Table IV. Integral Enthalpies of Solution and Relative Partial Molal Heat Contents of Aqueous Dipotassium Orthophosphate Solutions at 25 °C

Concn of K_2HPO_4, m	Heat of soln, $-\Delta H$, cal/mol	Rel molal heat content, cal/mol: Apparent, of K_2HPO_4, $-\phi L$	Partial, of K_2HPO_4, $-\bar{L}_2$	Partial, of H_2O, $-\bar{L}_1$
0	4939	0	0	0.00
0.5	5202	263	527	−2.38
1.0	5447	508	945	−7.89
2.0	5746	807	1148	−12.30
3.0	5838	899	1019	−6.49
4.0	5832	893	701	13.87
5.0	5747	808	213	53.64
6.0	5600	661	−376	112.12
7.0	5407	468	−998	184.91
8.0	5187	248	−1583	263.86
9.0	4955	16	−2063	337.13
9.988[a]	4733	−206	−2367	388.74

[a] Saturated solution.

The observed values of the differential enthalpies of solution from Table II were fitted to a polynomial in molality. The equation giving the best fit was

$$-\mathrm{d}(\Delta H)/\mathrm{d}n_2 = 4939 + 998m + 330.0m^2 - 493.9m^3 + 111.5m^4 \quad (2)$$

The standard deviation of the observed values from eq 2 is ±23 cal/mol.

If the amount of solvent is held constant, say 1000 g, n_2 of eq 2 can be replaced by m, and integration of this equation with respect to m over the concentration range of the measurements and division by m gives the equation for ΔH, the integral enthalpy of solution, in calories per mole.

$$-\Delta H = 4939 + 499m + 110.0m^2 - 123.5m^3 + 22.3m^4 \quad (3)$$

Enthalpies of Dilution

The enthalpies of dilution, ΔH_D, in calories per mole, for the solutions listed in Table I were determined by diluting a weighed amount of each solution with a weighed amount of distilled water in the calorimeter, measuring the enthalpy change, Q, and dividing by the number of moles of K_2HPO_4, n_2, involved in the dilution.

The enthalpy of dilution is equal to the difference in the integral enthalpy of solution of the final, ΔH_F, and the initial, ΔH_I, solution so

$$\Delta H_I = \Delta H_F - \Delta H_D \quad (4)$$

The molalities of the final solutions were calculated from the weights and concentrations of the initial solutions and the weight of distilled water used to dilute them. The value for ΔH_F for each measurement then was calculated using eq 3. Equation 4 was used to calculate the integral enthalpy of solution of K_2HPO_4 in water to the concentrations shown in Table I. The measured values and the integral enthalpy of solution for each measurement are shown in Table III.

The average values for the integral enthalpies of solution from Table III were fitted to a polynomial in molality.

$$-\Delta H = 5205 + 407.8m - 74.18m^2 + 2.866m^3 \quad (5)$$

with a standard deviation of ±12 cal/mol.

Equation 5 was used to calculate the integral enthalpies of solution at even molalities to saturation. These values, together with partial molal quantities calculated by conventional methods (*1*), are shown in Table IV.

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Low-Temperature Heat Capacity and Entropy of Dipotassium Orthophosphate

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The low-temperature heat capacity of dipotassium orthophosphate, K_2HPO_4, was measured over the range 9–316 K by adiabatic calorimetry. The heat capacity, C_p, entropy, $S°$, and Planck function, $(G° - H_0°)/T$, at 298.15 K were calculated to be 33.77, 42.80, and −21.85 cal mol^{-1} deg^{-1}, respectively. The heat capacity showed only normal sigmate behavior.

In a continuing program of the measurement of thermochemical properties of materials of interest in fertilizer technology, the heat capacity of dipotassium orthophosphate, K_2HPO_4, was measured by adiabatic calorimetry over the temperature range 9–316 K. Related thermodynamic properties were derived.

Materials and Apparatus

Dipotassium orthophosphate was prepared by recrystallizing the reagent-grade salt from distilled water and drying it by vacuum desiccation over $MgClO_4$. Chemical analysis showed the material to contain 40.7% P_2O_5 and 54.1% K_2O (stoichiometric, 40.75% P_2O_5 and 54.08% K_2O). The calorimeter was charged with 77.7580 g or 0.446 415 mol. The weight was corrected for buoyancy in air on the basis of a density of 2.54 g/cm^3 (*1*), and the gram formula weight was taken as 174.183 37. Its heat capacity ranged from 50% of the total at 10 K to 58% 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.

