Heat Capacity and Enthalpy of Phosphoric Acid

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Measurements of the enthalpy and derived heat capacity values for phosphoric acid were extended into the ranges of concentration (72.3–84.8% P_2O_5) and of temperature (25–200°C) that are of direct interest in the technology of superphosphoric acid. The results were combined with previous data to form a general equation for heat capacity from which values were calculated at even intervals over the concentration range water to crystalline P_2O_5 and over the temperature range 15–200°C or to the approximate boiling point.

Measurements of the heat capacity and enthalpy of phosphoric acid were extended into the ranges of concentration and temperature that are of direct interest in the technology of superphosphoric acid. The enthalpies of phosphoric acids containing 72.3–84.8% P_2O_5 were measured over the temperature range 25–200°C and their heat capacities were calculated from the results. The heat capacities were smooth continuations of those determined previously by solution calorimetry at lower concentrations and temperatures (*3*). Unpublished results, measured by low-temperature calorimetry, for liquids obtained by fusion of crystalline orthophosphoric acid and crystalline phosphoric acid hemihydrate are in agreement over the temperature range in which they were determined. A comparison with the data of Smirnova et al. (*7*) who measured the mean heat capacity between 25° and 100°C (which may be interpreted as the heat capacity at 62.5°C), shows good agreement except at the highest P_2O_5 concentrations where the separation becomes as much as 0.04 cal-g^{-1}. Heat capacities at 62.5°C are shown in Figure 1.

The change in heat capacity that reflects the increase of condensed phosphate species at concentrations above 70% P_2O_5 is apparent in Figure 1, but the heat capacity curve appears to make a smooth continuation to the slightly extrapolated value for crystalline P_2O_5 (*1*). This may indicate that with increasing concentration there is a continuous development of order in the liquid system, and that the increase in both ring species and three-dimensional cross linkages results in a smooth transition into the crystalline system.

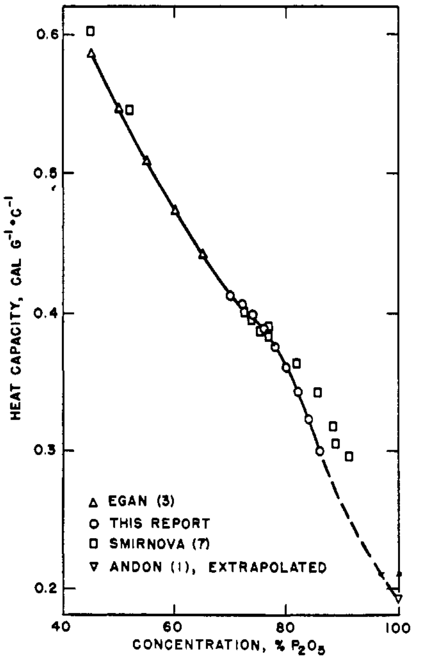

Figure 1. Heat capacity of phosphoric acid at 62.5°C

MATERIALS AND PROCEDURE

The phosphoric acid samples were taken from stock solutions used in earlier work (*5*). The stock solutions had been prepared by dissolving 2.8 kg of reagent P_2O_5 in 1050 ml of reagent H_3PO_4 (85%) at 145°C and filtering the hot solution through a coarse glass frit into a phosphoric acid reagent bottle for storage. Portions of the stock acid (85.2% P_2O_5) were diluted with reagent H_3PO_4 to form solutions of the desired concentration, and the diluted solutions were heated for 6 hr at 100°C to ensure equilibrium distribution of the phosphate species. Final concentrations were determined by the gravimetric quimociac method for phosphorus (*2*). Analyses before and after the heat capacity measurements agreed to within 0.1% P_2O_5.

The high-temperature drop calorimeter (*4*) was used for the measurements, even though the relatively low temperatures of this study produced heat effects smaller than desirable, with consequent loss of precision. The calorimeter and measuring equipment were modified in certain respects. The water bath temperature was maintained at 25.17°C wth an average deviation of ±0.10°C for the entire period of the measurements.

The current through the block thermometer, a copper-manganin bridge, was maintained constant at 8 mA by a constant-current source (Princeton Applied Research Corp., Model TC-100.2AR). A digital voltmeter (Hewlett Packard, Model DY-2401C) and a Leeds & Northrup rotary switch were used to measure the bridge unbalance and to monitor the current through the bridge by measuring the potential across a 10-Ω standard resistor in series with the bridge.

