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

| Run No.[a] | Molality, $m_2$ | $\Delta H$, 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., $\Delta H$, 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 $H_8KFe_3(PO_4)_6$-$6H_2O$. 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 the salt, as calculated from x-ray data, was 2.41 grams per cc.

The calorimeter (*1*) contained 67.5000 grams (vacuum) or 0.075617 mole of $H_8KFe_3(PO_4)_6 \cdot 6H_2O(c)$. The National Bureau of Standards supplied a calibration table for the platinum resistance thermometer in 1° intervals down to 10° K. The table was extended to 7° K. by smooth extrapolation of first and second differences. Temperatures were read to four decimal places and were so used in the calculation of small temperature differences; they were rounded to two decimal places in the final tabulation. The calculations were made on an IBM 704 computer (*1*). The defined calorie is taken as 4.1840 absolute joules—the ice point as 273.15° K. (*5*).

## RESULTS

The observed molar heat capacities are listed in Table I, and molar thermodynamic properties at integral temperatures are listed in Table II. The average deviation of the observed from the smoothed heat capacities was 0.1% except at temperatures below 20° K. where the small magnitudes impaired the accuracy.

The measured heat capacities went through small broad humps below 36° K. The hump was present at the lowest measured temperature, 7.78° K.; it went through a broad maximum at about 8.5° K. and apparently disappeared between 12° and 14.5° K. A second (or continued) hump appeared with a broad maximum at about 24.5° K., and disappeared above 36° K. A plot of $C_p/T$ *vs.* $T$ indicated that the hump was decreasing rapidly below 7.78° K., and the observed heat capacities were arbitrarily joined smoothly to the "normal" curve at 7° K. The "normal" curve was established from a least-squares fourth-power polynomial calculated from two observed points between 12° and 15° K. and seven points between 36° and 51° K.; the curve passed smoothly through the origin. It was not decided whether there are two adjacent small humps or one continuous hump, but the hump is believed to be a magnetic effect traceable to the iron content of the compound. Similar, larger humps were observed in the heat-capacity curve of strengite, $FePO_4 \cdot 2H_2O$ (*2*). In the present study

