	8.4	7115	13.35	17.86
913 (ℓ)	9.9	7791	14.09	17.86
1000	10.0	8657	15.00	18.64
1100	10.0	9657	15.95	19.47
1200	10.0	10657	16.81	20.23
1300	10.0	11657	17.61	20.94
1400	10.0	12657	18.35	21.61
1500	10.0	13657	19.03	22.23
1600	10.0	14657	19.68	22.82
1700	10.0	15657	20.29	23.38
1800	10.0	16657	20.86	23.91
1900	10.0	17657	21.41	24.42
2000	10.0	18657	21.92	24.89
2100	10.0	19657	22.41	25.35
2200	10.0	20657	22.88	25.79
2300	10.0	21657	23.32	26.20
2400	10.0	22657	23.74	26.60
2500	10.0	23657	24.15	26.99

TABLE III. Pu MONATOMIC GAS

T, °K	$H_T - H_{298}$	$S_T - S_{298}$	$-\left(\frac{F_T - H_{298}}{T}\right)_g$	ΔH_T	ΔS_T	$-\log_{10}K_p$
298	0	0	47.73	91870	35.43	59.66
400	580	2.59	48.87	90650	33.15	42.29
500	1129	2.87	48.36	90180	31.21	32.60
600	1709	3.96	48.84	89730	30.40	26.04
700	2299	4.87	49.32	89420	29.92	21.38
800	3392	6.32	49.81	89100	29.50	17.90
900	3478	6.35	50.22	88340	28.54	15.22
1000	4186	7.09	50.63	87400	27.52	13.09
1100	4926	7.79	51.04	87140	27.27	11.35
1200	5666	8.43	51.44	86880	27.05	9.91
1300	6406	9.04	51.84	86620	26.86	8.69
1400	7146	9.57	52.20	86360	26.65	7.66
1500	7886	10.07	52.55	86100	26.47	6.76
1600	8626	10.55	52.89	85840	26.30	5.98
1700	9366	11.00	53.22	85580	26.14	5.29
1800	10110	11.42	53.54	85320	25.99	4.68
1900	10850	11.83	53.85	85060	25.85	4.13
2000	11590	12.21	54.15	84800	25.72	3.65
2100	12330	12.57	54.43	84540	25.59	3.21
2200	13070	12.92	54.71	84280	25.47	2.81
2300	13810	13.25	54.97	84020	25.36	2.44
2400	14550	13.55	55.22	83760	25.24	2.11
2500	15290	13.86	55.48	83500	25.14	1.81

For vaporization: ΔC_p = -3.1 cal/deg/g-atom (298 - 913°K)

ΔC_p = -2.6 cal/deg/g-atom (913 - 2500°K)

Analytic expression: $\log p \text{ (atm)} = 27.535 - 22923/T - 5.988 \log T$

Boiling point at 1 atm: 3727°K

ΔH_o^o = 91800 cal/g-atom