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Fundamental Research Branch

HEATS OF FORMATION OF PHOSPHORUS OXIDES

Progress Report on Work Performed in the Period June 1, 1963, to November 30, 1963, Under Contract CMLMC-PA-2B-RFP-129

By

E. P. Egan, Jr., and B. B. Luff

Wilson Dam, Alabama

Tennessee Valley Authority
Office of Agricultural and Chemical Development
Wilson Dam, Alabama
January 27, 1964

Director,
Directorate for Industrial and Engineering Services
Edgewood Arsenal, Maryland 21010

Attention: Contract Project Officer

Gentlemen:

We transmit herewith the third semiannual progress report on our work on the determination of the heats of formation of phosphorus oxides. The report covers work performed under contract CMLMC-PA-2B-RFP-129 during the period June 1, 1963, to November 30, 1963.

We are distributing copies as follows:

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Very truly yours,

K. L. Elmore

K. L. Elmore, Chief
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HEATS OF FORMATION OF PHOSPHORUS OXIDES

Progress Report on Work Performed in the Period June 1, 1963, to November 30, 1963, Under Contract CMLMC-PA-2B-RFP-129

This is the third semiannual report on the determination of the heat of formation from the elements at 25° C. of phosphoric oxide, $P_4O_{10}(c)$, in a bomb calorimeter. The first report, which covered the period June 1 to November 30, 1962, contained descriptions of the bomb calorimeter, the operation of the calorimeter, the measurement of temperature, and the calibration of the calorimeter with standard benzoic acid. Results were reported for the combustion of phosphorus purified by a wet-chemical method and sealed in thin-walled glass ampoules, and of phosphorus coated with a film of Lucite.

The second semiannual report, which covered the period December 1, 1962, to May 31, 1963, described the combustion of distilled phosphorus coated with Lucite, the construction of a separate oxygen jacket to fit on the outside of the bomb so that uncoated phosphorus could be used, and the preliminary results obtained from combustion of phosphorus in the jacketed bomb.

Correction Terms for P_4O_6 and HPO_3

Titration of the bomb washings indicated that a small amount of P_4O_6 was formed in all the combustions. Correction for the presence of P_4O_6 was based on the reaction

$$P_4O_6(liq) + 2O_2(g) = P_4O_{10}(c) \qquad (1)$$

The heat of formation from the elements of $P_4O_6(liq)$ has been reported as -540.0 kcal./mole (9); combination of this value with the reported heat of formation of $P_4O_{10}(c)$ of -720.0 kcal./mole (10) and the correction of $nRT = 1.185$ kcal./mole yields the value for the heat of combustion at constant volume of P_4O_6 (equation 1) of -172.015 kcal./mole which was used in previous corrections for P_4O_6. A more recent value for the heat of formation of P_4O_6 (5) is -392 kcal./mole when the heat of formation of P_4O_{10} is taken as -713 kcal./mole (6) or -399 kcal./mole at constant pressure when the heat of formation of P_4O_{10} is taken as -720 kcal./mole (10). The heat of reaction of equation 1 at constant pressure at 25° C. then becomes -321.0 kcal./mole, and addition of the term nRT = 1.185 kcal./mole yields -319.815 kcal./mole at constant volume for equation 1. This value was used for all combustion corrections in this report.

It was assumed that water formed in the combustion of an organic coating would react immediately with the P_4O_{10} to form a condensed phosphoric acid. The only condensed phosphoric acid for which any thermal datum is available is HPO_3. In previous reports (1, 2) the heat of reaction of

$$2H_2O(liq) + P_4O_{10}(c) = 4HPO_3(s) \tag{2}$$

was based on a heat of formation of $P_4O_{10}(c)$ of -720 kcal./mole (10) and of HPO_3 of -228.2 kcal./mole (10) to yield a heat of reaction of -14.041 kcal./mole of HPO_3. This heat of formation of HPO_3 is not well defined, and it is obvious from the results of the combustions of coated phosphorus reported previously (1, 2) and in this report that the correction for HPO_3 is in error, but there appears to be no better way to correct for the water formed in the combustions. If the correction for HPO_3 is omitted, the calculated values for the heat of combustion of phosphorus agree more closely, but it is unreasonable to eliminate the correction entirely.

In 1903 Giran (4) reported the following thermal values for the formation of HPO_3 from H_2O and P_4O_{10}.

$$P_4O_{10}(c) + 2H_2O(liq) = 4HPO_3(s) \qquad \Delta H = -42.54 \text{ kcal.} \tag{3}$$

$$P_4O_{10}(amorph) + 2H_2O(liq) = 4HPO_3(s) \qquad \Delta H = -28.58 \text{ kcal.} \tag{4}$$

Equation 3 yields -10.635 kcal./mole HPO_3 and equation 4 yields -7.145 kcal./mole HPO_3. The P_4O_{10} formed in the present combustions is the hexagonal crystalline modification, and the best compromise appeared to be to use the value of -7.145 kcal./mole HPO_3 as a correction for the water formed in the combustion process. This compromise is not unreasonable, since both the heat of formation of HPO_3 and the actual occurrence of the reaction in equation 2 are uncertain. This value of the heat of reaction for equation 2 has been used in all the combustion corrections in this report. The standard corrections and the primary data used in reduction to standard conditions are listed in Appendix A.

Phosphorus Coated with Lucite

The combustion of samples of phosphorus coated with Lucite has been discussed and the results are tabulated in previous reports (1, 2). These data were recalculated on the basis of the corrections for P_4O_6 and HPO_3 discussed above and are listed in Table I. The values listed in Table I are selected values, and the basis for the elimination of other values from the table are discussed in the final section of this report. All the values for combustions of Lucite-coated phosphorus are included in a table in Appendix D.

Jacketed Bomb

Operation of the Bomb: The jacketed bomb, Figure 1, was described in a previous report (2). After the jacket was flushed and filled with oxygen, the jacket valve was closed, and the bomb was assembled. To prevent blowing of solid P_4O_{10} from the bomb into the jacket during the rapid expansion of gas in the combustion, a loose glass-wool plug was placed in the 1/16-inch gas transfer line in the bomb head. During a combustion with the jacketed bomb, the jacket valve was opened at the start of the combustion period and 15 seconds was allowed for the oxygen in the jacket to enter the main bomb before the phosphorus sample was ignited.

Because of the increased mass and volume of the jacketed bomb which required a larger calorimeter bucket containing more water, the temperature rise was slower than with the bomb without the jacket. During the combustion period, which for the jacketed bomb was increased from the normal 15 minutes to 25 or 30 minutes, the temperature readings were taken at the rates of 6 to 8 readings per minute during the first 8 minutes, 2 readings per minute for the next 12 to 19 minutes, and 1 reading per minute during the last 5 minutes. There were thus obtained about 80 temperature readings during the combustion period, so that the temperature-rise curve was well defined. A typical temperature-rise pattern for a jacketed-bomb combustion is included in Appendix B.

TABLE I

Selected Heats of Combustion of Lucite-Coated Phosphorus

Weight, grams				$-\Delta E_c$, cal.					$-\Delta E_c$, kcal./mole
P_4	Lucite	P_4 equiv. of P_4O_6	ΔT, °C.	Substance	Lucite	HPO_3	P_4O_6	P_4	P_4
				Wet-method-purified phosphorus					
0.4128	0.0035	0.0017	1.05305	2405.052	22.289	1.998	4.388	2385.153	715.865
0.6009	0.0061	0.0019	1.53552	3508.494	38.847	3.483	4.905	3471.069	715.675
0.6547	0.0059	0.0023	1.67036	3816.892	37.573	3.369	5.937	3781.888	715.683
0.5452	0.0061	0.0019	1.39538	3187.976	38.847	3.483	4.905	3150.551	715.954
0.7309	0.0096	0.0023	1.87466	4284.129	61.136	5.481	5.937	4223.449	715.919
0.6547	0.0008	0.0022	1.65695	3786.251	5.095	4.457	5.679	3786.379	716.533
0.7025	0.0117	0.0024	1.80783	4131.265	75.509	6.680	6.195	4056.271	715.377
0.7380	0.0047	0.0025	1.87872	4293.444	29.931	2.683	6.453	4267.283	716.390
0.7133	0.0019	0.0024	1.80557	4126.161	12.100	1.085	6.195	4119.172	715.471
0.7654	0.0043	0.0026	1.94604	4447.419	27.384	2.455	6.712	4424.292	716.160
0.7037	0.0039	0.0025	1.78756	4084.954	24.836	2.227	6.453	4064.344	715.579
				Distilled phosphorus					
0.67482	0.00248	0.00227	1.70593	3898.279	15.793	1.416	5.860	3886.929	713.630
0.59653	0.00323	0.00201	1.51924	3471.287	20.570	1.844	5.189	3454.062	717.385
0.60270	0.00478	0.00195	1.53262	3501.877	30.440	2.729	5.034	3473.741	714.086
0.65215	0.00310	0.00211	1.65538	3782.655	19.742	1.770	5.447	3766.590	715.575
0.65987	0.00144	0.00213	1.66895	3813.691	9.170	0.822	5.498	3809.197	715.203
0.63546	0.00260	0.00205	1.61089	3680.896	16.558	1.484	5.292	3668.146	715.176
0.67981	0.00413	0.00260	1.72912	3947.908	26.301	2.358	6.712	3925.960	715.505
0.63146	0.00332	0.00230	1.60633	3667.299	21.143	1.896	5.937	3650.198	716.185
0.56846	0.00707	0.00210	1.45371	3318.557	45.024	4.037	5.421	3274.917	713.764
0.72697	0.01083	0.00300	1.86438	4256.987	68.969	6.183	7.744	4189.579	714.017
0.62680	0.01211	0.00160	1.61824	3694.491	77.120	6.914	4.130	3614.587	714.470

