Table I. Enthalpy of Solution of K_2HPO_4 in 9.93 *m* HCl at 40 °C

sample wt, g	cor temp rise, °C	−enthalpy of soln, cal/sample	$-\Delta H_2$,[a] cal/mol
8.442 60	0.6527	463.8	9570
8.647 70	0.6690	475.1	9570
8.828 08	0.6820	484.5	9560
9.024 76	0.6969	496.3	9578
9.224 17	0.7128	506.7	9568

[a] $\Delta H_2 = -9550 - 2.13w$, std dev = 7, w = 8.904 98, ΔH_2 = −9569 cal/mol.

Table II. Enthalpy of Solution of H_2O in 9.93 *m* HCl at 40 °C

sample wt, g	cor temp rise, °C	−enthalpy of soln, cal/sample	$-\Delta H_3$,[a] cal/mol
4.944 40	0.1768	125.4	457.0
7.965 80	0.2825	201.6	456.0
10.999 52	0.3882	278.6	456.3
14.008 15	0.4898	352.9	453.8
17.043 63	0.5913	428.3	452.7

[a] $\Delta H_3 = -459.1 + 0.357w$, std dev = 0.7, w = 0.460 48, ΔH_3 = −458.9 cal/mol.

Table III. Enthalpy of Solution of $K_4P_2O_7$ in 9.93 *m* HCl + Stoichiometric H_2O at 40 °C

sample wt, g	cor temp rise, °C	−enthalpy of soln, cal/sample	$-\Delta H_4$,[a] cal/mol
8.405 38	1.0012	711.94	27 981
8.410 33	0.9991	710.97	27 926
8.444 30	1.0059	716.18	28 018
8.445 04	1.0066	715.24	27 979
8.517 45	1.0134	721.13	27 969

[a] $\Delta H_4 = -27974 - 0.110w$, std dev = 38, w = 8.444 50, ΔH_4 = −27 975 cal/mol.

was too small to determine accurately its enthalpy of solution so the sample size of water was varied over a range several times greater than the stoichiometric amount.

Results of determinations of ΔH_2, ΔH_3, and ΔH_4 are listed in Tables I, II, and III, respectively. Straight line equations of the enthalpies of solution as a function of sample weight, *w*, were fitted to the observed values by the "least-squares" method. These equations were solved where *w* was the average weight of $K_4P_2O_7$ or the stoichiometric amount of H_2O or K_2HPO_4 corresponding to that weight. The equations along with the standard deviations and the values of ΔH_2, ΔH_3, and ΔH_4 for the specified values of *w* also are listed in Tables I, II, and III. Substitution of these calculated values of the enthalpies of solution in eq 5 gives 9296 ± 39 cal (standard deviation) for the enthalpy of reaction 1 at 40 °C. This value was adjusted by −154 ± 2 cal (standard deviation) to give 9142 ± 39 cal (standard deviation) for the enthalpy of reaction 1 at 25 °C according to the equation

$$\Delta H_1(25\ ^\circ\mathrm{C}) = \Delta H_1(40\ ^\circ\mathrm{C}) + \int_{40\ ^\circ\mathrm{C}}^{25\ ^\circ\mathrm{C}} \Delta C_P \, dT \qquad (6)$$

where ΔC_P is the difference in heat capacity between the products and the reactants, and *T* is the temperature in °C. The heat capacity equations were derived from the data of Osborne et al. (*5*) for water and the data of Luff and Reed (*2*, *4*) for K_2HPO_4 and $K_4P_2O_7$.

The standard enthalpy of formation of $H_2O(l)$ (*6*) is −68.315 kcal/mol and the standard enthalpy of formation of $K_2HPO_4(c)$ (*3*) is −425.4 kcal/mol. Substituting these enthalpies of formation and the enthalpy of reaction 1 at 25 °C in the equation

$$\Delta H_f^\circ(K_4P_2O_7) = 2\Delta H_f^\circ(K_2HPO_4) - \Delta H_f^\circ(H_2O) + \Delta H_1 \qquad (7)$$

gives −773.3 kcal/mol as the standard enthalpy of formation of $K_4P_2O_7$.

