at 1 *m*. The densities of Na_2SO_4 agree to within $\pm 20 \times 10^{-6}$ g cm^{-3} from 0 to 0.6 *m*. Our value is higher than the data of Lee by 60×10^{-6} g cm^{-3} at 1 *m*. The measured densities of $MgSO_4$ agree with the data of Lee to within 25×10^{-6} g cm^{-3}.

The 1-atm density equations obtained in this study have been combined with the high-pressure sound speeds (*2*) to derive high-pressure equations of state for NaCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$ aqueous solutions. The results will be presented in a future publication (*4*).

Acknowledgment

A. Lo Surdo and P. Chetirkin performed the sulfate and chloride analysis.

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Received for review February 29, 1980. Accepted July 21, 1980. We acknowledge the support of the Office of Naval Research (N00014-75-C-0173) and the oceanographic section of the National Science Foundation (OCE-73-00351-A01) for this study. Chen-Tung A. Chen acknowledges the support of the School of Oceanography, Oregon State University, where some of the data analysis was made.

Thermodynamic Properties of Magnesium Potassium Orthophosphate Hexahydrate

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The low-temperature heat capacity of magnesium potassium orthophosphate hexahydrate, $MgKPO_4 \cdot 6H_2O$, was measured by adiabatic calorimetry over the temperature range 10–316 K. The standard enthalpy of formation at 298.15 K was determined with a solution calorimeter. Related thermodynamic properties and the solubility product constant were derived.

Introduction

Magnesium potassium orthophosphate hexahydrate, $MgKPO_4 \cdot 6H_2O$, may occur as a soil-fertilizer reaction product (*3*) or as a precipitate in liquid fertilizers containing potassium and prepared from wet-process phosphoric acid (*1*). It also is an excellent source of potassium and phosphorus for plants (*8*). Presented here are measurements of the heat capacity of magnesium potassium orthophosphate hexahydrate from 10 to 316 K, entropies and enthalpies at 298.15 K derived therefrom, and the enthalpy of formation at 298.15 K. The entropy and enthalpy of formation are combined with other values from the literature in the calculation of the solubility product constant, which is compared with the value derived from the direct measurements of solubilities.

Materials. Magnesium potassium orthophosphate hexahydrate was prepared by the method of Lehr et al. (*2*). Chemical analyses showed it to contain 17.4% K_2O, 15.2% MgO, and 26.8% P_2O_5 (stoichiometric: 17.68% K_2O, 15.13% MgO, and 26.63% P_2O_5); microscopic examination showed it to comprise an essentially homogeneous phase of $MgKPO_4 \cdot 6H_2O$.

Monopotassium orthophosphate was prepared by recrystallizing the reagent-grade salt from distilled water and drying it by vacuum desiccation over $MgClO_4$. It contained 34.6% K_2O and 52.1% P_2O_5 (stoichiometric: 34.61% K_2O and 52.15% P_2O_5). The magnesium chloride solution was prepared by dissolving the reagent-grade salt in distilled water. It contained 14.6% MgO and 25.2% Cl ($MgCl_2 \cdot 10.05H_2O$, based on the MgO analysis).

Low-Temperature Heat Capacity. The adiabatic calorimeter and the method of operation have been described previously (*10*), and the overall accuracy of our technique has been reported (*5*). The defined calorie was taken as 4.1840 absolute J and the ice point as 273.15 K.

The calorimeter was charged with 35.8460 g or 0.134 518 mol. The weight was corrected for bouyancy in air on the basis of a density of 1.83 g cm^{-3} (*2*), and the gram formula weight was taken as 266.4774. The air in the calorimeter was replaced with helium by evacuating to a pressure of 100 torr and then relieving to atmospheric pressure with helium. This cycle was repeated twice, and then the pressure was adjusted to give the same mass of helium as was used in the measurements on the empty calorimeter. The final observed weight of the calorimeter was 5 mg greater than the summation of the masses in each step of the preparation, evacuation, and sealing of the calorimeter. This difference (+0.01% based on the sample weight) was considered sufficiently small to assure that no appreciable alteration of the sample occurred during evacuation and sealing of the calorimeter. The heat capacity of the sample ranged from 28% of the total at 10 K to 49% at 300 K.