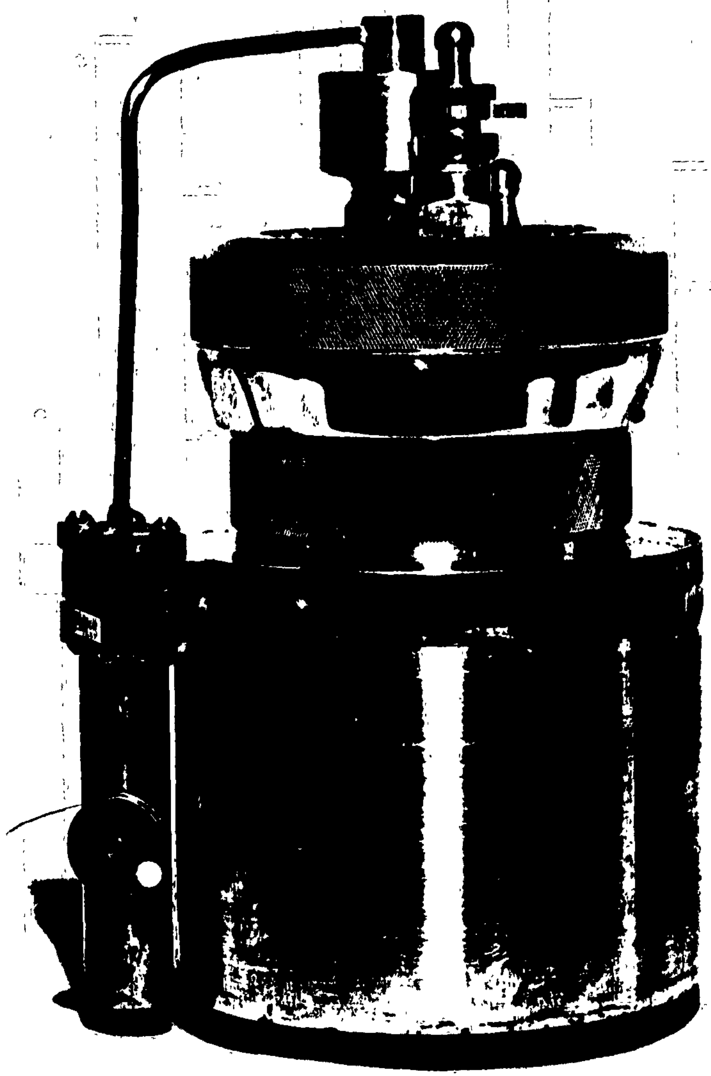

FIGURE I
COMBUSTION BOMB WITH OXYGEN JACKET

Bomb Calibration: Four measured expansions of oxygen from 40 atmospheres pressure in the jacket into the combustion bomb gave a temperature drop of 5.28 ± 0.12 millidegrees. Since this expansion took place at the start of the combustion period, and 15 seconds was allowed for expansion of the gas before the phosphorus sample was ignited, correction for the energy of expansion of the oxygen before ignition of the phosphorus was made by addition of 0.00528° to the corrected temperature rise to obtain the final corrected temperature rise that would have occurred, if the expansion of the oxygen had not cooled the system slightly.

Six measurements of the ignition of 5 inches of 36-gage platinum fuse wire gave a temperature rise of 0.38 ± 0.12 millidegrees which, converted to equivalent calories during the calibration of the bomb system with benzoic acid, gave an ignition energy of 1.088 cal.

Four standard benzoic acid calibrations were made of the bomb system with 40 atmospheres oxygen pressure in the jacket with the jacket valve closed, and the standard conditions of 1 gram of benzoic acid, 1 ml. of water, and 30 atmospheres oxygen pressure in the bomb proper. The reduction to standard conditions was made as described previously (1), and the results of the calibrations are listed in Table II.

TABLE II

Standard Benzoic Acid Calibrations of Jacketed Bomb

Wt. grams, of benzoic acid, m_s	$-E_B m_s$	ΔT, °C.	Δe_1	E_c cal./°C.	Dev., %
0.98699	6235.684	2.17602	0.449	2865.688	0.053
0.98761	6239.602	2.17734	0.450	2865.749	0.058
0.97746	6175.475	2.15737	0.440	2862.566	0.046
0.99428	6281.742	2.19426	0.458	2862.845	0.070
			Average	2864.212	±0.057

The benzoic acid samples were supported in thin glass cups (1), and the unburned residue was 0.2 mg. or less and was ignored. No nitric acid was found in the bomb washings after the combustion. A silica dish, a glass rod, and a platinum rod of the masses usually used in the combustion of phosphorus were added to the bomb.

Combustion of Phosphorus: Samples of phosphorus, either distilled or purified by the wet method, were weighed under water in weighing bottles. In the weighing procedure, the sample of phosphorus (through which a support hole had been punched under water) and a small beaker of acetone were introduced into a glove bag, and the bag was flushed and filled with deoxidized nitrogen. The phosphorus was dipped quickly into the acetone, waved briefly in the nitrogen gas stream, and placed on a small watch glass over which a rapid flow of nitrogen was passed for 10 minutes. The sample then was placed in a tared weighing bottle containing some distilled water. This weighing technique, checked by reweighing several samples, caused no significant change in weight of the sample. The weighed phosphorus was dried by the same procedure, except that the atmosphere was helium that had been passed through a charcoal trap in liquid nitrogen. The dried sample was mounted in the bomb on a short piece of platinum rod in 1 atmosphere of helium, with the fuse wire mounted to lay against the phosphorus, and the bomb was closed. The oxygen jacket was flushed and filled with oxygen, usually to 40 atmospheres pressure, and mounted on the bomb. The tube fitting that connected the jacket to the bomb was swept with helium in the glove bag while the phosphorus was being loaded into the bomb.

Under the usual conditions of combustion, nitrogen is assumed (12) to obey the same P-V-T relations as oxygen, whereas helium (8) is significantly different, so that it would simplify the gas corrections to standard conditions if nitrogen could be used as the inert atmosphere in the bomb in which the phosphorus sample is mounted. In a few trial combustions in which nitrogen was used as the inert gas, significant amounts of nitrogen oxides were formed. To avoid this complication, helium was used as the inert gas. The necessary correction factors for helium are given in Appendix A.

Uncoated phosphorus that was mounted in the bomb in a helium atmosphere and subjected to the oxygen from the jacket did not ignite spontaneously; it was necessary to ignite the phosphorus with a fuse wire. To check this point, a sample of phosphorus was mounted in helium in the bomb, and 30 atmospheres of oxygen pressure was admitted directly into the bomb. After 45 minutes the bomb was opened and the phosphorus had not ignited, but it ignited within a few seconds after the bomb was opened. This observation agrees with that of Semenoff (13) who found the upper limit for oxygen pressure, above which phosphorus does not react spontaneously with oxygen, is about 200 mm. Hg. In charging the bomb, the phosphorus was mounted in 1 atmosphere of helium and, when the oxygen was admitted to the bomb, the oxygen partial pressure passed rapidly through the lower pressure limit for spontaneous ignition (13), but the phosphorus did not ignite.

In every combustion of phosphorus in the jacketed bomb, both a yellow-to-orange and a brown-to-black residue were found on the silica dish when the bomb was opened. Each of these residues was estimated to weigh 1 mg. or less. The products of combustion were washed from the bomb with distilled water, and the washings were separated into two portions--those from the bomb walls, and those from the silica dish. Each solution was titrated iodometrically in acid and alkaline solution (14) to determine H_3PO_3 and H_3PO_2. No significant titrations were obtained for the washings from the bomb walls, and all the incompletely oxidized phosphorus was in the washings from the silica dish. No indication of unreacted elemental phosphorus was found in any of the combustions, except that a faint odor of phosphorus was detected when the bomb was first opened. There were no fumes.

On the assumption that the residue resulted from escape of a small part of the phosphorus from the intense combustion flame to the cold wall of the silica dish, several combustions were made with the initial bomb temperature at 35° or 50° C. With an initial temperature of 35° C. there was no apparent change in the quantity of residue, but with 50° C. the phosphorus melted and burned in the silica dish and the yellow-to-orange residue increased by a factor of 10 or more. In one combustion at 50° C., the bomb was opened in a dry nitrogen atmosphere, the solid P_4O_{10} was scraped from the silica dish, and part of the yellow-to-orange residue was scraped into a weighing bottle. Results of analysis of the residue are shown in the tabulation.

	Wt., mg.
Sample	11.19
P equivalent of H_3PO_3	1.1
P equivalent of H_3PO_2	0.5
Total P	4.8

These results indicate that the residue contained some P_4O_{10}, so that the ratio of phosphorus to oxygen in the residue is uncertain.

It is concluded that, as the intense flame dies out near the end of the combustion, a small amount of phosphorus on the relatively cold surface of the silica dish escapes complete combustion. Several exploratory combustions were made in which the purely mechanical arrangement of the parts of the bomb was altered in attempts to improve the conditions for combustion. The oxygen pressure in the jacket was varied between 10 and 55 atmospheres. The silica dish was raised from the bottom of the bomb on a short glass cylinder. A thin Vycor dish was substituted for the silica dish. The sample support was raised 3/4 inch higher in the bomb. The phosphorus sample was suspended on a platinum rod, a glass rod, or directly on the fuse wire. The power to the fuse wire was decreased so that the wire glowed rather than fused. Each change was intended to permit the phosphorus to burn longer in the gas space before it fell to the silica dish, or to raise the effective temperature of the dish, so that the combustion would be more nearly complete. None of the changes had any significant effect on the amount of incompletely oxidized residue.

Microscopic examination of the residue on the silica dish after each of these combustions showed loss of about 1 mg. of silica from the dish. The same effect was noted with the thin Vycor dish; thin flakes of Vycor glass floated in the solution in the dish when the residue was wetted with water.

The brown-to-black residue usually found after combustions in the jacketed bomb was first thought to result from reaction of platinum with oxygen or phosphorus in the intense phosphorus flame. In two combustions, however, 100 per cent of the platinum used as support rod and fuse wire was recovered, which indicated that the brown-black residue contained no platinum. One brown-black residue which was recovered separately weighed 0.7 mg. Spectrographic analysis indicated that its major constituent was silicon, and it was concluded that the brown-black residue probably was silicon monoxide. This residue was recovered quantitatively from only one run, however, and no attempt was made to correct for this small amount of impurity. Microscopic examination of the residue from several combustions indicated that the brown-black residue was intimately mixed with the yellow-orange residue so that separation was difficult or impossible, and that the brown-black residue was found along the grain boundaries of silica, where particles of silica had spalled off the silica dish.