Table I. Observed Molal Heat Capacity of $H_8KFe_3(PO_4)_6 \cdot 6H_2O(c)$

| Point[a] | $T$, ° K. | $C_p$, Cal./° K. | Point[a] | $T$, ° K. | $C_p$, Cal./° K. | Point[a] | $T$, ° K. | $C_p$, Cal./° K. | Point[a] | $T$, ° K. | $C_p$, Cal./° K. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 86 | 7.78 | 2.541 | 47 | 56.32 | 43.29 | 61 | 141.54 | 117.0 | 74 | 234.10 | 175.2 |
| 109 | 7.87 | 2.828 | 42 | 58.71 | 45.78 | 32 | 144.70 | 118.8 | 15 | 237.75 | 177.4 |
| 98 | 8.07 | 2.479 | 48 | 61.16 | 48.44 | 62 | 148.04 | 121.5 | 75 | 240.81 | 178.8 |
| 87 | 8.59 | 2.965 | 43 | 63.88 | 51.48 | 33 | 151.30 | 123.7 | 16 | 244.30 | 180.8 |
| 110 | 8.61 | 2.841 | 49 | 66.07 | 53.82 | 63 | 154.61 | 126.0 | 76 | 247.18 | 182.3 |
| 111 | 9.46 | 3.010 | 44 | 69.10 | 56.83 | 34 | 157.91 | 128.3 | 17 | 250.48 | 184.1 |
| 99 | 9.49 | 3.189 | 50 | 71.76 | 59.30 | 64 | 161.13 | 130.5 | 77 | 253.70 | 185.6 |
| 88 | 10.13 | 3.453 | 45 | 74.38 | 61.76 | 35 | 164.07 | 132.0 | 18 | 256.98 | 187.5 |
| 100 | 11.43 | 3.995 | 51 | 77.02 | 64.33 | 65 | 167.49 | 134.7 | 78 | 260.16 | 188.9 |
| 89 | 12.51 | 4.702 | 46 | 79.43 | 66.71 | 36 | 170.37 | 136.6 | 19 | 263.18 | 190.7 |
| 101 | 14.35 | 6.095 | 22 | 81.56 | 68.79 | 66 | 173.53 | 138.7 | 79 | 266.08 | 192.1 |
| 90 | 15.82 | 7.334 | 52 | 85.25 | 72.29 | 37 | 176.70 | 140.7 | 20 | 268.86 | 193.5 |
| 102 | 17.50 | 8.824 | 23 | 88.03 | 74.93 | 67 | 179.46 | 142.6 | 80 | 271.72 | 195.0 |
| 90 | 19.80 | 10.90 | 53 | 90.45 | 77.06 | 38 | 182.91 | 144.7 | 21 | 274.49 | 196.5 |
| 103 | 21.87 | 13.95 | 24 | 94.02 | 80.13 | 68 | 185.27 | 146.2 | 1 | 277.25 | 197.5 |
| 112 | 23.39 | 16.11 | 54 | 97.04 | 82.77 | 39 | 189.00 | 148.5 | 81 | 281.26 | 199.8 |
| 92 | 24.54 | 17.51 | 25 | 100.22 | 85.51 | 69 | 191.31 | 150.0 | 2 | 284.95 | 201.5 |
| 104 | 27.42 | 19.75 | 55 | 103.50 | 88.38 | 40 | 194.98 | 152.3 | 82 | 288.58 | 203.4 |
| 113 | 27.90 | 19.65 | 26 | 106.59 | 90.94 | 8 | 197.92 | 154.0 | 3 | 292.54 | 205.3 |
| 93 | 30.82 | 20.93 | 56 | 109.88 | 93.65 | 70 | 200.85 | 156.0 | 83 | 295.76 | 207.2 |
| 105 | 33.30 | 22.67 | 27 | 112.73 | 95.98 | 9 | 204.45 | 158.0 | 5 | 299.98 | 209.0 |
| 94 | 37.08 | 25.61 | 57 | 115.98 | 98.56 | 71 | 207.64 | 160.0 | 4 | 300.04 | 209.1 |
| 106 | 39.66 | 27.78 | 28 | 118.93 | 100.8 | 10 | 210.64 | 161.7 | 84 | 301.75 | 210.0 |
| 95 | 42.37 | 30.11 | 58 | 122.06 | 103.3 | 72 | 214.07 | 163.6 | 6 | 304.75 | 211.6 |
| 107 | 44.42 | 31.97 | 29 | 125.33 | 105.6 | 12 | 217.83 | 166.0 | 85 | 306.79 | 212.6 |
| 96 | 47.21 | 34.64 | 59 | 128.34 | 107.9 | 11 | 221.98 | 168.1 | 7 | 309.22 | 213.8 |
| 108 | 49.54 | 36.78 | 30 | 131.72 | 110.2 | 13 | 224.58 | 170.0 | | | |
| 97 | 51.71 | 38.86 | 60 | 134.84 | 112.4 | 73 | 228.48 | 172.1 | | | |
| 41 | 53.59 | 40.57 | 31 | 138.10 | 114.9 | 14 | 231.21 | 173.9 | | | |

[a] Numbered in chronological order.

Table II. Molal Thermodynamic Properties of $H_8KFe_3(PO_4)_6 \cdot 6H_2O(c)$

| $T$, ° K. | $C_p$, Cal./° K. | $S°$, Cal./° K. | $H° - H°_0$, Cal. | $T$, ° K. | $C_p$, Cal./° K. | $S°$, Cal./° K. | $H° - H°_0$, Cal. |
|---|---|---|---|---|---|---|---|
| 10 | 3.383 | 1.583 | 11.22 | 150 | 122.8 | 110.0 | 9,165 |
| 15 | 6.640 | 3.465 | 15.01 | 160 | 129.6 | 118.2 | 10,430 |
| 20 | 11.16 | 5.971 | 79.09 | 170 | 136.3 | 126.2 | 11,760 |
| 25 | 17.96 | 9.238 | 152.9 | 180 | 142.9 | 134.2 | 13,150 |
| 30 | 20.72 | 12.82 | 251.3 | 190 | 149.2 | 142.1 | 14,610 |
| 35 | 23.89 | 16.16 | 362.0 | 200 | 155.4 | 149.9 | 16,140 |
| 40 | 28.15 | 19.69 | 491.8 | 210 | 161.3 | 157.6 | 17,720 |
| 45 | 32.59 | 23.26 | 643.6 | 220 | 167.2 | 165.3 | 19,360 |
| 50 | 37.14 | 26.93 | 817.8 | 230 | 173.0 | 172.8 | 21,060 |
| 60 | 47.22 | 34.57 | 1239 | 240 | 178.5 | 180.3 | 22,820 |
| 70 | 57.66 | 42.65 | 1764 | 250 | 183.7 | 187.7 | 24,630 |
| 80 | 67.24 | 50.97 | 2388 | 260 | 189.0 | 195.0 | 26,500 |
| 90 | 76.66 | 59.44 | 3108 | 270 | 194.1 | 202.2 | 28,410 |
| 100 | 85.33 | 67.97 | 3919 | 280 | 199.1 | 209.4 | 30,380 |
| 110 | 93.79 | 76.51 | 4815 | 290 | 204.1 | 216.5 | 32,390 |
| 120 | 101.6 | 85.01 | 5792 | 300 | 209.1 | 223.5 | 34,460 |
| 130 | 109.1 | 93.44 | 6846 | 273.15 | 195.7 | 204.5 | 29,026 |
| 140 | 115.9 | 101.8 | 7971 | 298.15 | 208.2 | 222.2 | 34,074 |