The measured heat capacities were corrected for curvature and for small differences 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. Heat capacity and derived functions at round values

Table I. Observed Heat Capacity of Magnesium Potassium Phosphate Hexahydrate (cal K^{-1} mol^{-1})

T, K	C_p	T, K	C_p	T, K	C_p	T, K	C_p
9.67	0.4216	57.15	18.12	143.50	45.85	236.41	66.03
10.91	0.4953	57.62	18.30	146.69	46.67	239.49	66.63
12.24	0.7134	61.35	19.84	149.43	47.36	242.55	67.27
13.25	1.067	61.88	20.07	152.54	48.20	245.58	67.88
13.56	1.023	66.46	21.87	155.45	48.90	248.61	68.50
14.48	1.326	67.38	22.21	158.47	49.65	251.57	68.89
15.00	1.463	71.96	23.82	161.56	50.39	254.60	69.64
15.97	1.699	73.18	24.28	164.51	51.11	257.53	70.00
16.70	1.933	77.77	25.97	167.56	51.82	260.54	70.71
17.79	2.276	79.08	26.46	170.44	52.52	263.61	71.18
18.64	2.560	79.54	26.63	173.45	53.17	266.60	71.80
19.82	2.923	81.15	27.23	176.47	53.92	269.79	72.38
20.79	3.256	84.08	28.27	179.64	54.61	272.76	73.00
22.03	3.695	87.33	29.42	182.61	55.30	274.69	73.25
23.22	4.188	90.37	30.41	185.73	55.98	275.83	73.49
24.62	4.748	93.43	31.34	188.85	56.67	275.92	73.46
26.14	5.342	96.60	32.36	191.93	57.36	278.50	74.03
27.81	6.039	99.80	33.37	194.66	57.98	281.23	74.55
29.55	6.735	102.81	34.31	197.05	58.47	284.22	75.08
31.40	7.487	106.16	35.31	199.94	59.04	287.09	75.60
33.30	8.298	109.28	36.35	202.90	59.57	290.22	76.23
35.28	9.151	112.50	37.19	205.95	60.05	293.06	76.71
37.31	10.02	115.76	38.20	208.86	60.55	296.17	77.32
39.47	10.92	118.86	39.07	212.08	61.11	297.32	77.40
41.64	11.80	121.99	39.99	214.95	61.68	299.14	77.88
43.98	12.78	124.99	40.84	218.14	62.35	300.34	77.96
46.30	13.77	128.25	41.76	220.96	62.90	303.53	78.57
48.72	14.79	131.18	42.54	224.12	63.60	306.52	79.06
51.32	15.86	134.57	43.48	227.09	64.14	309.69	79.68
53.79	16.86	137.42	44.25	230.21	64.80	312.65	80.24
56.78	17.99	140.71	45.12	233.33	65.39	315.78	80.85

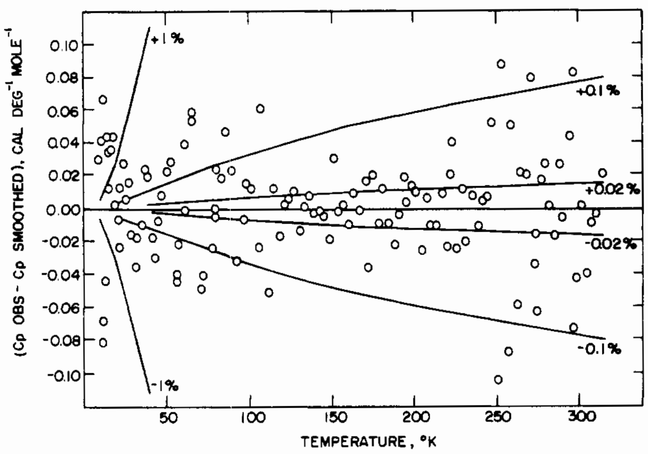

Figure 1. Deviations of observed heat capacities from smoothed values of magnesium potassium phosphate hexahydrate.

of temperature are shown in Table II. The deviations of the observed heat capacity values from the smoothed curve are shown in Figure 1.

Enthalpy of Formation. The standard enthalpy of formation of $MgKPO_4 \cdot 6H_2O$ was determined from published enthalpies of formation of KH_2PO_4, aqueous $MgCl_2$, aqueous HCl, and the enthalpy of the reaction

$$MgCl_2 \cdot 10.05H_2O + KH_2PO_4 = MgKPO_4 \cdot 6H_2O + 2(HCl \cdot 2.025H_2O) \quad (1)$$

at 298.15 K.