Selected results from the combustion of uncoated phosphorus in the jacketed bomb are listed in Table III. The complete results are listed in Appendix D, and the reasons for the selection of the results in Table III are given in the last section of this report. The calculations required in a typical combustion run are given in Appendix B.

TABLE III

Selected Heats of Combustion of Phosphorus in Jacketed Bomb

Weight, grams			$-\Delta E_c$, cal.			$-\Delta E_c$, kcal./mole
P_4	P_4 equiv. of P_4O_6	ΔT, °C.	Substance	P_4O_6	P_4	P_4
0.69164	0.0027	1.39210	3989.073	6.969	3996.042	715.821
0.64940	0.0052	1.30604	3742.392	13.423	3755.815	716.550
0.66332	0.0044	1.33147	3815.285	11.358	3826.643	714.742
0.79353	0.0058	1.59656	4575.130	14.972	4590.102	716.660
0.70120	0.0042	1.41148	4044.621	10.842	4055.463	716.561
0.74748	0.0057	1.50497	4312.598	14.714	4327.312	717.254
0.64067	0.0032	1.28919	3694.103	8.260	3702.363	715.977
0.82565	0.0031	1.66823	4780.560	8.002	4788.562	718.561
0.61694	0.0027	1.24560	3569.147	6.969	3576.116	718.163
0.53507	0.0150	1.05967	3051.352	38.720	3090.072	715.505
					Average	716.581
					Std. deviation of mean	0.351

Phosphorus Coated with Cellulose Acetate

Since combustions of phosphorus in the jacketed bomb did not give results of the desired quality, combustions were made with phosphorus coated with cellulose acetate.

Cellulose Acetate: A solution of cellulose acetate sheet in glacial acetic acid was used to coat phosphorus samples. Results of combustion analyses of the original sheet and of the film formed by drying the solution of the sheet in glacial acetic acid on a flat glass surface are shown in the tabulation.

	Composition, %		
	C	H	O
Original sheet	52.80	6.00	41.20
Dried film	52.95	6.00	41.05

The data show that the cellulose acetate comprises cellulose acetate 65 and cellulose butyrate 35 per cent; its molecular weight was calculated to be 317.713. Heats of combustion of the original sheet and of the dried film are listed in Table IV.

The data in Table IV show that the dried film contained some acetic acid. The results of combustions of the dried film were used in correcting for the combustion of the cellulose acetate-coated phosphorus samples.

Although the Lucite coating had been shown (1) to protect the phosphorus from oxidation before ignition, this coating was opaque and contained microscopic surface cracks. The cellulose acetate coating was transparent and showed no surface cracking. As with the Lucite, however, it was difficult to coat with cellulose acetate samples of distilled phosphorus that had been cut from a cast stick under water because of the sharp points and rough edges on the samples.

TABLE IV

Heat of Combustion of Cellulose Acetate Sheet

Weight of sheet, gram	ΔT, °C.	Corrected total heat developed, - calories	- Kcal./mole	Dev., %
		Original sheet		
0.52031	1.11230	4890.379	1553.74	0.00
0.52523	1.11798	4869.662	1547.16	0.43
0.51248	1.09787	4900.802	1557.05	0.21
0.52294	1.12043	4901.215	1557.18	0.22
		Average	1553.78	0.21
		Dried film		
0.56396	1.22704	4976.301	1581.04	0.15
0.52221	1.13548	4973.553	1580.16	0.09
0.52935	1.14412	4944.375	1570.89	0.50
0.51473	1.12047	4981.731	1582.76	0.26
		Average	1578.71	0.25

Bomb Calibration: The combustion bomb was recalibrated with standard benzoic acid before the combustion of phosphorus coated with cellulose acetate. The results of the calibration are shown in Table V.

The ignition energy used as a correction term in the benzoic acid calibration was 3.443 cal., the same as that used for the calibrations before the Lucite-coated phosphorus combustions because the conditions of calibration were unchanged. Chromatographic analysis showed no significant nitrogen in the oxygen, and no correction was required for nitric acid. No carbon monoxide was produced in the combustion in amounts detectable with a Mine Safety Appliances detector. The carbon residue from the combustions was insignificant and was neglected in the corrections.

TABLE V

Standard Benzoic Acid Calibration of Bomb Before Cellulose Acetate-Coated-Phosphorus Combustions

Wt., grams of benzoic acid, m_s	$-E_B m_s$	ΔT, °C.	Δe_1	E_c cal./°C.	Dev., %
1.00520	6350.733	2.78720	0.632	2279.138	0.014
1.00979	6379.732	2.80120	0.639	2278.090	0.032
1.01421	6407.657	2.81321	0.645	2278.282	0.024
1.00806	6368.802	2.79536	0.636	2278.943	0.005
1.01004	6381.312	2.79996	0.639	2279.663	0.037
			Average	2278.824	0.022

Combustion of Phosphorus: Both wet-purified (1) phosphorus and distilled phosphorus were used in the combustions. The yellow-to-orange and brown-to-black residues were significantly decreased in these combustions, and apparently were small enough to be ignored, but the amount of P_4O_6 was about the same as in all previous combustions. All the combustions were made under 30 atmospheres of oxygen pressure.

The selected values for the combustion of phosphorus coated with cellulose acetate are listed in Table VI, and all the values are listed in Appendix D.

There was no significant difference between the heats of combustion of wet-purified phosphorus and distilled phosphorus. Data from a typical cellulose acetate combustion are given in Appendix C.

TABLE VI

Selected Heats of Combustion of Cellulose Acetate-Coated Phosphorus

Weight, grams				$-\Delta E_c$, cal.					$-\Delta E_c$ kcal./mole
P_4	Cell. acet.	P_4 equiv. of P_4O_6	ΔT, °C.	Substance	Cell. acet.	HPO_3	P_4O_6	P_4	P_4
				Wet-method-purified phosphorus					
0.57640	0.00962	0.0028	1.47823	3375.596	47.881	4.092	7.228	3330.852	715.955
0.54895	0.00862	0.0036	1.40496	3208.117	42.903	3.666	9.293	3170.840	715.642
0.52092	0.00401	0.0022	1.32472	3024.691	19.959	1.706	5.679	3007.930	715.404
0.54906	0.00606	0.0019	1.39956	3195.780	30.162	2.577	4.905	3167.945	714.846
				Distilled phosphorus					
0.54897	0.00810	0.0034	1.40388	3205.626	40.315	3.445	8.777	3170.642	715.572
0.49537	0.00943	0.0034	1.27253	2905.375	46.935	4.011	8.777	2863.206	716.106
0.52363	0.00615	0.0033	1.33740	3053.665	30.610	2.616	8.519	3028.958	716.677
0.53358	0.01321	0.0019	1.38106	3153.438	65.749	5.619	4.905	3086.975	716.784
0.53026	0.01018	0.0022	1.36344	3113.175	50.668	4.330	5.679	3063.856	715.870
0.50742	0.01242	0.0011	1.31141	2994.235	61.817	5.283	2.840	2929.975	715.403
0.51376	0.01279	0.0020	1.32783	3031.767	63.658	5.440	5.163	2967.832	715.704

Evaluation of the Combustion Results

This study was started on the premise established by Prosen (11):

> "Although proper corrections may sometimes be applied for a very small amount of incomplete combustion, the products of incomplete combustion are usually so complex that it is better to strive for complete combustion."

Complete combustion was not obtained in any run. If the study had been terminated after the first five combustions of phosphorus coated with Lucite, the results would have been considered satisfactory in that the first five combustions were highly reproducible, and actually yielded a value near the finally selected heat of combustion. All the additional combustions were made in an attempt to account for the deviation of the result of the sixth combustion of Lucite-coated phosphorus.

A significant feature of this study is that no distinction was found between phosphorus purified by the wet method (1) and that further purified by distillation under vacuum at about 120° C.

No satisfactory method was found for quantitative separation or positive identification of the products of incomplete combustion. The dry residues could not be completely separated, and their dissolution in the bomb washings showed that they contained no red phosphorus. The results of the cellulose acetate-coated phosphorus combustions, in which the solid residues were significantly smaller than in any of the other combustions, although the analytically determined P_4O_6 remained about the same, indicate that P_4O_6 is a major constituent of the incomplete-combustion products and that the solid residues are minor constituents. Similar incomplete combustions were obtained in the study of the combustion of P_4O_6 to P_4O_{10} (5).

Analyses of the bomb washings for total phosphorus usually showed 99.6 to 99.8 per cent of the phosphorus charged. Analyses of phosphorus samples, either coated or uncoated, for total phosphorus, by a preliminary bromine oxidation method in a closed system showed 99.7 to 100.3 per cent of the sample weight. Determination of the principal constituent is not a desirable analytical technique, however, especially when the principal constituent is phosphorus and the methods of analysis are admittedly short of perfection.

The solid P_4O_{10} in the combustion products was shown by x-ray examination to be the hexagonal crystalline form.

When all the results listed in Appendix D, for both Lucite- and cellulose acetate-coated, and for both wet-purified and distilled phosphorus, are plotted as corrected temperature rise, ΔT, against $\underline{c}$, total combustibles (sum of weights of phosphorus and coating), the plot is a straight line, as shown in Figure 2. A similar plot for the combustion of phosphorus in the jacketed bomb, in which the total combustible is the weight of phosphorus, is included in Figure 2. The equations for the two lines in Figure 2 are:

For coated phosphorus:

$$\text{Corr. } \Delta T = -.00869 + 2.53978\underline{c} \tag{3}$$

For uncoated phosphorus:

$$\text{Corr. } \Delta T = -.01031 + 2.02824\underline{c} \tag{4}$$

The slope of the line for the coated phosphorus is larger than that for uncoated phosphorus because the heat of combustion per gram of coating material is higher than the heat of combustion per gram of phosphorus.

The values included in Appendix D that are omitted from Tables I, III, and VI were discarded largely on the basis of lack of fit to the straight lines in Figures 2, 3, and 4.

The average value of the heat of combustion of phosphorus for the combustions in the jacketed bomb (Table III) is 716.581 kcal./mole with a standard deviation from the mean of 0.351 kcal./mole.

