

THERMODYNAMIC PROPERTIES OF P₄

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The thermodynamic functions of P₄(g) calculated by Thyagarajan and Cleveland, (1960; 1961) were based upon frequencies corrected semiquantitatively for anharmonicities (Pistorius, 1958) which resulted in approximate zero order frequencies. A more accurate set of functions is obtained if the fundamentals rather than zero order frequencies are used in the rigid-rotor harmonic-oscillator approximation. This results in a partial correction for the anharmonicities (Herzberg, 1945). The functions in Table 1 are based

upon the assignment of Gutowski and Hoffman, (1950) and a P-P bond distance of 2.21°A. (Maxwell, Hendricks and Mosley, 1955).

A third law entropy of 66.9 ± 0.2 cal. deg.⁻¹ mole⁻¹ at 298.15°K. results from the calorimetric (Maples, 1949) and vapor pressure (Dainton and Kimberly, 1950) measurements in good agreement with the statistical value obtained with the fundamentals. The use of the approximate zero order frequencies leads to a value of 66.4 (Thyagarajan and Cleveland, 1961).

TABLE 1. Functions Derived from Fundamental Frequencies.

T°K	cal. mole ⁻¹ deg. ⁻¹			kcal. mole ⁻¹
	C _P ^o	S ^o	-(F ^o -H ^o) 298.15 ----- T	H ^o -H ^o 298.15
0	0.000	0.000	Infinite	-3.378
100	8.899	53.486	79.150	-2.566
200	13.294	61.010	68.285	-1.455
298.15	16.051	66.893	66.893	0.000
300	16.088	66.992	66.893	0.030
400	17.510	71.837	67.544	1.717
500	18.281	75.835	68.814	3.510
600	18.735	79.212	70.273	5.363
700	19.022	82.123	71.763	7.252
800	19.214	84.676	73.221	9.164
900	19.348	86.947	74.622	11.093
1000	19.445	88.991	75.958	13.033

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