The adiabatic calorimeter and the method of operation have been described previously (*4*) and the overall accuracy of our

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Table I. Observed Heat Capacity of Dipotassium Orthophosphate, cal deg^{-1} mol^{-1}

T, K	C_p	T, K	C_p	T, K	C_p	T, K	C_p
9.49	0.1799	55.32	10.90	146.52	23.30	240.39	30.06
9.70	0.1938	57.08	11.30	149.36	23.54	243.74	30.29
10.57	0.2439	58.93	11.73	152.73	23.83	246.50	30.46
11.28	0.3033	61.27	12.26	155.52	24.05	249.83	30.69
11.71	0.3518	63.47	12.76	159.01	24.35	252.56	30.84
13.05	0.4487	66.10	13.30	161.75	24.56	255.87	31.05
13.17	0.4789	68.75	13.81	165.17	24.82	258.56	31.22
14.59	0.6756	71.62	14.31	167.86	25.04	261.85	31.42
15.21	0.7556	74.64	14.83	171.24	25.31	264.52	31.58
16.08	0.8861	77.83	15.40	173.89	25.50	267.78	31.78
17.20	1.065	80.46	15.86	177.21	25.74	270.56	31.97
17.55	1.117	82.10	16.12	179.84	25.94	273.66	32.17
19.01	1.384	85.19	16.60	183.11	26.19	276.26	32.32
19.26	1.429	88.64	17.12	185.86	26.38	277.12	32.38
20.80	1.747	91.29	17.47	189.10	26.61	280.14	32.57
22.06	2.011	94.57	17.88	191.97	26.81	283.88	32.81
23.34	2.317	97.56	18.26	195.16	27.05	286.33	32.99
25.46	2.825	100.69	18.64	196.58	27.13	289.90	33.22
26.64	3.120	103.78	19.01	198.29	27.25	292.61	33.41
28.99	3.742	106.79	19.36	201.46	27.47	295.87	33.63
30.36	4.115	109.97	19.71	204.24	27.67	298.82	33.85
32.63	4.755	112.87	20.03	207.39	27.87	299.32	33.81
34.13	5.190	116.16	20.41	210.12	28.06	299.64	33.85
36.37	5.840	118.97	20.69	213.25	28.27	301.80	34.00
38.07	6.326	122.15	21.04	216.09	28.45	305.49	34.19
40.37	6.972	125.08	21.32	219.20	28.66	305.80	34.22
42.28	7.510	128.18	21.62	222.15	28.86	307.94	34.41
44.68	8.165	131.22	21.91	225.24	29.06	310.32	34.52
46.72	8.736	134.24	22.20	228.15	29.25	311.60	34.59
49.18	9.388	137.22	22.47	231.38	29.46	313.23	34.70
51.32	9.944	140.36	22.75	234.24	29.65	314.16	34.71
53.82	10.54	143.26	23.01	237.59	29.92	316.12	34.91

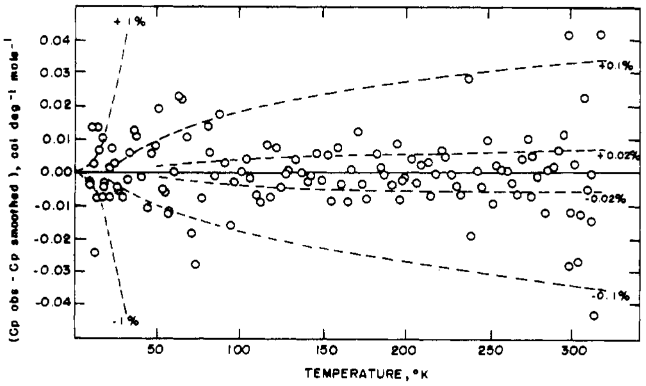

Figure 1. Deviations of observed heat capacities from smoothed values of dipotassium orthophosphate.

Table II. Molal Thermodynamic Properties of Dipotassium Orthophosphate

T, K	C_p, cal K^{-1}	$S°$, cal K^{-1}	$H° - H_0°$, cal	$(G° - H_0°)/T$, cal K^{-1}
5	0.0250	0.0085	0.0311	0.0023
10	0.2094	0.0681	0.5110	0.0170
15	0.7189	0.2359	2.666	0.0582
20	1.582	0.5535	8.289	0.1390
25	2.709	1.023	18.92	0.2665
30	4.022	1.631	35.69	0.4416
35	5.432	2.356	59.30	0.6620
40	6.869	3.176	90.07	0.9242
45	8.264	4.066	127.9	1.223
50	9.591	5.006	172.6	1.554
60	11.98	6.971	280.7	2.292
70	14.03	8.977	411.1	3.104
80	15.77	10.97	560.3	3.962
90	17.30	12.91	725.8	4.850
100	18.56	14.80	905.3	5.751
110	19.72	16.63	1097	6.657
120	20.81	18.39	1299	7.562
130	21.79	20.10	1513	8.461
140	22.72	21.75	1735	9.351
150	23.60	23.34	1967	10.23
160	24.42	24.89	2207	11.10
170	25.20	26.40	2455	11.96
180	25.95	27.86	2711	12.80
190	26.68	29.28	2974	13.63
200	27.37	30.67	3244	14.45
210	28.05	32.02	3521	15.25
220	28.72	33.34	3805	16.04
230	29.37	34.63	4096	16.82
240	30.05	35.89	4393	17.59
250	30.69	37.13	4696	18.35
260	31.30	38.35	5006	19.09
270	31.93	39.54	5323	19.83
280	32.56	40.72	5645	20.55
290	33.23	41.87	5974	21.27
300	33.89	43.01	6310	21.98
310	34.56	44.13	6651	22.67
273.15	32.13	39.91	5423	20.06
298.15	33.77	42.80	6247	21.85

technique has been reported (*2*). The defined calorie was taken as 4.1840 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 read from a large scale plot of C_p/T against T^2 that extrapolated smoothly 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 the figure.