A plot of the heat of combustion of the Lucite-coated phosphorus from Appendix D against the weight of coating shows a definite trend. The equation for a least-squares straight line representing the points between the dashed lines in Figure 3 is

$$-\Delta E_c^\circ, \text{ kcal./mole} = 716.291 - 0.1870\underline{W} \tag{5}$$

where $\underline{W}$ is the weight, mg., of the coating. The standard error of the intercept is 0.874 kcal./mole, and the standard error of the slope is 0.0812.

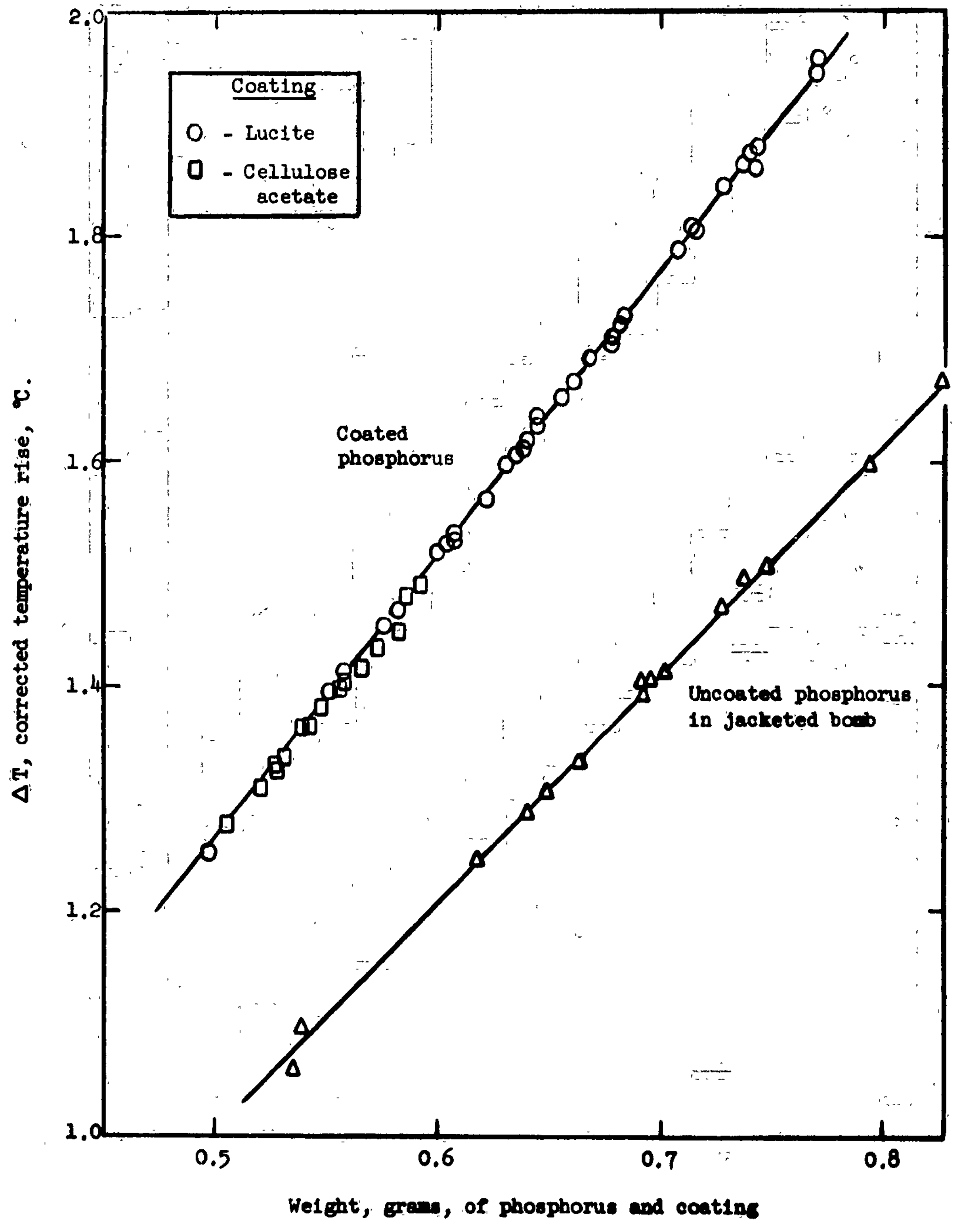

Figure 2

Relation Between Weight of Combustibles and Temperature Rise

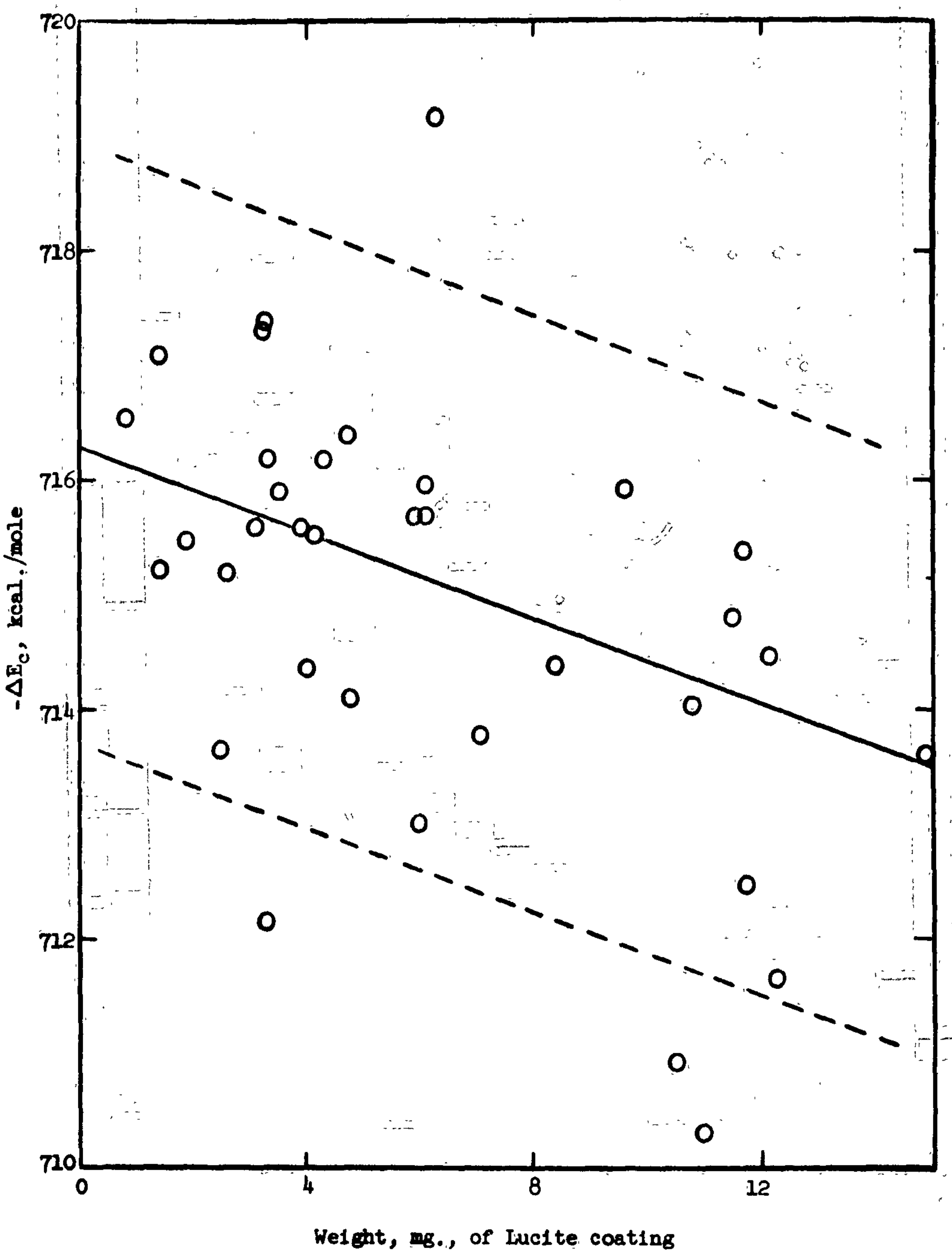

Figure 3

Relation Between Weight of Lucite Coating and Heat of Combustion of Phosphorus

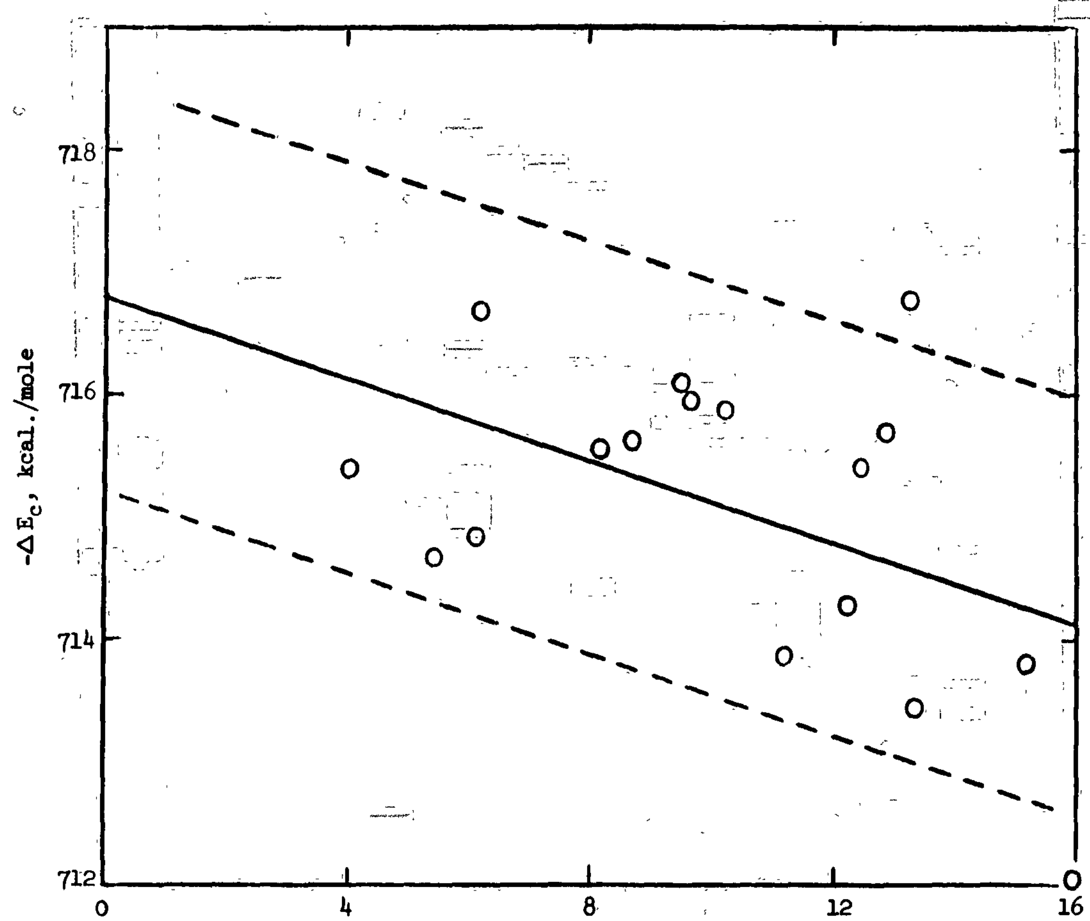

Figure 4

Relation Between Weight of Cellulose Acetate Coating and Heat of Combustion of Phosphorus