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Low-Temperature Heat Capacity and Entropy of Tetrapotassium Pyrophosphate

Basil B. Luff* and Robert B. Reed

Division of Chemical Development, National Fertilizer Development Center, Tennessee Valley Authority, Muscle Shoals, Alabama 35660

In a continuing program of measurement of thermochemical properties of materials of interest in fertilizer technology, the heat capacity of tetrapotassium pyrophosphate, $K_4P_2O_7$, was measured by adiabatic calorimetry over the temperature range 10–317 K. Related thermodynamic properties were derived.

Materials and Apparatus

Tetrapotassium pyrophosphate was prepared by heating reagent-grade dipotassium orthophosphate in a platinum dish at 600 °C for 21 h and allowing it to cool in a desiccator over $MgClO_4$. Chemical analysis showed the material to contain 57.1% K_2O and 42.98% P_2O_5 (stoichiometry: 57.0% K_2O and 42.97% P_2O_5). None of the P_2O_5 was in the ortho form. The calorimeter was charged with 88.3417 g or 0.267589 mol. The weight was corrected for bouyancy in air on the basis of a density of 2.61 g/cm^3 (*1*), and the gram formula weight was taken as 330.3514. Its heat capacity ranged from 46% of the total at 10 K to 60% at 300 K. Air in the calorimeter was removed and replaced with the same mass of helium used in measurements on the empty calorimeter; the helium facilitated heat transfer and thermal equilibrium.

Table I. Observed Heat Capacity of Tetrapotassium Pyrophosphate (cal deg^{-1} mol^{-1})

T, K	C_p	T, K	C_p	T, K	C_p	T, K	C_p
10.10	0.3099	56.39	19.17	144.26	41.98	232.29	53.56
11.40	0.4493	58.83	20.21	147.23	42.44	235.32	53.93
11.42	0.4110	61.10	21.17	150.08	42.94	238.35	54.22
12.68	0.6080	63.63	22.22	152.99	43.37	241.36	54.58
12.86	0.6462	66.01	23.13	155.95	43.86	244.50	54.89
13.91	0.8386	68.78	24.12	158.81	44.27	247.48	55.22
14.51	0.9580	71.13	24.89	161.89	44.74	250.59	55.53
15.28	1.111	74.25	25.94	164.86	45.15	253.54	55.86
16.36	1.368	76.43	26.67	167.79	45.57	256.63	56.13
16.92	1.517	79.26	27.61	170.98	46.03	259.56	56.45
18.35	1.905	81.08	28.18	173.86	46.43	262.62	56.75
18.74	2.047	84.26	29.17	177.00	46.84	265.53	57.02
20.40	2.551	87.48	30.10	179.84	47.22	268.57	57.31
20.96	2.738	90.46	30.89	182.94	47.66	271.45	57.64
23.02	3.505	93.72	31.70	185.74	48.04	274.47	57.91
23.70	3.758	96.55	32.39	188.81	48.45	275.08	57.92
26.26	4.838	99.88	33.18	191.57	48.79	277.05	58.11
26.77	5.062	102.59	33.83	194.60	49.19	280.00	58.43
29.46	6.276	105.78	34.53	195.44	49.28	283.16	58.72
30.06	6.561	108.60	35.15	196.51	49.41	286.08	58.99
32.63	7.790	111.67	35.82	199.42	49.79	289.21	59.30
33.53	8.243	114.59	36.45	202.51	50.16	292.11	59.59
36.00	9.490	117.56	37.05	205.39	50.51	295.22	59.87
37.13	10.06	120.40	37.63	208.44	50.87	298.11	60.13
39.62	11.28	123.47	38.21	211.29	51.20	299.46	60.17
41.00	11.96	126.22	38.77	214.31	51.55	302.35	60.46
43.58	13.23	129.40	39.35	217.28	51.87	305.40	60.73
45.19	14.05	132.26	39.89	220.26	52.22	308.28	60.94
47.99	15.39	135.36	40.44	223.37	52.61	311.31	61.23
49.58	16.15	138.33	40.98	226.30	52.88	314.17	61.46
52.72	17.58	141.35	41.50	229.37	53.27	317.17	61.75
54.26	18.27						