The enthalpy of reaction 1 was determined by the scheme

$$\text{ampule } KH_2PO_4 + \text{solvent} = \text{solution A} \quad (2)$$

$$\text{ampule } MgCl_2 \cdot 10.05H_2O + \text{solution A} = \text{solution B} \quad (3)$$

$$\text{stoich } HCl \cdot 2.025H_2O + \text{solvent} = \text{solution C} \quad (4)$$

$$\text{ampule } MgKPO_4.6H_2O + \text{solution C} = \text{solution B} \quad (5)$$

$$\Delta H_1 = \Delta H_2 + \Delta H_3 - 2(\Delta H_4) - \Delta H_5 \quad (6)$$

Table II. Molal Thermodynamic Properties of Magnesium Potassium Phosphate Hexahydrate

T, K	C_p, cal K^{-1}	$S°$, cal K^{-1}	$H° - H_0°$, cal	$-[(G° - H_0°)/T]$, cal K^{-1}
5	0.0555	0.0184	0.0694	0.0045
10	0.4330	0.1457	1.092	0.0366
15	1.419	0.4854	5.444	0.1224
20	2.982	1.097	16.26	0.2840
25	4.871	1.961	35.80	0.5292
30	6.939	3.031	65.29	0.8545
35	9.024	4.257	105.2	1.251
40	11.13	5.599	155.6	1.710
45	13.24	7.032	216.5	2.221
50	15.30	8.534	287.9	2.777
60	19.29	11.68	460.9	3.996
70	23.15	14.94	673.3	5.326
80	26.80	18.28	923.1	6.736
90	30.27	21.63	1029	8.204
100	33.42	24.99	1527	9.715
110	36.50	28.32	1877	11.26
120	39.41	31.62	2257	12.82
130	42.23	34.89	2665	14.39
140	44.93	38.12	3101	15.97
150	47.52	41.31	3563	17.55
160	50.02	44.45	4051	19.13
170	52.40	47.56	4563	20.71
180	54.70	50.62	5099	22.29
190	56.94	53.64	5657	23.86
200	59.04	56.61	6237	25.43
210	60.74	59.53	6836	26.98
220	62.62	62.40	7453	28.53
230	64.74	65.24	8091	30.06
240	66.74	68.03	8748	31.58
250	68.71	70.80	9426	33.10
260	70.56	73.53	10120	34.60
270	72.40	76.23	10840	36.09
280	74.29	78.90	11570	37.57
290	76.16	81.53	12320	39.04
300	77.94	84.15	13090	40.50
310	79.75	86.73	13880	41.95
273.15	72.99	77.07	11070	36.56
298.15	77.62	83.67	12950	40.23

Table III. Enthalpy of Solution of KH_2PO_4 in 4.010 m HCl at 25 °C

solvent wt, g	sample wt, g	cor temp rise, °C	enthalpy of soln, cal/sample	ΔH_2, cal/mol
901.512	5.003 83	−0.2915	233.5	6350
901.479	5.021 66	−0.2924	234.0	6341
901.057	5.042 52	−0.2941	235.5	6355
901.825	5.060 97	−0.2944	235.9	6343
901.846	5.082 38	−0.2957	236.8	6340
			av	6346
			std dev	3

where ΔH_1 is the enthalpy of reaction 1 in calories; ΔH_2, ΔH_3, and ΔH_5 are the enthalpies of reactions 2, 3, and 5, respectively, in cal/mol of the materials in the ampules; and ΔH_4 is the enthalpy of reaction 4 in cal/mol $HCl \cdot 2.025H_2O$ calculated from published values of the enthalpies of formation of aqueous HCl.

The solution calorimeter, the method of measurement, and the corrections applied have been described (*4*). The overall accuracy of our technique was checked by measuring the enthalpy of solution of Tris (Bureau of Standards No. 724) in 0.100 N HCl at 25 °C. The average of eight measurements was −7115 cal/mol with a standard deviation of ±6 cal/mol. This is in good agreement with other reported values. The calorimetric solvent was prepared by diluting reagent-grade hydrochloric acid with distilled water to 4.010 m (12.75%) HCl, as determined by alkalimetric titration.

The observed enthalpies of solution of KH_2PO_4 in 4.010 m HCl (ΔH_2) and of $MgCl_2 \cdot 10.05H_2O$ in 4.010 m HCl, to which the stoichiometric amount of KH_2PO_4 had been added (ΔH_3), are listed in Tables III and IV, respectively. The observed enthalpies of solution of $MgKPO_4 \cdot 6H_2O$ in 4.092 m (12.98%) HCl, ΔH_5, are

Table IV. Enthalpy of Solution of $MgCl_2 \cdot 10.05H_2O$ in 4.010 m HCl plus Stoichiometric KH_2PO_4 at 25 °C

solvent wt, g	sample wt, g	KH_2PO_4 added, g	cor temp rise, °C	−enthalpy of soln, cal/sample	$-\Delta H_3$, cal/mol
901.891	10.156 70	5.003 44	0.0654	51.5	1402
901.719	10.197 82	5.023 45	0.0662	52.1	1412
901.754	10.242 91	5.045 97	0.0661	52.1	1404
901.658	10.272 81	5.060 29	0.0663	52.3	1405
901.578	10.321 08	5.084 17	0.0668	52.7	1409
901.638	10.356 03	5.101 72	0.0666	52.5	1402
					av 1406
					std dev 2