A similar plot, shown in Figure 4, for the cellulose acetate-coated phosphorus combustions gave

$$-\Delta E_c^\circ,\ \text{kcal./mole} = 716.769 - 0.1666\underline{W} \qquad (6)$$

The standard error of the intercept is 0.338 kcal./mole, and the standard error of the slope is 0.0450.

It is obvious that the corrections for the combustion of the coating are not entirely adequate, or the slopes in equations 5 and 6 would be zero.

A further correlation of the combustion of coated phosphorus that supported the extrapolation of equations 5 and 6 to zero coating resulted from a calculation on the basis of the weight of coating per unit weight of phosphorus. The term (wt. P_4)$^{-1}$ was used as a multiplier of the weight of coating, ΔE_c° substance, and ΔE_c° ($P_4O_6 \rightarrow P_4O_{10}$) from Appendix D. When the results were calculated to heat of combustion at constant volume, and a least-squares straight line fitted to ΔE_c° and $\underline{u}$, mg. coating per gram of phosphorus, the equations were

For Lucite coating:

$$-\Delta E_c^\circ,\ \text{kcal./mole} = 716.267 + 0.74214\underline{u} \qquad (7)$$

For cellulose acetate coating:

$$-\Delta E_c^\circ,\ \text{kcal./mole} = 716.079 + 0.62530\underline{u} \qquad (8)$$

These calculations include the correction for P_4O_6, but the correction for the coating is included in the equations, and no assumptions about the heat of combustion of the coating or the formation of HPO_3 are involved. The slopes in equations 7 and 8 are positive because the heat of combustion of the coating is included in the equations.

The slopes of equations 5 and 7, and of equations 6 and 8 differ because the Lucite and cellulose acetate form different amounts of H_2O and CO_2 per gram of coating material.

The intercepts of equations 5, 6, 7, and 8 at zero coating give values of $-\Delta E_c^\circ$ that are close to the average value from Table III:

	$-\Delta E_c^\circ$, kcal./mole
Uncoated phosphorus	716.581
Lucite-coated phosphorus, equation 5	716.291
equation 7	716.267
Cellulose acetate-coated phosphorus, equation 6	716.769
equation 8	716.079
Average	716.397

This average value represents the heat of combustion of phosphorus at constant volume under standard conditions. Since 5 moles of oxygen are consumed in the formation of 1 mole of P_4O_{10} from 1 mole of P_4, the subtraction of the term 5RT = 2.962 kcal. (R = 1.98725, T = 298.15° K.) yields -719.359 kcal./mole for the heat of combustion of phosphorus at constant pressure, or, since the combustion yields 1 mole of P_4O_{10} per mole of P_4, the heat of formation of P_4O_{10}(c). This value is compared in Table VII with other values from the literature.

TABLE VII

Heat of Formation of P_4O_{10}(c)

Source	Reference	$-\Delta H^\circ f$, kcal./mole
Abria (1846)	4	703.0
Andrews (1848)	4	712.6
Favre (1853)	4	738.0
Giran (1903)	4	738.8
NBS (selected, 1952)	10	720.0[a]
Holmes (1962)	6	713.2
This work		719.4

[a] Recalculated from Giran's result (4).

From the results of the present work

$$P_4(\alpha, \text{white}, c) + 5O_2(g) = P_4O_{10}(c, \text{hex})$$

$$\Delta H°f = -719.4 \pm 2.0 \text{ kcal./mole}$$

In this study, the results of 44 of the 68 combustions are within 2.0 kcal. of the value $\Delta H°f = 719.4$ kcal. Most of the other 24 results can be discarded as those of faulty runs.

It is difficult to reconcile the heat of combustion of phosphorus at constant pressure of -713.2 kcal./mole reported recently by Holmes (6) with the present results. Holmes measured temperatures with a glass thermometer graduated in 0.01° C.; in the present measurements, a platinum resistance thermometer precise to less than 0.0002° C. was used, together with a detailed method of calculation of the corrected temperature rise (7). With a bomb-calibration factor of about 2300 cal. per degree, a temperature difference of 0.001° C. is significant.

Holmes (6) found, in agreement with the present results, that the P_4O_{10} on the walls of the bomb contained no P_4O_6. He assumed that the yellow-orange residue was red phosphorus, but he does not state whether the equivalent amount of phosphorus was subtracted from the weight of the sample.

If the corrections for $P_4O_6 \rightarrow P_4O_{10}$ listed in Table III are ignored, the average value for the heat of combustion at constant volume is -714.8 kcal./mole rather than -716.4 kcal./mole. If the weight of phosphorus equivalent to P_4O_6 listed in Table III is considered as unburned phosphorus, as Holmes did, and this value is subtracted from the initial weight of phosphorus, the average value for the heat of combustion at constant volume is -719.0 kcal./mole rather than -716.4 kcal./mole. In any event, it is difficult to account for the low values reported by Holmes. Only 4 of the 68 values listed in Appendix D are less than -712 kcal./mole for the heat of combustion at constant volume.

Dainton and Kimberley (3) established a chain-reaction mechanism for the oxidation of phosphorus at low pressures with P_4O as the first intermediate. In the present study, the direct calorimetric measurements appear to be straightforward and satisfactorily reproducible, but the chemistry of the combustion is definitely not straightforward, as shown by the variation of the measured heat of combustion under presumably identical conditions.

The normal combustion of benzoic acid in oxygen is complete in 12 to 15 seconds. It is estimated that the oxidation of phosphorus is complete in about 5 seconds and that the flame temperature of phosphorus burning in oxygen is above 5000° K. The steep temperature gradients in the process could account for part of the difficulty in obtaining satisfactory combustions. The chemistry of the combustion process under the conditions existing in a combustion bomb needs further clarification to establish satisfactory conditions for reproducible combustions.

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APPENDIX A

Primary Data Used in Reduction of Phosphorus Combustions to Standard Conditions

The reduction to standard conditions was based on the 100-term correction procedure of Hubbard, Scott, and Waddington (7). Terms involving a solution phase were omitted. The pertinent terms are listed in Appendixes B and C.

In combustions of phosphorus with the jacketed bomb, the phosphorus sample was suspended in the bomb in 1 atmosphere of helium. Since the P-V-T relations for helium (8) differ from those for oxygen, it was necessary to modify some of the correction terms for the gas phase. The PV equation for helium at 25° C. (8) is taken as

$$PV = nRT(1.09094 + 540 \times 10^{-6} P) \tag{9}$$

and that for oxygen (7) as

$$PV = nRT[1 - \{890 - 11.3(25°\ C.)\}\ 10^{-6}\ P] \tag{10}$$

For the jacketed bomb, the initial moles of gas were determined by applying equation 9 to the helium in the bomb at 1 atmosphere pressure and equation 10 to the oxygen in the jacket at 40 atmospheres, and adding the results. The volume of the bomb to the jacket valve was 0.34088 liter and the volume of the jacket to the jacket valve was 0.17270 liter.

For the combined gases, after the oxygen had been admitted to the bomb by opening the jacket valve, the coefficients of equations 1 and 2 were combined on the basis of the respective mole fractions of oxygen and helium to yield at 25° C.

$$PV = nRT(1.0038 - 560 \times 10^{-6} P) \tag{11}$$

The densities and heat capacities of the various substances used in the combustions are given in the tabulation.

Substance	Density, grams/cc.	C_p, cal./gram (25° C.)
P_4	1.828	0.183
P_2O_5	2.30	0.184
SiO_2 (vitreous)	2.20	0.1764
Glass (Pyrex)	2.23	0.17
Platinum	21.45	0.0325
Lucite	0.945	0.343
Cellulose acetate-butyrate	1.30	0.30
HPO_3	2.35	0.2551

Substance	Gram formula weight
P_4	123.8952
P_4O_{10}	283.8922
Lucite	100.11831
Cellulose acetate butyrate	317.713

The energy-of-compression terms for the substances in the bomb, $(\partial E/\partial P)_T$, were estimated to be -0.005 cal./gram for P_4 and -0.007 cal./gram for both coating materials from similar data given in reference 7.

APPENDIX B

Sample Calculation of Correction for Combustion of Phosphorus in Jacketed Bomb

Statement numbers correspond to those listed by Hubbard, Scott, and Waddington (7).

Statement No.	Term	Symbol	Value
1	Formula	P_4	
2	Mass P_4	m'	0.70120 gram
3	Molecular wt. P_4	m'	123.8952 gram
4	Moles P_4	n' = m'/m'	0.0056596 mole
5	Density P_4	d'	1.828 gram/ml.
6	Volume P_4	v' = m'/1000 d'	0.0003836 liter
14	Mass glass	m'"	1.85127 gram
	Mass SiO_2	m""	16.53772 gram
17	Density glass	d'"	2.23 gram/cc.
	Density SiO_2	d""	2.20 gram/cc.
18	Volume glass	v'" = m'"/1000 d'"	0.000830 liter
	Volume SiO_2	v"" = m""/1000 d""	0.007517 liter
26	Volume bomb	Bomb 0.34088 liter Jacket 0.17270 liter	0.51358 liter
28	p_i(gas)		40.0 atm.
31	v_i (gas) = v_{bomb} - v' - v"' - v""		0.50485 liter

APPENDIX B (Contd.)

