Heat of Solution of Monoammonium and Monopotassium Phosphates at 25° C.

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The heats of solution at 25° C. of $NH_4H_2PO_4$ and KH_2PO_4 were measured over the concentration range infinite dilution to saturation. The endothermic heats of solution at infinite dilution are ΔH = 3888 cal. per mole for $NH_4H_2PO_4$ and ΔH = 4705 cal. per mole for KH_2PO_4.

THE INTEGRAL heats of solution of monoammonium and monopotassium phosphates were measured as part of a possible refinement of the entropies of aqueous phosphate ions. Relative partial molal quantities were calculated from the observed heats of solution.

MATERIALS AND APPARATUS

The solution calorimeter has been described (*1*). The first sample of salt was dissolved in distilled water and successive increments of salt (about 25 g. in 850 ml. of solution) were added until the solution approached saturation (*4*). The measurements were repeated for each salt. The conversion of measured heat effects to integral heats of solution was described in a previous article (*1*). In the previous work, the solute, H_3PO_4, dissolved exothermically; both $NH_4H_2PO_4$ and KH_2PO_4 dissolved endothermically. The base temperature was 0° C. = 273.15° K. (*5*) and one defined calorie = 4.1840 absolute joules.

Potassium dihydrogen phosphate was dried at 105° C. Salt from the same source had been found repeatedly (by TVA) to have essentially stoichiometric composition. Monoammonium phosphate was recrystallized from distilled water and dried by vacuum desiccation over P_2O_5. All weights were corrected to vacuum.

RESULTS

KH_2PO_4. The measured integral heats of solution of KH_2PO_4(c), listed in Table I, are represented with an average deviation of ±0.05% by

$$\Delta H = 4704.81 - 302.4488m + 44.7608m^2 \qquad (1)$$

in which *m* is the concentration, molality, of KH_2PO_4.

The relative partial molal quantities listed in Table II were obtained from Equation 1 by conventional methods (*2*). The integral heats of solution in Table II may be compared with those of Khomyakov *et al.* (*3*), which were measured at 23° C. The Russian data have about the same intercept but a steeper slope, and yield a value for ΔH about 60 cal. per mole lower at saturation, than the present value. The intercept in Equation 1, 4705 cal. per mole KH_2PO_4, represents the heat of solution at infinite dilution, and is the value of significance in entropy calculations. The data of Khomyakov (*3*) show an intercept of 4697 cal. per mole.

$NH_4H_2PO_4$. The measured integral heats of solution at 25° C. for $NH_4H_2PO_4$(c) are listed in Table III, the calculated relative partial molal quantities in Table IV. The integral heats of solution are represented with an average deviation of ±0.08% by

$$\Delta H = 3887.95 - 80.4247m + 19.5397m^2 - 1.5249m^3 \qquad (2)$$

in which *m* is the concentration, molality, of $NH_4H_2PO_4$.

Table I. Observed Integral Heat of Solution KH_2PO_4(c) in Water at 25° C.

Run No.[a]	Concn., of KH_2PO_4 Molality	ΔH, Cal./Mole	Dev. From Eq. 1, %
1	0.0852	4684.2	0.10
10	0.1492	4660.2	−0.01
9	0.2140	4627.2	−0.32
11	0.2827	4625.1	0.05
2	0.3367	4615.8	0.17
12	0.4620	4574.8	0.00
3	0.5567	4553.0	0.06
13	0.7048	4513.1	−0.02
4	0.7704	4499.7	0.03
14	0.9582	4454.3	−0.04
5	0.9738	4453.0	0.01
6	1.1765	4411.3	0.01
15	1.2045	4403.1	−0.05
16	1.3855	4370.1	−0.04
7	1.4447	4362.8	0.04
17	1.5613	4341.6	0.00
8	1.7125	4318.9	0.02
18	1.7586	4311.5	0.00

[a] Numbered in chronological order.

Table II. Relative Partial Molal Quantities for KH_2PO_4 Solutions at 25° C.

		Relative Molal Heat Content, Cal./Mole		
Concn., of KH_2PO_4 Molality	Heat of Soln., ΔH, Cal./Mole	Apparent, of KH_2PO_4, $-\phi_2$	Partial, of KH_2PO_4, $-\bar{L}_2$	Partial, of H_2O, $\bar{L}_1$
0	4705	0.0	0.0	0.0
0.2	4646	58.7	115.6	0.205
0.4	4591	113.8	220.5	0.769
0.6	4539	165.4	314.6	1.613
0.8	4492	213.3	398.0	2.662
1.0	4447	257.7	470.6	3.836
1.2	4406	298.5	532.5	5.060
1.4	4369	335.7	583.7	6.254
1.6	4335	369.3	624.1	7.343
1.78[a]	4307	397.4	652.0	8.139

[a] Saturated solution.