Table V. Enthalpy of Solution of $MgKPO_4 \cdot 6H_2O$ in 4.092 m HCl at 25 °C

wt 4.092 m HCl, g	sample wt, g	cor temp rise, °C	−enthalpy of soln, cal/sample	$-\Delta H_5$, cal/mol
906.968	9.87693	0.0454	35.4	954
906.847	9.88679	0.0462	36.0	972
907.095	9.88982	0.0471	36.7	990
907.102	9.89309	0.0460	35.8	965
907.046	9.89508	0.0467	36.4	981
907.079	9.90350	0.0460	35.9	966
				av 971
				std dev 5

listed in Table V. The concentration and the amount of the HCl solution in which the $MgKPO_4 \cdot 6H_2O$ was to be dissolved were calculated from the average weight of calorimetric solvent (901.632 g) used for the measurements listed in Tables III and IV and the stoichiometric amount of $HCl \cdot 2.025H_2O$ (5.414 79 g) for the average weight of $MgKPO_4 \cdot 6H_2O$ (9.890 87 g) listed in Table V.

The enthalpy of solution of 5.414 79 g (0.0742 mol) of $HCl \cdot 2.025H_2O$ in 901.632 g (3.1541 mol) of 4.010 m HCl ($HCl \cdot 13.844H_2O$)

$$3.1541(HCl \cdot 13.844H_2O) + 0.0742(HCl \cdot 2.025H_2O) = 3.2282(HCl \cdot 13.572H_2O) \quad (7)$$

calculated from a smooth curve through the published enthalpies of formation of HCl solutions (*7*) is −320 cal. Dividing ΔH_7 by 0.0742 gives −4309 cal/mol for ΔH_4. Substituting the average values for ΔH_2, ΔH_3, and ΔH_5 and the calculated value for ΔH_4 in eq 6 gives 14 529 cal for ΔH_1.

The standard enthalpies of formation of H_2O and HCl in $2.025H_2O$ are −68.315 kcal/mol and −33.76 kcal/mol, respectively (*7*). The standard enthalpy of formation of $MgCl_2$ in $10.05H_2O$ is −185.66 kcal/mol (*6*), and the standard enthalpy of formation of KH_2PO_4 is −376.1 kcal/mol (*4*). Substituting these enthalpies of formation and the enthalpy of reaction 1 in eq 8

$$\Delta H_f^\circ(MgKPO_4 \cdot 6H_2O) = \Delta H_f^\circ(MgCl_2 \text{ in } 10.05H_2O) + \Delta H_f^\circ(KH_2PO_4) + 6[\Delta H_f^\circ(H_2O)] - 2[\Delta H_f^\circ(HCl \text{ in } 2.025H_2O)] + \Delta H_1 \quad (8)$$

gives −889.6 kcal/mol as the standard enthalpy of formation of $MgKPO_4 \cdot 6H_2O$.

Solubility Product Constant. The enthalpies of formation and entropies at 298.15 K required in the calculation of solubility product constants are listed in Table VI. Substitution of these values in the equation

Table VI. Enthalpies of Formation and Entropies at 298.15 K

substance	ΔH_f°, kcal mol^{-1}	S°, cal mol^{-1} K^{-1}
$MgKPO_4 \cdot 6H_2O$ (c)	−889.6	83.67
Mg^{2+}(aq)	−110.41[a]	−28.2[a]
K^{1+}(aq)	−60.04[a]	24.5[a]
PO_4^{3-}(aq)	−305.3[b]	−53[b]
H_2O (l)	−68.315[b]	16.71[b]

[a] Reference *6*. [b] Reference *7*.

$$MgKPO_4 \cdot 6H_2O(c) + aq = Mg^{2+}(aq) + K^{1+}(aq) + PO_4^{3-}(aq) + 6H_2O(l) \quad (9)$$

gives

$$\Delta H(aq-c) = 3960 \text{ cal mol}^{-1} \quad (10)$$

$$\Delta S(aq-c) = -40.11 \text{ eu} \quad (11)$$

Substitution of these values in the equation

$$\ln K_{sp} = \frac{\Delta H(aq-c) - T\Delta S(aq-c)}{-RT} \quad (12)$$

gives 2.1×10^{-12} as the solubility product constant, K_{sp}, of $MgKPO_4 \cdot 6H_2O$. This value may be compared with 2.4×10^{-11}, as calculated by direct solubility measurements (*9*).

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Received for review March 31, 1980. Accepted July 24, 1980.