

composition. $\text{HTl}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ decomposes to $\text{Tl}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ if left exposed to air at room temperature (2).

Weighed amounts of $\text{HTl}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ and premixed sulfuric acid solution were taken in a closed Erlenmeyer flask and agitated with a magnetic stirrer in an oil bath ($\pm 0.5^\circ\text{C}$) for 2 h, until all the salt dissolved. The solution was slowly cooled and allowed to equilibrate (until no change in concentration in the supernatant was observed) at the temperature under consideration (25 or 0°C). An ice bath was used for regulating the lower temperature ($\pm 1^\circ\text{C}$). The amount of $\text{HTl}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ in the saturated solution was determined by an iodometric titration using KI and $\text{Na}_2\text{S}_2\text{O}_3$. Thallium salts are extremely toxic and must be handled very carefully.

Results and Discussion

The results are given in Table I. The solubility of $\text{HTl}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ is expressed as grams of the salt dissolved in 100 g of the premixed acid solution. Also presented in Table I are the data

of Meyer. The data were correlated by the following least-squares expression

$$\ln(s) = 13.02 - ((1314/T) + 0.19a)$$

with a correlation coefficient of 0.9. The solubility of $\text{HTl}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ seems to be very dependent on the acid concentration.

Glossary

- s* solubility, g of salt/100 g of acid solution
T absolute temperature, K
a acid concentration, %

Literature Cited

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Enthalpy of Solution of Dipotassium Orthophosphate at 25°C

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Measurements were made of the enthalpy of solution at 25°C of dipotassium orthophosphate in water over the concentration range 0.06–2.33 *m*. Measurements also were made of the enthalpies of dilution to near infinite dilution of dipotassium orthophosphate solutions ranging from 3.12 to 9.99 *m*. The results were combined to determine the enthalpy of solution over the entire concentration range, and the partial molal heat contents were derived.

The integral enthalpy of solution of dipotassium orthophosphate was measured as part of a possible refinement of the entropies of aqueous phosphate ions. Relative partial molal quantities were calculated from the enthalpy of solution.

Materials and Apparatus

Reagent-grade dipotassium orthophosphate was recrystallized from distilled water. The crystals were filtered by suction on fritted glass and dried under vacuum desiccation over magnesium perchlorate for several days. Then, they were ground lightly to pass a 20-mesh screen and dried to constant weight under vacuum over magnesium perchlorate. Chemical analysis of the product showed it to contain 54.1% K_2O and 40.7% P_2O_5 (stoichiometric, 54.08% K_2O and 40.75% P_2O_5).

The dipotassium orthophosphate solutions were prepared by dissolving the recrystallized salt in distilled water. The concentrations of these solutions are shown in Table I.

The saturated solution was prepared by dissolving the recrystallized salt in distilled water at 70°C until no more would dissolve readily. The solution was allowed to cool to room temperature in a capped plastic bottle with periodic stirring. After several days the supernatant liquid was decanted from the rather large crystals that had developed. All solutions were stored in capped plastic bottles until used.

The solution calorimeter has been described (2). The initial bulk charge of liquid for each experimental run was weighed and placed in the calorimeter. Each addition to the bulk liquid was

Table I. Dipotassium Orthophosphate Solutions

Composition, %		$[\text{K}_2\text{HPO}_4], m$
K_2O	P_2O_5	
19.1	14.29	3.119
22.0	16.49	3.924
24.7	18.63	4.832
27.8	20.83	6.048
29.6	22.48	6.995
32.4	24.26	8.526
34.6	25.64	9.988 ^a

^a Saturated solution.

contained in a thin-walled glass bulb that was suspended from a glass rod inside the hollow stirrer shaft. The bulb was crushed against the bottom of the Dewar flask to start the solution period.

The calorimeter system was calibrated electrically immediately before and after each measurement. The platinum resistance thermometer was calibrated by the National Bureau of Standards. The Wenner potentiometer, Ayrton shunt, and standard resistors used in the energy measurements were calibrated against standard resistors and a potentiometer calibrated by the Redstone Arsenal, Huntsville, Ala., and traceable to the National Bureau of Standards. The defined calorie was taken as 4.1840 absolute J.

Conventional "normal" and "reverse" readings of the resistance of the platinum resistance thermometer on a Leeds and Northrup G-2 Mueller bridge were made during rating periods to establish heat-leak corrections. Only normal readings were taken during the solution period, and to these were applied both the usual bridge corrections and an adjustment to compensate for the absence of reverse measurements. The observed temperature rise was the difference between the temperatures at the end and at the beginning of the solution period as calculated from linear equations for the rating periods. The correction to the observed temperature rise for heat leak was calculated by in-

Table II. Observed Differential Enthalpies of Solution of Dipotassium Orthophosphate Solutions

K ₂ HPO ₄		-Q, cal	-Δ(ΔH)/Δn ₂ , cal/mol
Av molality, <i>m</i>	Grams added		
Series A			
0.0572	17.079 43	490.528	5002.61
0.1745	17.489 75	507.426	5053.55
0.2988	18.925 95	570.971	5254.88
0.4282	18.709 37	579.193	5392.26
0.5568	18.465 12	589.281	5558.75
0.8220	20.786 68	690.230	5783.83
0.9519	16.002 76	538.707	5863.60
1.0728	18.089 09	614.601	5918.12
1.2055	19.060 43	653.407	5971.15
1.4032	17.772 16	616.500	6042.26
1.5306	17.199 95	599.436	6070.47
1.6577	17.464 21	610.448	6088.45
1.7907	18.609 28	651.629	6099.26
1.9249	17.497 73	612.424	6096.45
2.0593	18.477 36	647.453	6103.45
2.1942	17.369 27	607.259	6089.75
2.3315	18.931 72	660.714	6078.97
Series B			
0.1189	17.460 55	503.025	5018.09
0.2350	16.531 18	490.418	5167.36
0.3477	16.267 20	496.514	5316.50
Series C			
0.0636	19.028 53	542.945	4970.01
0.0615	18.371 96	527.424	5000.47
0.0631	18.878 97	540.574	4986.95