The data in Tables II and IV may be compared to those of Khomyakov (*3*) at 23° C., which start about 40 cal. per mole higher than the present data at *m* = 0 and are 20 cal. lower at saturation. The intercept in Equation 2, 3888 cal. per mole $NH_4H_2PO_4$, represents the heat of solution at infinite dilution. The Russian data give an intercept of 3926 cal. per mole.

Table III. Observed Integral Heat of Solution in Water at 25° C. for $NH_4H_2PO_4(c)$

Run No.[a]	Molality, m_2	ΔH, Cal./Mole	Dev., %, From Eq. 2
12	0.1603	3877.3	0.04
1	0.2899	3861.0	–0.14
13	0.4524	3860.0	0.12
2	0.6049	3844.4	–0.04
14	0.7591	3839.7	0.06
3	0.9246	3825.2	–0.10
15	1.0646	3825.3	0.07
23	1.0667	3825.4	0.07
4	1.2175	3812.0	–0.11
16	1.3893	3812.2	0.06
24	1.3732	3811.9	0.04
5	1.5456	3799.3	–0.14
25	1.6890	3803.0	0.07
17	1.7255	3801.3	0.05
6	1.8834	3790.5	–0.14
26	2.0093	3795.6	0.07
18	2.0431	3794.2	0.05
7	2.1941	3784.9	–0.12
27	2.3089	3791.3	0.10
19	2.3401	3789.2	0.05
8	2.4778	3781.2	–0.11
28	2.6238	3785.3	0.04
20	2.6494	3785.6	0.05
9	2.7739	3778.7	–0.10
29	3.0006	3783.4	0.06
21	3.0019	3783.5	0.06
10	3.0914	3778.8	–0.06
22	3.2860	3783.1	0.07
11	3.3812	3778.2	–0.06

[a] Numbered in chronological order.

Table IV. Relative Partial Molal Quantities for $NH_4H_2PO_4$ Solutions at 25° C.

		Relative Molal Heat Content, Cal./Mole		
Concn., of $NH_4H_2PO_4$ Molality	Heat of Soln., ΔH, Cal./Mole	Apparent, of $NH_4H_2PO_4$, $-\phi_2$	Partial, of $NH_4H_2PO_4$, $-\bar{L}_2$	Partial, of H_2O, $\bar{L}_1$
0.0	3888	0.0	0.0	0.0
0.4	3859	29.15	55.36	0.189
0.8	3835	52.62	94.29	0.601
1.2	3817	71.01	119.2	1.041
1.6	3803	84.91	132.3	1.366
2.0	3793	94.89	136.0	1.482
2.4	3786	101.6	132.7	1.348
2.8	3782	105.5	124.7	0.970
3.2	3781	106.8	113.8	0.409
3.6	3781	107.4	104.0	–0.227
3.62[a]	3781	107.4	103.4	–0.266

[a] Saturated solution.

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Low Temperature Heat Capacity and Entropy of the Potassium Iron Phosphate $H_8KFe_3(PO_4)_6 \cdot 6H_2O$

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The heat capacity of $H_8KFe_3(PO_4)_6 \cdot 6H_2O$ was measured over the range 10° to 300° K. There is a small hump in the heat-capacity curve between 7° and 36° K. At 298.15° K. the entropy is 222.17 e.u. and the enthalpy is 34,074 cal. per mole.

ONE OF THE compounds formed by the reaction of phosphate fertilizers with soil minerals (*3*) is a potassium iron phosphate with the empirical formula $H_8KFe_3(PO_4)_6 \cdot 6H_2O$. As part of a continuing program of the determination of the thermodynamic properties of compounds of interest in fertilizer technology, the low temperature heat capacities of this compound were measured over the temperature range 10° to 300° K., and the entropy and enthalpy at 298.15° K. were derived therefrom.

APPARATUS AND MATERIALS

Iron(II) phosphate solution was prepared by dissolving 25.2 grams of high-purity iron wire in a mixture of 285 grams of 85% phosphoric acid and 285 grams of distilled water. The solution was filtered, diluted to 2 liters, and oxidized with 50% hydrogen peroxide. To the iron(III) phosphate slurry was added, with vigorous stirring, a solution of 135 grams of KH_2PO_4 in 1.5 liters of water. The resulting slurry stood at room temperature overnight and became a rigid gel which was redispersed with some difficulty and transferred to a polyethylene bottle. Digestion at 50° C. for 72 hours produced crystalline potassium iron phosphate. The crystals were washed five times at room temperature with distilled water acidified with 10 ml. of 85% phosphoric acid per liter to lower the pH to 1.4 (hydrous iron(III) phosphate forms at pH 1.6), five times with water at 50°, and then with acetone. They were air dried for 1 week and dried for 1 week under vacuum. Chemical analysis gave 4.41% K, 18.77% Fe, and 20.86% P, (stoichiometric values are: 4.38% K, 18.77% Fe, 20.82% P). The optical and x-ray properties of the crystals agreed with previously reported values (*3, 4*). The density of