The bridge unbalance was calibrated against a quartz thermometer in the block well at five temperatures that covered the working range of the block, 24.5–25.2°C. From these five pairs of values of bridge unbalance and temperature, an equation was developed from which the block temperatures at the end of the heating periods in subsequent measurements were calculated. The equation fitted the observed temperatures to within ±0.001°C.

The thermal equivalent of the calorimeter block was determined by passing a direct electric current through the calibration heater in the block for 600 sec and measuring the change in bridge unbalance. The quotient of the calories supplied to the block divided by the corrected change in bridge unbalance in millivolts is the thermal equivalent of the block in calories per millivolt. The values obtained by the electrical calibration are shown in Table I.

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Table I. Electrical Equivalent of Copper Block, Calories per Millivolt

V	Amp[a]	Cal	Corr temp rise, mV	Cal/mV
10.09555	0.0947294	137.1428	0.21289	644.19
12.72686	0.1194206	217.9509	0.33859	643.69
17.11029	0.1605531	393.9438	0.61255	643.13
19.00924	0.1783722	486.2394	0.75576	643.38
21.32061	0.2000624	611.6787	0.94963	644.12
23.34161	0.2190288	733.1457	1.13858	643.91
			Av =	643.74
			Std. dev. =	0.17

[a] All tests were made with current flowing for 600 sec.

Table II. Enthalpy of Empty Crucible Above 25°C

Cruc. no.	Furnace temp, °C	Final block temp, °C	$H_T - H_{25}$, cal-g^{-1} Observed	$H_T - H_{25}$, cal-g^{-1} Equation 2
5	100.37	25.00	2.74	2.71
6	100.10	25.00	2.69	2.70
5	125.25	24.99	3.54	3.62
6	125.02	25.00	3.55	3.61
5	150.00	25.00	4.49	4.52
6	150.04	25.00	4.51	4.52
5	175.01	25.00	5.42	5.43
6	175.02	25.00	5.46	5.43
5	200.36	25.00	6.29	6.36
6	200.32	25.00	6.49	6.36
			Std. dev. =	0.06

Table III. Enthalpy and Heat Capacity of Alumina Above 25°C

Temp, °C	$H_T - H_{25}$, cal-g^{-1} This work	$H_T - H_{25}$, cal-g^{-1} NBS	Heat capacity, cal-g^{-1} °C^{-1} This work	Heat capacity, cal-g^{-1} °C^{-1} NBS
25	...	...	0.189	0.185
51.85	5.08	5.15	0.200	0.198
76.85	10.21	10.23	0.210	0.208
96.85	14.49	14.47	0.218	0.216
126.85	21.20	21.09	0.230	0.225
146.85	25.87	25.64	0.238	0.231
176.85	33.18	32.69	0.249	0.238
196.85	38.25	37.50	0.255	0.243

The temperature of the sample in the furnace was measured with a Wenner potentiometer and a platinum-platinum-rhodium thermocouple that was mounted just above the sample crucible. The working thermocouple was calibrated at each furnace temperature against a standard thermocouple that had previously been calibrated against a quartz thermometer in a sand bath over the temperature range covered in the measurements. The quartz thermometer was calibrated at 150° and 200°C against a platinum resistance thermometer that had been calibrated by the National Bureau of Standards.

The accuracy of this method of obtaining the temperature of the sample was checked at 125° and 200°C by placing the probe of the quartz thermometer in the furnace in the position normally occupied by the sample crucible. The temperature indicated by the quartz thermometer and that indicated by the standard thermocouple at the same working thermocouple voltage agreed within ±0.3°C.

The operating procedure for the enthalpy measurements was similar to procedures used in the calibration of the calorimeter block. The furnace temperature varied only a few hundredths of a degree from the average value which was taken as the temperature of the sample at the time it was dropped into the block.