Statement No.	Term	Symbol	Value
34	n_i (gas)	0.28940 mole O_2 0.01245 mole He	0.30185 mole
49	$v_f (gas) = \frac{p_i (gas)\ v_i (gas)}{24.4644[1.0038 - 0.00056 p_i (gas)]}$		0.50453 liter
56	$n_f (O_2 + N_2\ tot) = n_i (gas) - 5n'$		0.27355 mole
62	$n_f (gas) = n_f (O_2 + N_2\ tot) + n_f (CO_2\ tot)$		0.27355 mole
64	$\mu_f (gas) = \mu_f (O_2)$		0.00060 atm.$^{-1}$
65	$p_f (gas) = \left\{ [v_f (gas)/ 24.4644 n_f (gas)] + \mu_f (gas) \right\}^{-1}$		13.12010 atm.
68	$(\partial E/\partial P)_{P_4}$		-0.005 cal./gram atm.
74	$\mathcal{E}_{calor}$		-2864.212 cal./°C.
75	$\mathcal{E}_i (cont) = C_v (O_2)\ n_i (gas) + m'C'_p$		1.62888 cal./°C.
76	$\mathcal{E}_f (cont) = C_v (O_2)\ n_f (gas) + C_v (CO_2)\ n_f (CO_2) + m_{P_2O_5} C_{pP_2O_5}$		1.65310 cal./°C.
77	$\Delta E(ign)$		1.088 cal.

APPENDIX B (Contd.)

Temperature Corrections

Foreperiod, t, min.	R, ohms Corr.	R, ohms Calc.	Diff.
1	27.89811	27.89811	.00000
2	27.89866	27.89866	.00000
3	27.89920	27.89920	.00000
4	27.89973	27.89973	.00000
5	27.90027	27.90027	.00000
6	27.90082	27.90082	.00000
7	27.90135	27.90135	.00000
8	27.90190	27.90190	.00000
9	27.90243	27.90243	.00000
10	27.90298	27.90298	.00000
11	27.90352	27.90352	.00000
12	27.90407	27.90406	.00001
13	27.90459	27.90459	.00000
14	27.90513	27.90513	.00000

15 min. = t_i T_i = 23.54780° C.

Afterperiod, t, min.	R, ohms Corr.	R, ohms Calc.	Diff.
41	28.05356	28.05357	-.00001
42	28.05376	28.05376	.00000
43	28.05394	28.05394	.00000
44	28.05412	28.05412	.00000
45	28.05432	28.05431	.00001
46	28.05450	28.05449	.00001
47	28.05468	28.05468	.00000
48	28.05484	28.05484	.00000
49	28.05503	28.05503	.00000
50	28.05520	28.05520	.00000
51	28.05542	28.05539	.00003
52	28.05557	28.05557	.00000
53	28.05572	28.05574	-.00002
54	28.05593	28.05593	.00000
55	28.05611	28.05611	.00000

40 min. = t_f T_f = 25.01115° C.

APPENDIX B (Contd.)

Combustion Period

t, min.	°C.	Δt, min.	°C - °C$_o$	Av.(°C - °C$_o$)
15.0	23.54780			
15.95333	23.60656	0.95333	0.05874	0.02937
16.08167	23.70560	0.12834	0.15778	0.10826
16.22	23.80464	0.13833	0.25683	0.20731
16.375	23.90369	0.15500	0.35587	0.30635
16.53833	24.00284	0.16333	0.45502	0.40545
16.71667	24.10189	0.17834	0.55408	0.50455
16.82833	24.15132	0.11166	0.60351	0.57879
16.95167	24.20105	0.12334	0.65323	0.62837
17.08333	24.25048	0.13166	0.70266	0.67795
17.235	24.30010	0.15167	0.75229	0.72748
17.40833	24.34964	0.17333	0.80182	0.77706
17.6	24.39927	0.19167	0.85145	0.82664
17.81167	24.44870	0.21167	0.90088	0.87617
18.06	24.49843	0.24833	0.95061	0.92575
18.17667	24.51824	0.11667	0.97043	0.96052
18.36333	24.54786	0.18666	1.00005	0.98524
18.49	24.56768	0.12667	1.01986	1.00996
18.71333	24.59819	0.22333	1.05038	1.03512
18.86667	24.61790	0.15334	1.07009	1.06023
19.03	24.63772	0.16333	1.08990	1.08000
19.21	24.65752	0.18000	1.10972	1.09981
19.42167	24.67745	0.21167	1.12963	1.11968
19.62167	24.69726	0.20000	1.14945	1.13954
19.73	24.70717	0.10833	1.15935	1.15440
19.84833	24.71698	0.11833	1.16916	1.16426
19.97	24.72688	0.12167	1.17907	1.17411
20.09167	24.73679	0.12167	1.18898	1.18402
20.23167	24.74670	0.14000	1.19888	1.19393
20.37167	24.75660	0.14000	1.20879	1.20384
20.52	24.76661	0.14833	1.21880	1.21379
20.685	24.77652	0.16500	1.22870	1.22375
20.84667	24.78643	0.16167	1.23861	1.23366
21.02333	24.79633	0.17666	1.24852	1.24357
21.20333	24.80624	0.18000	1.25843	1.25347
21.40667	24.81605	0.20334	1.26824	1.26333
21.61333	24.82596	0.20666	1.27814	1.27319
21.83667	24.83586	0.22334	1.28805	1.28310
22.07833	24.84577	0.24166	1.29796	1.29300
22.19333	24.85073	0.11500	1.30291	1.30043

APPENDIX B (Contd.)

Combustion Period

t, min.	°C.	Δt, min.	°C - °C_o	Av.(°C - °C_o)
22.31833	24.85568	0.12500	1.30787	1.30539
22.43667	24.86063	0.11834	1.31282	1.31034
22.58167	24.86569	0.14500	1.31787	1.31535
22.71667	24.87064	0.13500	1.32283	1.32035
22.87333	24.87559	0.15666	1.32778	1.32530
23.0	24.88005	0.12667	1.33224	1.33001
23.5	24.89442	0.5	1.34660	1.33942
24.0	24.90512	0.5	1.35730	1.35195
24.5	24.91641	0.5	1.36860	1.36295
25.0	24.92612	0.5	1.37831	1.37345
25.5	24.93494	0.5	1.38713	1.38272
26.0	24.94237	0.5	1.39456	1.39084
26.5	24.94881	0.5	1.40100	1.39778
27.0	24.95486	0.5	1.40704	1.40402
27.5	24.96021	0.5	1.41239	1.40972
28.0	24.96486	0.5	1.41705	1.41472
28.5	24.96922	0.5	1.42141	1.41923
29.0	24.97299	0.5	1.42517	1.42329
29.5	24.97626	0.5	1.42844	1.42681
30.0	24.97913	0.5	1.43132	1.42988
30.5	24.98220	0.5	1.43439	1.43285
31.0	24.98438	0.5	1.43657	1.43548
31.5	24.98666	0.5	1.43885	1.43771
32.0	24.98894	0.5	1.44113	1.43999
32.5	24.99082	0.5	1.44301	1.44207
33.0	24.99261	0.5	1.44479	1.44390
33.5	24.99439	0.5	1.44658	1.44568
34.0	24.99617	0.5	1.44836	1.44747
34.5	24.99756	0.5	1.44975	1.44905
35.0	24.99954	0.5	1.45173	1.45074
36.0	25.00202	1.0	1.45420	1.45297
37.0	25.00450	1.0	1.45668	1.45544

APPENDIX B (Contd.)

Combustion Period

t, min.	°C.	Δt, min.	°C - °C_0	Av.(°C - °C_0)
38.0	25.00648	1.0	1.45866	1.45767
39.0	25.00886	1.0	1.46104	1.45985
40.0	25.01115	1.0	1.46334	1.46219

$$t_m = t_f - (T_f - T_i)^{-1} \int_{t_i}^{t_f} (T - T_i)dt = 18.48109 \text{ min.}$$

$$\Delta T_{corrn} = (dT/dt)_i(t_m - t_i) + (dT/dt)_f(t_f - t_m) = 0.05715° \text{ C.}$$

$$\text{Corr. } \Delta T = T_f - (T_i + \Delta T_{corrn}) = 1.40618° \text{ C.}$$

Statement No.	Term	Symbol	Value
78	Initial temp.	T_i	23.54780° C.
79	Final temp.	T_f	25.01115° C.
80	Temp. correction	T_{corrn}	0.05715° C.
	Oxygen expansion		0.00528° C.
	Corr. $\Delta T = T_f - (T_i + \Delta T_{corrn}) + .00528$		1.41148° C.
83	ΔE_i (sub)$]_1^{P_i} = m'(\partial E/\partial P)_{P_4}(P_i - 1)$		-0.042 cal.
85	ΔE_i (gas)$]_0^{P_i} = [(\partial E/\partial P)_T O_2 \text{ (gas)}]P_i \text{ (gas) } n_i \text{ (gas)}$		-5.9745 cal.

APPENDIX B (Contd.)

Statement No.	Term Symbol	Value
86	$\Delta E\ (IBP) = \mathcal{E}_{calor}\ (\Delta T_{corrn})$ $+ \mathcal{E}_i\ (cont)\ (T_i - 25)$ $+ \mathcal{E}_f\ (cont)\ (25 - T_f + \Delta T_{corrn})$ $+ \Delta E\ (ign)$	-4043.997 cal.
93	$\Delta E_f\ (gas)]^{o}_{P_f} = [(\partial E/\partial P)_T\ O_2\ (gas)]\ P_f\ (gas)\ n_f\ (gas)$	5.3940 cal.
95	$n\Delta E_c^{\circ}$ (sub) = sum of items 81 through 94	-4044.621 cal.
97	$\Delta E_c^{\circ}\ (P_4O_6 \rightarrow P_4O_{10}) = n_{P_4O_6}\ (-319{,}815)$	-10842 cal.
98	$\Delta E_c^{\circ}\ (compd) = n\Delta E_c^{\circ}\ (sub) + \Delta E_c^{\circ}\ (P_4O_6 \rightarrow P_4O_{10})$	-4055.463 cal.
99	$Cal./gram = \Delta E_c^{\circ}\ (compd)/m'$	-5783.603 cal.
100	Kcal./mole = (cal./gram)(123.8952)(0.001)	-716.561 kcal./mole

APPENDIX C

Sample Calculation of Corrections for Combustion of Phosphorus Coated with Cellulose Acetate

Statement numbers correspond to those listed by Hubbard, Scott, and Waddington (7).