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Standard Enthalpies of Formation of Monopotassium and Dipotassium Orthophosphate

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The standard enthalpies of formation of monopotassium orthophosphate, KH_2PO_4, and dipotassium orthophosphate, K_2HPO_4, are −376.1 and −425.4 kcal mol^{-1}, respectively. They were determined from the enthalpies of solution of KCl, $H_3PO_4 \cdot 13.88H_2O$, $H_3PO_4 \cdot 1.51H_2O$, KH_2PO_4, K_2HPO_4, and H_2O in 4 *m* HCl at 25 °C, the standard enthalpies of formation of KCl, aqueous HCl, and $H_3PO_4 \cdot 100H_2O$, and the enthalpies of dilution of H_3PO_4 solutions.

The enthalpies of formation of monopotassium and dipotassium orthophosphate are important quantities in the development of processes for the manufacture of potassium phosphate fertilizers. These values were determined from published enthalpies of formation of KCl, $H_3PO_4 \cdot 100H_2O$, and aqueous HCl, enthalpies of dilution of H_3PO_4, and the enthalpies of reaction

$$KCl + H_3PO_4 \cdot 13.88H_2O = KH_2PO_4 + HCl \cdot 13.88H_2O \quad (1)$$

and

$$K_2HPO_4 + H_3PO_4 \cdot 1.51H_2O = 2KH_2PO_4 + 1.51H_2O \quad (2)$$

at 25 °C.

Materials

Reagent monopotassium orthophosphate, KH_2PO_4 (gram formula weight = 136.0893), dipotassium orthophosphate, K_2HPO_4 (gram formula weight = 174.1834), and potassium chloride, KCl (gram formula weight = 74.555), were recrystallized from distilled water and dried by vacuum desiccation over $MgClO_4$. Chemical analyses of the products along with the stoichiometric values are listed in Table I. Recrystallized reagent phosphoric acid was diluted to yield $H_3PO_4 \cdot 1.51H_2O$ (gram formula weight = 125.2158, 56.68% P_2O_5 by chemical analysis) and $H_3PO_4 \cdot 13.88H_2O$ (gram formula weight = 348.0741, 20.39% P_2O_5 by chemical analysis). The calorimetric solvent was prepared by diluting reagent-grade hydrochloric acid with distilled water to 4.001 *m* (12.73%) HCl as determined by alkalimetric titration.

Table I. Chemical Analyses of Salts Used in Enthalpy of Solution Measurements

	Composition, %					
	P_2O_5		K_2O		Cl	
Salt	Anal.	Stoich	Anal.	Stoich	Anal.	Stoich
KH_2PO_4	52.1	52.15	34.6	34.61		
K_2HPO_4	40.7	40.75	54.1	54.08		
KCl			63.4	63.18	47.5	47.55

Table II. Enthalpy of Solution of $H_3PO_4 \cdot 13.88H_2O$ in 4.001 *m* HCl at 25 °C

Sample wt, g	Cor temp rise, °C	Enthalpy of soln, cal/sample	ΔH_3,[a] cal/mol
21.148 46	−0.0264	22.55	371
21.578 10	−0.0270	23.04	372
21.854 01	−0.0281	23.93	381
21.883 38	−0.0278	23.71	377
22.287 33	−0.0284	24.24	379

[a] $\Delta H_3 = 199 + 8.14w$, std dev = 3, w = 21.75026, ΔH_3 = 376.

Calorimeter

The solution calorimeter, the method of measurement, and the corrections applied have been described (*2*), with the exception that the Wenner potentiometer and Aryton shunt were replaced by a digital voltmeter (Hewlett-Packard, Model 3490A) that measured the voltage drop directly across the calorimeter heater as well as across a standard resistor in series with the heater. The defined thermochemical calorie (1 cal = 4.1840 absolute J) was used to convert electrical energy to thermal energy.

Procedure

The enthalpy of reaction 1 was determined by the scheme

$$\text{ampule } H_3PO_4 \cdot 13.88H_2O + \text{solvent} = \text{solution D} \quad (3)$$

$$\text{ampule KCl} + \text{solution D} = \text{solution E} \quad (4)$$

$$\text{ampule } HCl \cdot 13.88H_2O + \text{solvent} = \text{solution F} \quad (5)$$

$$\text{ampule } KH_2PO_4 + \text{solution F} = \text{solution E} \quad (6)$$

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