tegration by the trapezoidal rule of the heat leak as a function of time from measurements taken at 0.5-min intervals. The calculation was simplified by the linear relationship of heat leak to temperature over the temperature range of the measure-

ments. Raoult's law was applied to correct for the heat of vaporization of water into the vapor space above the calorimeter liquid for each measurement. The corrections were less than 0.02% of the observed enthalpies of solution and were applied to the two calibration periods as well as to the solution period so that any deviations of vapor pressure from those of ideal solutions were essentially cancelled. A correction for the energy of bulb breaking (1.1 ± 0.1 cal) was based on the results of ten measurements in which bulbs filled with water were broken in the calorimeter containing water. The average temperature for all the solution periods was 25.04 ± 0.06 °C, and no corrections were applied to convert the enthalpies of solution to 25.00 °C.

Enthalpies of Solution

The differential enthalpies of solution over the concentration range 0.057–2.332 *m* dipotassium orthophosphate were determined from three series of measurements. In series A the salt was added to distilled water in successive increments to a final concentration of 2.404 *m*. Series B was similar to series A to a final concentration of 0.404 *m*. In series C the salt was added to distilled water for each measurement. The concentration for each measurement in molality of K₂HPO₄, *m*, is the average concentration during the solution period. The differential enthalpy of solution for each solution was calculated from the equation

$$d(\Delta H)/dn_2 = Q/n_2 \quad (1)$$

where *Q* is the observed enthalpy change in calories, *n*₂ is the number of moles of K₂HPO₄ added, and Δ*H* is the integral enthalpy of solution. The gram formula weight of K₂HPO₄ is 174.183 37. The measured values and the differential enthalpy of solution for each measurement are shown in Table II.

Table III. Observed Integral Enthalpies of Solution of Dipotassium Orthophosphate Solutions

<i>m</i>	Initial soln		Final soln, molality	<i>Q</i> , cal	Δ <i>H</i> ₀ , cal/mol	Δ <i>H</i> _f , cal/mol	Δ <i>H</i> _i , cal/mol
	<i>m</i>	g					
3.119	25.186 94		0.059	43.693	858.42	-4969	-5827
	26.893 60		0.063	47.037	865.48	-4971	-5836
	24.235 02		0.057	42.074	859.08	-4968	-5827
Av -5830 ± 4							
3.924	27.050 28		0.073	54.394	862.71	-4976	-5839
	26.364 22		0.071	53.011	862.65	-4975	-5838
	26.367 65		0.071	53.086	863.76	-4975	-5839
	25.330 11		0.068	50.823	860.80	-4974	-5834
Av -5838 ± 2							
4.832	28.442 45		0.086	59.489	797.19	-4983	-5780
	26.386 98		0.080	54.498	787.19	-4980	-5767
	26.350 47		0.080	54.257	784.80	-4980	-5764
	29.349 92		0.089	60.572	786.61	-4984	-5771
Av -5770 ± 5							
6.048	29.363 60		0.100	52.231	603.96	-4990	-5594
	27.732 98		0.095	50.637	619.96	-4987	-5607
	27.286 03		0.093	50.250	625.29	-4986	-5612
	26.706 36		0.091	48.234	613.24	-4985	-5599
Av -5603 ± 6							
6.995	30.767 06		0.112	38.176	393.53	-4996	-5390
	31.423 88		0.115	38.583	389.41	-4998	-5387
	29.809 36		0.109	38.242	406.88	-4994	-5401
	31.341 96		0.115	38.852	393.15	-4997	-5391
Av -5392 ± 4							
8.526	25.326 64		0.101	7.557	86.91	-4990	-5077
	31.001 45		0.124	6.736	63.29	-5002	-5065
	28.430 03		0.113	7.143	73.18	-4997	-5070
	29.361 50		0.117	7.445	73.86	-4999	-5073
Av -5071 ± 4							
9.988	29.296 65		0.124	-29.408	-275.35	-5002	-4727
	27.886 30		0.118	-27.426	-269.78	-4999	-4730
	29.543 81		0.125	-28.471	-264.35	-5003	-4739
Av -4732 ± 5							

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

Concn of K ₂ HPO ₄ , <i>m</i>	Heat of soln, -Δ <i>H</i> , cal/mol	Rel molal heat content, cal/mol		
		Apparent, of K ₂ HPO ₄ , -φ <i>L</i>	Partial, of K ₂ HPO ₄ , - <i>L</i> ₂	Partial, of H ₂ O, - <i>L</i> 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

$$-d(\Delta H)/dn_2 = 4939 + 998m + 330.0m^2 - 493.9m^3 + 111.5m^4 \quad (2)$$

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 K₂HPO₄, 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 K₂HPO₄ 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.

Literature Cited

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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, K₂HPO₄, was measured over the range 9–316 K by adiabatic calorimetry. The heat capacity, C_p , entropy, S° , and Planck function, $(G^\circ - H_0^\circ)/T$, 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 sigmoid behavior.

In a continuing program of the measurement of thermochemical properties of materials of interest in fertilizer technology, the heat capacity of dipotassium orthophosphate, K₂HPO₄, 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 MgClO₄. Chemical analysis showed the material to contain 40.7% P₂O₅ and 54.1% K₂O (stoichiometric, 40.75% P₂O₅ and 54.08% K₂O). 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/cm³ (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