The correction to the observed temperature rise was calculated by the equation given by White (*10*)

$$n = [V_R + (V_R - V_A)(\theta_x - \theta_R)/(\theta_R - \theta_A)]T_x \qquad (1)$$

where

n = temperature rise correction, mV
V_R = slope of afterperiod, mV/min
V_A = slope of foreperiod, mV/min
θ_R = average temperature in afterperiod, mV
θ_A = average temperature in foreperiod, mV
θ_x = average temperature in heating period, mV
T_x = duration of heating period, min; 20 min in all measurements

V_R, V_A, θ_R, and θ_A were calculated from equations expressing the constant rates of change of bridge unbalance during the fore- and afterperiods. θ_x was obtained by tabular integration of the readings of time and bridge unbalance during the heating period and dividing by T_x. The correction, n, was subtracted from the observed bridge unbalance change during the heating period to give the temperature rise resulting from dropping the hot sample into the block.

A least-squares fit to temperature of the enthalpy above 25°C of the empty crucibles gives the equation

$$H_T - H_{25} = -0.959 + 0.03652\ T \qquad (2)$$

where $H_T - H_{25}$ is enthalpy of the crucible, cal-g^{-1}, and T is temperature, °C. The observed values and those calculated from Equation 2 are compared in Table II.

The sample crucibles were suspended from platinum-rhodium electrodes by platinum fuse wires that passed through small silica rings attached to the crucibles. Corrections for the energy supplied by the fused silica rings were calculated from the equation of Southard (*8*).

The observed enthalpy of each sample in cal-g^{-1} as a function of temperature was fitted by the least-squares method to a second-degree equation of the form

$$H_T - H_{25} = A_0 + A_1T + A_2T^2 \qquad (3)$$

In Table III the enthalpy of the alumina sample calculated from Equation 3 and the heat capacity calculated from the first derivative of that equation are compared with the certificate values for a standard alumina sample from the National Bureau of Standards.

The observed enthalpy increases of the phosphoric acid samples as a function of temperature and concentration were fitted by the least-squares method to the polynomial equation

$$H_T - H_{25} = B_0 + B_1T + B_2C + B_3CT + B_4TC^2 + B_5CT^2 \qquad (4)$$

where

$H_T - H_{25}$ = enthalpy above 25°C, cal-g^{-1}
T = temperature, °C
C = concentration, % P_2O_5
$B_0 = -2.762 \times 10$
$B_1 = -9.449 \times 10^{-1}$
$B_2 = 2.388 \times 10^{-1}$
$B_3 = 4.0492 \times 10^{-2}$
$B_4 = -3.0667 \times 10^{-4}$
$B_5 = 2.914 \times 10^{-6}$

The standard deviation of Equation 4 is ±0.4 cal-g^{-1}. The observed values and those calculated from Equation 4 are shown in Table IV.

The enthalpy above 25°C of phosphoric acids at even intervals of temperature and of concentration were calculated by Equation 4; the results are shown in Table V. Equation 4 was differentiated to give an equation for heat capacity that was solved at convenient intervals of temperature and concentration; the results are shown in Table VI for the concentration

Table IV. Enthalpy Above 25°C of Phosphoric Acid

% P_2O_5								
72.3			79.2			84.8		
Furnace temp, °C	$H_T - H_{25}$, cal-g^{-1} Observed	$H_T - H_{25}$, cal-g^{-1} Equation 4	Furnace temp, °C	$H_T - H_{25}$, cal-g^{-1} Observed	$H_T - H_{25}$, cal-g^{-1} Equation 4	Furnace temp, °C	$H_T - H_{25}$, cal-g^{-1} Observed	$H_T - H_{25}$, cal-g^{-1} Equation 4
50.41	9.11	9.32	50.43	8.81	8.95	50.40	7.36	7.55
50.42	9.35	9.32	50.46	8.91	8.96	50.51	7.26	7.58
75.14	19.11	19.36	75.25	17.50	18.07	75.15	15.71	15.34
75.12	19.25	19.35	75.14	18.71	18.03	75.12	15.83	15.33
100.19	29.64	29.80	75.09	18.09	18.01	100.23	22.68	23.54
100.04	29.67	29.74	75.31	17.13	18.09	100.06	22.78	23.48
125.01	39.95	40.40	100.06	26.86	27.47	125.01	32.14	31.94
125.03	40.41	40.41	100.14	27.80	27.50	125.01	32.70	31.94
150.05	50.98	51.36	125.01	37.45	37.21	150.01	41.05	40.73
150.14	51.65	51.40	125.02	37.88	37.22	150.03	40.76	40.74
175.03	62.99	62.55	150.03	47.20	47.27	175.02	50.14	49.84
175.00	62.09	62.54	150.04	47.46	47.28	175.01	49.89	49.83
200.10	74.24	74.05	175.03	58.17	57.61	200.22	58.84	59.32
200.44	74.42	74.21	175.04	57.50	57.61	200.50	59.11	59.43
			200.03	68.18	68.24			
			200.16	67.58	68.29			