Statement No.	Term	Symbol	Value
1	Formula	P_4	
2	Mass P_4	m'	0.52363 gram
3	Molecular wt. P_4	m'	123.8952 gram
4	Moles P_4	n' = m'/m'	0.0042264
5	Density P_4	d'	1.828 gram/ml.
6	Volume P_4	v' = m'/1000 d'	0.00028644 liter
7	Formula cell. acet.	-	-
8	Mass cell. acet.	m"	0.00615 gram
9	Mol. wt. cell. acet.	m"	317.713 gram
10	Moles cell. acet.	n" = m"/m"	0.0000194 gram
11	Density cell. acet.	d"	1.3 gram/cc.
12	Volume cell. acet.	v" = m"/1000 d"	0.000005 liter
14	Mass glass	m'"	1.84671 gram
	Mass SiO_2	m""	16.51022 gram
17	Density glass	d'"	2.23 gram/cc.
	Density SiO_2	d""	2.20 gram/cc.

APPENDIX C (Contd.)

Statement No.	Term	Symbol	Value
18	Volume glass	$v''' = m'''/1000\ d'''$	0.000828 liter
	Volume SiO_2	$v'''' = m''''/1000\ d''''$	0.007505 liter
26	Volume bomb		0.33807 liter
28	p_i (gas)		30.0 atm.
31	v_i (gas) = $v_{bomb} - v' - v'' - v''' - v''''$		0.32945 liter
34	n_i (gas) = $\dfrac{p_i\ (gas)\ v_i\ (gas)}{24.4644\ [1 - 0.00061 p_i\ (gas)]}$		0.41149 mole
49	v_f (gas) = $v_{bomb} - v_{P_2O_5} - v''' - v'''' - v_{HPO_3}$		0.32920 liter
50	n_f (CO_2 tot) = (m'' x 1.94014)/44.01		0.000097 mole
56	n_f (O_2 + N_2 tot) = n_i (gas) - 5n' - 6n"		0.38988 mole
62	n_f (gas) = n_f (O_2 + N_2 tot) + n_f (CO_2 tot)		0.38989 mole
63	X (CO_2) = n_f (CO_2)/n_f (gas)		0.000248
64	μ_f (gas) = $\mu(O_2)\left\{1 + 3.21\ X\ (CO_2)[1 + 1.33\ X\ (CO_2)]\right\}$		0.00088 atm.$^{-1}$
65	p_f (gas) = $\left\{[v_f\ (gas)/24.4644 n_f\ (gas)] + \mu_f\ (gas)\right\}^{-1}$		28.2596 atm.
68	$(\partial E/\partial P)_{P_4}$		-0.005 cal./gram atm.
	$(\partial E/\partial P)_{cell.\ acet.}$		-0.007 cal./gram atm.
72	E_c (cell. acet.)		-1578.71 kcal./mole
74	$\mathcal{E}_{calor}$		2278.824 cal./°C.

APPENDIX C (Contd.)

Statement No.	Term	Symbol	Value
75	$\mathcal{E}_i$ (cont)	$= C_v\ (O_2)\ n_i\ (gas) + m'C_p' + m''C_p'' + 0.17\ m_{glass} + 0.1764 m_{SiO_2} + 0.0325 m_{Pt}$	5.41312 cal./°C.
76	$\mathcal{E}_f$ (cont)	$= C_v\ (O_2)\ n_f\ (gas) + C_v\ (CO_2)\ n_f\ (CO_2) + m_{P_2O_5} C_{pP_2O_5} + 0.17 m_{glass} + 0.1764 m_{SiO_2} + 0.0325 m_{Pt} + 0.2551 m_{HPO_3}$	5.43038 cal./°C.
77	ΔE (ign)		3.443 cal.

Temperature Corrections

Foreperiod, t, min.	R, ohms Corr.	R, ohms Calc.	Diff.
1	27.90433	27.90434	-.00001
2	27.90500	27.90500	.00000
3	27.90568	27.90567	.00001
4	27.90631	27.90633	-.00002
5	27.90698	27.90699	-.00001
6	27.90767	27.90766	.00001
7	27.90834	27.90832	.00002
8	27.90899	27.90899	.00000
9	27.90966	27.90965	.00001
10	27.91031	27.91031	.00000
11	27.91096	27.91096	.00000
12	27.91162	27.91163	-.00001
13	27.91228	27.91228	.00000
14	27.91294	27.91294	.00000

15 min. = t_i $\qquad$ T_i = 23.62642° C.

APPENDIX C (Contd.)

Afterperiod, t, min.	R, ohms Corr.	Calc.	Diff.
31	28.05245	28.05244	.00001
32	28.05264	28.05264	.00000
33	28.05284	28.05284	.00000
34	28.05304	28.05305	-.00001
35	28.05325	28.05326	-.00001
36	28.05347	28.05347	.00000
37	28.05369	28.05368	.00001
38	28.05387	28.05387	.00000
39	28.05407	28.05408	-.00001
40	28.05428	28.05428	.00000
41	28.05448	28.05448	.00000
42	28.05469	28.05469	.00000
43	28.05491	28.05491	.00000
44	28.05511	28.05511	.00000
45	28.05533	28.05532	.00001

30 min. = t_f T_f = 24.99953° C.

Combustion Period

t, min.	°C.	Δt, min.	°C - °C_o	Av.(°C - °C_o)
15.0	23.62642			
15.21333	23.79890	0.21333	0.17247	0.08623
15.31167	23.99709	0.09834	0.37066	0.27156
15.48167	24.19530	0.17000	0.56887	0.46977
15.595	24.29436	0.11333	0.66793	0.61840
15.72	24.39352	0.12500	0.76709	0.71751
15.87833	24.49268	0.15833	0.86625	0.81667
16.10167	24.59244	0.22334	0.96601	0.91613
16.40667	24.69151	0.30500	1.06508	1.01555
16.62	24.74095	0.21333	1.11452	1.08980
16.88833	24.79058	0.26833	1.16416	1.13934
17.02667	24.81040	0.13834	1.18397	1.17406
17.17333	24.83012	0.14666	1.20369	1.19383
17.34833	24.84993	0.17500	1.22350	1.21359
17.44667	24.85984	0.09834	1.23341	1.22846

APPENDIX C (Contd.)

t, min.	°C.	Δt, min.	°C - °C$_0$	Av.(°C - °C$_0$)
17.55667	24.86985	0.11000	1.24342	1.23841
17.68667	24.87976	0.13000	1.25332	1.24837
17.82333	24.88966	0.13666	1.26323	1.25828
17.98	24.89957	0.15667	1.27314	1.26819
18.165	24.90948	0.18500	1.28305	1.27809
18.37833	24.91929	0.21333	1.29286	1.28795
18.62833	24.92920	0.25000	1.30276	1.29781
19.0	24.94158	0.37167	1.31515	1.30896
19.5	24.95288	0.5	1.32644	1.32080
20.0	24.96110	0.5	1.33467	1.33056
20.5	24.96674	0.5	1.34032	1.33749
21.0	24.97140	0.5	1.34497	1.34264
21.5	24.97497	0.5	1.34854	1.34676
22.0	24.97794	0.5	1.35151	1.35003
22.5	24.98022	0.5	1.35379	1.35265
23.0	24.98250	0.5	1.35607	1.35493
23.5	24.98418	0.5	1.35775	1.35691
24.0	24.98557	0.5	1.35914	1.35845
25.0	24.98844	1.0	1.36201	1.36058
26.0	24.99033	1.0	1.36390	1.36296
27.0	24.99310	1.0	1.36667	1.36528
28.0	24.99459	1.0	1.36816	1.36741
29.0	24.99726	1.0	1.37083	1.36949
30.0	24.99953	1.0	1.37310	1.37197

$$t_m = t_f - (T_f - T_i)^{-1} \int_{t_i}^{t_f} (T - T_i)dt = 16.13142$$

$$\Delta T_{corrn} = (dT/dt)_i(t_m - t_i) + (dT/dt)_f(t_f - t_m) = 0.03571° \text{ C.}$$

$$\text{Corr. } \Delta T = T_f - (T_i + \Delta T_{corrn}) = 1.3373° \text{ C.}$$

APPENDIX C (Contd.)

Statement No.	Term	Symbol	Value
78	Initial temp.	T_i	23.62642° C.
79	Final temp.	T_f	24.99953° C.
80	Temp. correction	ΔT_{corrn}	0.03571° C.
	Corrected ΔT		1.33739° C.
83	$\Delta E_i\ (\text{sub})]_1^{P_i} = [m'(\partial E/\partial P)'_T + m''(\partial E/\partial P)''_T](P_i - 1)$		-0.077 cal.
85	$\Delta E_i\ (\text{gas})]_0^{P_i} = [(\partial E/\partial P)_T\ O_2\ (\text{gas})]P_i\ (\text{gas})\ n_i\ (\text{gas})$		-16.418 cal.
86	$\Delta E\ (\text{IBP}) = \mathcal{E}_{calor}\ (T_i - T_f + \Delta T_{corrn}) + \mathcal{E}_i\ (\text{cont})\ (T_i - 25) + \mathcal{E}_f\ (\text{cont})\ (25 - T_f + \Delta T_{corrn}) + \Delta E\ (\text{ign})$		-3051.836 cal.
93	$\Delta E_f\ (\text{gas})]_{P_f}^{0} = (\partial E/\partial P)_T\ O_2\ (\text{gas}) \{1 + 1.69X\ (CO_2)\ [1 + X\ (CO_2)]\}\ P_f\ (\text{gas})\ n_f\ (\text{gas})$		14.669 cal.
95	$n\Delta E_c^\circ$ (sub) = sum of items 81 through 94		-3053.665 cal.
96	ΔE_c° (cell. acet.) = n" (-1578,710)		-30.610 cal.