the magnetic effect in $H_8KFe_3(PO_4)_6 \cdot 6H_2O$ probably is "swamped" by the nonmagnetic centers in the structure.

The entropy of $H_8KFe_3(PO_4)_6 \cdot 6H_2O(c)$ is 222.17 e.u. at 298.15° K. with an estimated uncertainty of 0.50 e.u. The calculated entropy at 298.15° K., using the "normal" heat capacity values below 36° K., is 220.96 e.u. The excess entropy contributed by the anomalous hump was calculated in two increments—0.18 e.u. (7° to 12.5° K.) and 1.03 e.u. (12.5° to 36° K.). The enthalpy, $H^\circ - H_0^\circ$, at 298.15° K. is 34,074 cal. per mole, of which 34,046 cal. per mole represents the enthalpy using the "normal" heat capacity values below 36° K., and 1.61 (7° to 12.5° K.) and 26.08 (12.5° to 36° K.) cal. per mole represent the excess enthalpy under the hump. Curvature corrections to observed heat capacities were made as required (*1*).

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# Low Temperature Heat Capacity and Entropy of Basic Potassium Aluminum Phosphate


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**The heat capacity of $KAl_2(PO_4)_2OH \cdot 2H_2O$ was measured over tne range 10° to 300° K. At 298.16° K. the entropy is 70.43 e.u. and the enthalpy is 11,800 cal. per mole.**


A BASIC potassium aluminum phosphate (*3, 5*) of the minyulite type, $KAl_2(PO_4)_2OH \cdot 2H_2O$, is of interest in soil-fertilizer relationships. As part of a continuing program of the determination of thermodynamic properties of compounds of interest in fertilizer technology, the low temperature heat capacities of basic potassium aluminum phosphate were measured over the temperature range 10° to 300° K., and the entropy and enthalpy at 298.16° K. were derived therefrom.

## MATERIALS AND APPARATUS

The basic potassium aluminum phosphate was prepared by dissolving 18 grams of aluminum metal (supplied by Consolidated Aluminum Corp., Jackson, Tenn., who reported it iron-free and 99.994% pure) in a mixture of 300 grams of 85% phosphoric acid and 350 ml. of distilled water. The solution was filtered, diluted to 2 liters, and adjusted to pH 6.12 with 20% KOH solution. The precipitate was redispersed in 3 liters of hot water, and, after standing overnight at 75° C., the precipitate was again redispersed in 3 liters of water and digested at 95° C. until crystalline. The product was washed with hot water and dried over $CaCl_2$ in a vacuum at room temperature.

The crystals were 30 to 50 microns long; a few were not optically clear but showed "veiling." Chemical analysis gave 11.5% K, 16.06% Al, 18.32% P, and less than 0.005% Fe (stoichiometric values are: 11.64% K, 16.05% Al, 18.44% P).

The calorimeter (*1, 2*) contained 96.139 grams (vacuum) or 0.28609 mole of $KAl_2(PO_4)_2OH \cdot 2H_2O(c)$. Temperatures were read to four decimal places and were so used in the calculation of small differences, but were rounded to two places in the tables. The calculations were made on an IBM 704 computer (*2*). One defined calorie was taken as 4.1840 absolute joules—the ice point as 273.16° K. This work was completed before adoption in this laboratory of the change of the ice point to 273.15° K. (*4*).