Table V. Enthalpy of Phosphoric Acid, $H_T - H_{25}$, Cal-G^{-1}

Temp, °C	% P_2O_5 70	75	80	85
40	4.9	5.3	5.1	4.3
50	9.0	9.2	8.7	7.4
60	13.0	13.1	12.2	10.4
70	17.2	17.1	15.9	13.6
80	21.4	21.1	19.5	16.8
90	25.6	25.1	23.2	20.0
100	29.8	29.2	27.0	23.3
110	34.1	33.3	30.8	26.6
120	38.5	37.5	34.7	30.0
130	42.8	41.7	38.6	33.4
140	47.3	46.0	42.5	36.9
150	51.7	50.3	46.5	40.4
160	56.2	54.6	50.5	44.0
170	60.8	59.0	54.6	47.7
180	65.3	63.4	58.8	51.3
190	70.0	67.9	62.9	55.1
200	74.6	72.4	67.2	58.8

range 70–85% P_2O_5 and the temperature range 25–200°C.

The values in Table VI fall into three groups. Those from the literature for water (*6*), phosphoric acid (*3*), and P_2O_5 (*1*) are reported to four decimal places; those determined in the present study are reported to three decimal places, and those obtained by interpolation or extrapolation through use of Equation 5 are reported to two decimal places.

The heat capacity values of Egan et al. (*3*) at each temperature were fitted to third-degree equations in % P_2O_5 and cal-g^{-1} by the method of least squares. The standard deviation of the equations for the several temperatures ranged from 0.0004–0.0016 cal-g^{-1} °C^{-1}. The results are shown in Table VI for the concentration range 0–60% P_2O_5 and the temperature range 15–80°C.

The heat capacities calculated from the present measurements over the temperature range 25–200°C were combined with previous data to develop a general equation for heat capacity for concentrations from 30–100% (crystalline) P_2O_5 and at temperatures from 15–200°C or to the boiling point.

The data used to develop the general equation comprised

Table VI. Heat Capacity of Phosphoric Acid, Cal-G^{-1} °C^{-1}

P_2O_5, wt %	Temperature, °C 15	25	40	50	60	70	80	90	100
0	1.0004	0.9990	0.9987	0.9992	1.0001	1.0013	1.0030	1.0050	1.0076
5	0.9436	0.9454	0.9482	0.9498	0.9519	0.9538	0.9552	0.96	0.96
10	0.8896	0.8931	0.8984	0.9016	0.9045	0.9067	0.9080	0.91	0.91
15	0.8365	0.8414	0.8487	0.8528	0.8569	0.8595	0.8609	0.86	0.87
20	0.7846	0.7907	0.7995	0.8044	0.8093	0.8124	0.8141	0.82	0.82
25	0.7343	0.7411	0.7511	0.7571	0.7621	0.7658	0.7678	0.77	0.78
30	0.6856	0.6931	0.7038	0.7097	0.7156	0.7199	0.7223	0.71	0.71
35	0.6391	0.6469	0.6579	0.6640	0.6702	0.6751	0.6778	0.67	0.68
40	0.5948	0.6028	0.6138	0.6202	0.6263	0.6316	0.6346	0.64	0.64
45	0.5533	0.5612	0.5716	0.5780	0.5841	0.5898	0.5928	0.60	0.61
50	0.5146	0.5223	0.5319	0.5379	0.5441	0.5499	0.5529	0.57	0.57
55	0.4792	0.4865	0.4949	0.5006	0.5065	0.5122	0.5151	0.53	0.54
60	0.4473	0.4540	0.4608	0.4662	0.4717	0.4771	0.4795	0.50	0.50
65	0.42	0.43	0.44	0.44	0.44	0.45	0.46	0.46	0.47
70	0.38	0.397	0.403	0.407	0.411	0.415	0.420	0.424	0.428
75	0.35	0.378	0.385	0.389	0.393	0.398	0.402	0.406	0.411
80	0.31	0.343	0.350	0.355	0.360	0.364	0.369	0.374	0.378
85	0.28	0.294	0.301	0.306	0.311	0.316	0.321	0.326	0.331
90	0.25	0.25	0.27	0.27	0.28	0.28	0.29	0.30	0.30
95	0.21	0.22	0.24	0.24	0.24	0.25	0.26	0.26	0.27
100	0.1740	0.1783	0.1848	0.1891	0.22	0.22	0.23	0.23	0.24