APPENDIX C (Contd.)

Statement No.	Term	Symbol	Value
97	ΔE_c° (HPO$_3$) = n_{HPO_3} (-7145)		-2.616 cal.
	ΔE_c° (P$_4$O$_6$ $\rightarrow$ P$_4$O$_{10}$) = $n_{P_4O_6}$ (-319,815)		-8.519 cal.
98	ΔE_c° (compd) = nΔE_c° (sub) - ΔE_c° (cell. acet.) - ΔE_c° (HPO$_3$) + ΔE_c° (P$_4$O$_6$ $\rightarrow$ P$_4$O$_{10}$)		-3028.958 cal.
99	Cal./gram = ΔE_c° (compd)/m'		-5784.539 cal./gram
100	Kcal./mole = (cal./gram)(123.8952)(0.001)		-716.677 kcal./mole

APPENDIX D

Heat of Combustion of Phosphorus

Weight, grams				$-\Delta E_c$, cal.					$-\Delta E_c$, kcal./mole
P_4	Coating	P_4 equiv. of P_4O_6	ΔT, °C.	Substance	Coating	HPO_3	P_4O_6	P_4	P_4
Lucite coating, wet-method-purified phosphorus									
0.4128	0.0035	0.0017	1.05305	2405.052	22.289	1.998	4.388	2385.153	715.865
0.6009	0.0061	0.0019	1.53552	3508.494	38.847	3.483	4.905	3471.069	715.675
0.6547	0.0059	0.0023	1.67036	3816.892	37.573	3.369	5.937	3781.888	715.683
0.5452	0.0061	0.0019	1.39538	3187.976	38.847	3.483	4.905	3150.551	715.954
0.7309	0.0096	0.0023	1.87466	4284.129	61.136	5.481	5.937	4223.449	715.919
0.6366	0.0084	0.0021	1.62953	3723.495	53.494	4.796	5.421	3670.626	714.378
0.6547	0.0008	0.0022	1.65695	3786.251	5.095	0.457	5.679	3786.379	716.533
0.6569	0.0115	0.0022	1.69099	3864.040	73.236	6.566	5.679	3789.918	714.801
0.6440	0.0014	0.0022	1.63298	3731.423	8.916	0.799	5.679	3727.387	717.039
0.7025	0.0117	0.0024	1.80783	4131.265	74.509	6.680	6.195	4056.271	715.377
0.7380	0.0047	0.0025	1.87872	4293.444	29.931	2.683	6.453	4267.283	716.390
0.7133	0.0019	0.0024	1.80557	4126.161	12.100	1.085	6.195	4119.172	715.471
0.7654	0.0043	0.0026	1.94604	4447.419	27.384	2.455	6.712	4424.292	716.160
0.6742	0.0040	0.0023	1.71068	3909.120	25.473	2.284	5.937	3887.300	714.355
0.7037	0.0039	0.0025	1.78756	4084.954	24.836	2.267	6.453	4064.344	715.579
0.7254	0.0032	0.0023	1.84491	4216.119	20.379	1.827	5.937	4199.851	717.316

APPENDIX D (Contd.)

Weight, grams				$-\Delta E_c$, cal.					$-\Delta E_c$, kcal./mole
P_4	Coating	P_4 equiv. of P_4O_6	ΔT, °C.	Substance	Coating	HPC_3	P_4O_6	P_4	P_4
Lucite coating, distilled phosphorus									
0.49391	0.00330	0.0017	1.25063	2856.961	21.015	1.884	4.905	2838.966	712.142
0.67482	0.00248	0.0023	1.70593	3898.279	15.793	1.416	5.860	3886.929	713.630
0.59653	0.00323	0.0020	1.51924	3471.287	20.570	1.844	5.189	3454.062	717.385
0.76396	0.00626	0.0028	1.95616	4470.558	39.866	3.574	7.357	4434.475	719.161
0.60270	0.00478	0.0020	1.53262	3501.877	30.440	2.729	5.034	3473.741	714.086
0.65215	0.00310	0.0021	1.65538	3782.655	19.742	1.770	5.447	3766.590	715.575
0.65987	0.00144	0.0021	1.66895	3813.691	9.170	0.822	5.498	3809.197	715.203
0.63014	0.00600	0.0020	1.60298	3662.792	38.210	3.426	5.266	3626.423	713.010
0.63546	0.00260	0.0020	1.61089	3680.896	16.558	1.484	5.292	3668.146	715.176
0.67981	0.00413	0.0026	1.72912	3947.908	26.301	2.358	6.716	3925.960	715.505
0.63146	0.00332	0.0023	1.60633	3667.299	21.143	1.896	5.937	3650.198	716.185
0.56846	0.00707	0.0021	1.45371	3318.557	45.024	4.037	5.421	3274.917	713.764
0.61131	0.01101	0.0022	1.56613	3575.418	70.115	6.286	5.679	3504.696	710.302
0.72697	0.01083	0.0030	1.86438	4256.987	68.969	6.183	7.744	4189.579	714.017
0.57179	0.01055	0.0021	1.46692	3348.762	67.186	6.023	5.421	3280.974	710.920
0.62680	0.01211	0.0016	1.61824	3694.491	77.120	6.914	4.130	3614.587	714.470
0.61362	0.01757	0.0022	1.59653	3644.838	111.891	10.031	5.679	3528.595	712.454
0.54281	0.01491	0.0020	1.41270	3224.764	94.951	8.513	5.163	3126.462	713.608
0.67060	0.01175	0.0025	1.72237	3931.359	74.828	6.709	6.453	3856.276	712.458
0.59225	0.01226	0.0022	1.52576	3481.242	78.075	7.000	5.679	3401.846	711.646

APPENDIX D (Contd.)

Weight, grams				$-\Delta E_c$, cal.					$-\Delta E_c$, kcal./mole
P_4	Coating	P_4 equiv. of P_4O_6	ΔT, °C.	Substance	Coating	HPO_3	P_4O_6	P_4	P_4
Celluluse acetate coating, distilled phosphorus									
0.54897	0.00810	0.0034	1.40388	3205.626	40.315	3.445	8.777	3170.642	715.572
0.49537	0.00943	0.0034	1.27253	2905.375	46.935	4.011	8.777	2863.206	716.106
0.57094	0.01100	0.0035	1.44959	3310.128	54.749	4.679	9.035	3259.735	707.369
0.52363	0.00615	0.0033	1.33740	3053.665	30.610	2.616	8.519	3028.958	716.677
0.55578	0.01589	0.0021	1.43410	3274.687	79.088	6.758	5.421	3194.262	712.069
0.53358	0.01321	0.0019	1.38106	3153.438	65.749	5.619	4.905	3086.975	716.784
0.55030	0.01327	0.0025	1.41637	3234.163	66.047	5.644	6.453	3168.925	713.456
0.53080	0.01113	0.0016	1.36402	3114.503	55.396	4.734	4.130	3058.503	713.892
0.53026	0.01018	0.0022	1.36344	3113.175	50.668	4.330	5.679	3063.856	715.870
0.50742	0.01242	0.0011	1.31141	2994.235	61.817	5.283	2.840	2929.975	715.403
0.53350	0.01510	0.0015	1.38018	3151.428	75.156	6.422	3.872	3073.722	713.813
0.51376	0.01279	0.0020	1.32783	3031.767	63.658	5.440	5.163	2967.832	715.704
Cellulose acetate coating, wet-method-purified phosphorus									
0.51422	0.00540	0.0035	1.30795	2986.359	26.877	2.297	9.035	2966.220	714.676
0.57640	0.00962	0.0028	1.47823	3375.596	47.881	4.092	7.228	3330.852	715.955
0.54895	0.00862	0.0036	1.40496	3208.117	42.903	3.666	9.293	3170.840	715.642
0.57996	0.01217	0.0028	1.48986	3402.154	60.572	5.176	7.228	3343.633	714.291
0.52092	0.00401	0.0022	1.32472	3024.691	19.959	1.706	5.679	3007.930	715.404
0.54906	0.00606	0.0019	1.39956	3195.780	30.162	2.577	4.905	3167.945	714.846

APPENDIX D (Contd.)

Weight, grams				$-\Delta E_c$, cal.					$-\Delta E_c$, kcal./mole
P_4	Coating	P_4 equiv. of P_4O_6	ΔT, °C.	Substance	Coating	HPO_3	P_4O_6	P_4	P_4
Jacketed bomb, wet-method-purified phosphorus									
0.79353	-	0.0058	1.59656	4575.130	-	-	14.972	4590.102	716.660
0.70120	-	0.0042	1.41148	4044.621	-	-	10.842	4055.463	716.561
0.74748	-	0.0057	1.50497	4312.598	-	-	14.714	4327.312	717.254
0.53507	-	0.0150	1.05967	3051.352	-	-	38.720	3090.072	715.505
Jacketed bomb, distilled phosphorus									
0.69164	-	0.0027	1.39210	3989.073	-	-	6.969	3996.042	715.821
0.64940	-	0.0052	1.30604	3742.392	-	-	13.423	3755.815	716.550
0.66332	-	0.0044	1.33147	3815.285	-	-	11.358	3826.643	714.742
0.69428	-	0.0027	1.40502	4026.100	-	-	6.969	4033.069	719.707
0.64067	-	0.0032	1.28919	3694.103	-	-	8.260	3702.363	715.977
0.73694	-	0.0031	1.49547	4285.361	-	-	8.002	4293.363	721.805
0.72368	-	0.0057	1.47027	4213.127	-	-	14.714	4227.841	723.813
0.69272	-	0.0048	1.40401	4023.204	-	-	12.390	4035.594	721.779
0.82565	-	0.0031	1.66823	4780.560	-	-	8.002	4788.562	718.561
0.61694	-	0.0027	1.24560	3569.147	-	-	6.969	3576.116	718.163
0.53890	-	0.0010	1.09577	3139.146	-	-	2.581	3141.727	722.295