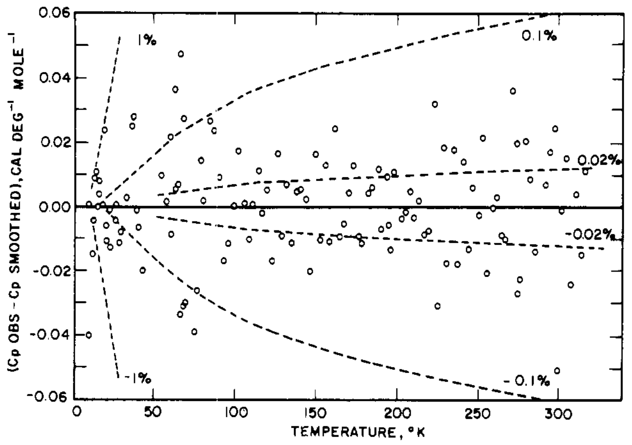

Figure 1. Deviations of observed heat capacities from smoothed values of tetrapotassium pyrophosphate.

Table II. Molal Thermodynamic Properties of Tetrapotassium Pyrophosphate

T, K	C_p, cal/K	$S°$, cal/K	$H° - H_0°$, cal	$-(G° - H_0°)/T$, cal/K
5	0.0360	0.0122	0.0452	0.0032
10	0.3000	0.0982	0.7380	0.0244
15	1.049	0.3405	3.849	0.0839
20	2.422	0.8166	12.29	0.2022
25	4.303	1.551	28.92	0.3942
30	6.539	2.529	55.91	0.6653
35	8.966	3.718	94.62	1.014
40	11.47	5.078	145.7	1.436
45	13.94	6.573	209.3	1.922
50	16.33	8.167	285.0	2.466
60	20.73	11.54	470.7	3.695
70	24.53	15.03	697.5	5.064
80	27.84	18.52	959.6	6.529
90	30.76	21.98	1253	8.054
100	33.21	25.35	1573	9.616
110	35.46	28.62	1917	11.20
120	37.55	31.80	2282	12.78
130	39.47	34.88	2667	14.36
140	41.26	37.87	3071	15.94
150	42.91	40.77	3492	17.49
160	44.45	43.59	3929	19.04
170	45.89	46.33	4381	20.56
180	47.26	48.99	4846	22.07
190	48.59	51.58	5326	23.55
200	49.85	54.11	5818	25.02
210	51.05	56.57	6322	26.46
220	52.19	58.97	6839	27.89
230	53.32	61.32	7366	29.29
240	54.42	63.61	7905	30.67
250	55.48	65.85	8455	32.03
260	56.49	68.05	9014	33.38
270	57.46	70.20	9584	34.70
280	58.41	72.31	10160	36.01
290	59.38	74.37	10750	37.29
300	60.27	76.40	11350	38.56
310	61.12	78.39	11960	39.82
273.15	57.76	70.87	9766	35.11
298.15	60.11	76.03	11240	38.33

The adiabatic calorimeter and the method of operation have been described previously (*4*) and the overall accuracy of our technique has been reported (*2*). The defined calorie was taken as 4.1844 absolute J and the ice point was 273.15 K. The measured heat capacities were corrected for curvature (*3*) and for a small difference in the amount of eutectic solder relative to the empty calorimeter. Because small temperature differences were important, temperatures were measured to four decimal places; but these were rounded to two decimal places in the final tabulation. The heat capacities below 10 K were from a large-scale plot of C_p/T against T^2 extrapolated to 0 K. Observed molal heat capacities are shown in Table I.

Results and Discussion

Smoothed heat capacities and derived functions at round values of temperature are shown in Table II. The heat capacity curve had the normal sigmate shape and showed no thermal anomalies. The deviations of the observed heat capacity values from the smoothed curve are shown in Figure 1.

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