(*Continued on next page*)

Table VI. *(Continued)*

P_2O_5, wt %	Temperature, °C 110	120	130	140	150	160	170	180	190	200
40	0.65									
45	0.61									
50	0.58				Boiling region					
55	0.54	0.55								
60	0.51	0.51	0.52	0.52						
65	0.47	0.48	0.48	0.49	0.49	0.50				
70	0.432	0.436	0.440	0.444	0.448	0.452	0.456	0.460	0.464	0.469
75	0.415	0.420	0.424	0.428	0.433	0.437	0.441	0.446	0.450	0.454
80	0.383	0.388	0.392	0.397	0.402	0.406	0.411	0.416	0.420	0.425
85	0.336	0.341	0.346	0.351	0.356	0.361	0.366	0.370	0.375	0.380
90	0.31	0.31	0.32	0.32	0.33	0.33	0.34	0.34	0.35	0.35
95	0.27	0.28	0.29	0.29	0.30	0.30	0.31	0.31	0.32	0.32
100	0.24	0.25	0.25	0.26	0.26	0.27	0.27	0.28	0.28	0.29

140 points; 8 points for crystalline P_2O_5 from 0–56.85°C (*1*), 10 points for liquid H_3PO_4 from 26–58°C, 8 points for liquid $2H_3PO_4 \cdot H_2O$ from 24–40°C (*9*), 64 points for acid concentrations in the range 32–68% P_2O_5 at temperatures from 15–80°C, and 50 points from this report for acid strengths in the range 70–86% P_2O_5 over the temperature range 25–200°C. The 9 points given for water in Table VI are taken from Osborne et al. (*6*).

The equation was of the form

$$C_p = B_0 + B_1T + B_2n + B_3T^2 + B_4n^2 + B_5Tn \qquad (5)$$

where

C_p = heat capacity, cal-g^{-1} °C^{-1}
T = temperature, °C
n = concentration, expressed as % P_2O_5
$B_0 = 8.90487 \times 10^{-1}$
$B_1 = 5.33763 \times 10^{-4}$
$B_2 = -7.77818 \times 10^{-3}$
$B_3 = -7.42939 \times 10^{-7}$
$B_4 = 5.64683 \times 10^{-6}$
$B_5 = 2.12033 \times 10^{-6}$

Addition of more terms did not improve the fit significantly. The standard deviation was 0.009 cal-g^{-1} °C^{-1}. A corresponding equation in units of $P_2O_5 \cdot nH_2O$ and cal (mole P_2O_5)$^{-1}$ gave similar results. The results of interpolations and extrapolations through use of Equation 5 are shown in Table VI as values shown to two decimal places.

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Enthalpy of Formation of Phosphoryl Triamide

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The enthalpy of formation of crystalline phosphoryl triamide, $PO(NH_2)_3$, from the elements in their standard states at 25°C is −143.2 kcal mol^{-1}. It was determined from its enthalpy of solution in 4*m* HCl at 25°C and from published values for the enthalpies of formation of H_3PO_4, $NH_4H_2PO_4$, and H_2O and for the enthalpy of dilution of H_3PO_4.

In a continuing study of the thermal properties of compounds with potential application in fertilizer technology, measurements were made to determine the standard enthalpy of formation of phosphoryl triamide, $PO(NH_2)_3$. This compound has a high plant nutrient content and good physical properties and was an excellent source of both nitrogen and phosphorus in greenhouse tests (*7*).

MATERIALS AND APPARATUS

Phosphoryl Triamide. The $PO(NH_2)_3$ samples were taken from the material removed from the low-temperature

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