[CONTRIBUTION FROM THE DIVISION OF CHEMICAL DEVELOPMENT, TENNESSEE VALLEY AUTHORITY[1]]

Low Temperature Heat Capacity, Entropy and Heats of Formation and Hydration of Monocalcium Phosphate

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Thermodynamic values for the anhydrous and monohydrated forms of monocalcium phosphate at 298.16°K. were derived from measurements of the heats of solution of the two forms of the salt and measurements of the heat capacity of the monohydrate at 10 to 345°K. For $Ca(H_2PO_4)_2 \cdot H_2O$ (c) the entropy is 62.10 ± 0.10 cal. per mole per degree; the heat content, $H^0 = H_0^0$, is 9950 cal. per mole; and the heat of formation is −816,820 cal. per mole. For $Ca(H_2PO_4)_2$ (c) the heat of formation is −746,040 cal. per mole, and the heat of hydration to $Ca(H_2PO_4)_2 \cdot H_2O$ (c) is −2460 cal. per mole.

Although monocalcium phosphate long has been ubiquitous as the principal phosphatic component of superphosphate and as a major component of baking powders, only rough estimates have been reported for the thermodynamic properties of the salt. This paper describes measurements of the low temperature heat capacity of monocalcium phosphate monohydrate, $Ca(H_2PO_4)_2 \cdot H_2O$, and of the heats of solution of the monohydrated and anhydrous forms of the salt. The measurements were used in the derivation of several thermodynamic properties at 298.16°K.—the entropy and heat content of the monohydrate, the heat of hydration of the anhydrous salt to the monohydrate and the heats of formation of both forms of the salt.

Materials. Monocalcium Phosphate Monohydrate.—Reagent grade monocalcium phosphate monohydrate was dissolved to near saturation in a 50% solution of reagent grade phosphoric acid at 100°. The hot solution was filtered through fritted glass and cooled to room temperature. The crystals of monocalcium phosphate were filtered off, dissolved in a fresh portion of acid and recrystallized three times. In the final recrystallization, the solution was cooled slowly with constant stirring to produce unagglomerated thin plate crystals. These crystals were filtered off on fritted glass, washed free of acid with anhydrous acetone and dried in a vacuum desiccator.

Petrographic, X-ray and spectrographic examination showed that the crystals were quite pure monocalcium phosphate monohydrate, and the composition shown by chemical analysis was 22.45% CaO and 56.20% P_2O_5 as compared with stoichiometric values of 22.25% CaO and 56.31% P_2O_5. The crystals were 25- to 50-μ rhombic plates and showed polysynthetic twinning, with as many as seven single crystals per unit. The contribution to the entropy by the strain induced in the twinned crystals upon change in temperature was estimated to be negligible.

Anhydrous Monocalcium Phosphate.—Boiling 80% phosphoric acid, prepared from crystalline phosphoric acid hemihydrate and distilled water, was saturated with crystalline monocalcium phosphate monohydrate, and the hot solution was filtered through fritted glass. The filtrate was held at 130° for 3 days to crystallize anhydrous monocalcium phosphate. The crystals were collected on a fritted glass filter and washed free of acid with anhydrous acetone. The product was dried at 80° for 3 hours, passed through a 60-mesh screen to remove large agglomerates that might contain free acid and stored in a vacuum desiccator.

A microscopic examination showed that the crystals were pure anhydrous monocalcium phosphate with no contaminating phase. The composition shown by chemical analysis was 23.94% CaO and 60.63% P_2O_5 as compared with stoichiometric values of 23.95% CaO and 60.65% P_2O_5.

Calcium Hydroxide.—Calcium carbonate, prepared from recrystallized calcium nitrate and ammonium carbonate, was heated in a platinum dish at 900° and finally at 1100°. The resultant calcium oxide was treated with an excess of water, placed immediately in an autoclave and heated at 150° for 72 hours.[2] The product was stored in a vacuum desiccator over calcium oxide to remove excess water and form crystalline calcium hydroxide. The average of six chemical analyses of the product corresponded to 100.02% $Ca(OH)_2$. Microscopic examination showed the presence of an insignificant amount of unreacted calcium oxide as cores in the calcium hydroxide crystals.

Phosphoric Acid.—Phosphoric acid hemihydrate, $2H_3PO_4 \cdot H_2O$, was crystallized from reagent grade phosphoric acid and dissolved in distilled water to form an acid containing 84.40% H_3PO_4. The phosphate content of the solution was checked by quadruplicate determination as magnesium pyrophosphate.

Apparatus.—The low temperature calorimeter described previously[3] was used without modification.

The solution calorimeter used for determinations of heats of formation and hydration was similar to that used by Southard.[4] The Dewar flask had a capacity of 875 ml.; its inside diameters were 85 mm. in the body and 50 mm. in the neck. The Dewar flask was supported in a constant temperature bath by paraffin-saturated cork rings that were clamped between stainless steel plates. A flanged stainless steel collar, fitted closely around the neck of the Dewar flask, was silver soldered to the top plate. A small stainless steel plate, provided with three small stuffing boxes for the thermometer supports and with a stainless steel ball-bearing guide 4 inches long for the stirrer, was bolted to the flanged collar through a Tygon gasket.

The stirrer shaft was a $^1/_4$-inch stainless steel tube. The portion of the shaft that extended into the Dewar flask had walls 0.008 inch thick. The stirrer blades thrust the liquid downward.

The thermometer–heater assembly hung from three $^1/_8$-in. Inconel tubes with 0.004-in. walls. Silver soldered to the lower end of the tubes was a copper tube 5.5 in. long and $1^7/_8$ in. in diameter with a wall thickness of 0.01 in. The thermometer–heater was wound on the copper tube, and the electrical leads were brought out through the Inconel tubes.

The thermometer, a copper–manganin bridge,[5,6] occupied the bottom 4.75 in. of the copper tube. The bridge had a total resistance of 225 ohms, and the resistances of the copper and manganin coils were adjusted to give an unbalance of 7 mvolts at 25°. The sensitivity of the thermometer was about 2 mvolts per degree. The bridge unbalance was read with a precision of 0.2 microvolt on a Wenner thermocouple potentiometer. The bridge current was maintained constant at 4 milliamperes by adjusting a Helipot in the bridge current circuit to maintain a voltage drop of 40 mvolts, as measured on a White potentiometer, across a 10-ohm standard resistor. The standard cells for the potentiometers were checked against saturated standard cells—certified by the National Bureau of Standards and maintained at 25°.

A 100-ohm constantan heater was wound on the top $^1/_2$ in. of the copper tube. Current and potential leads were soldered to the heater. The potential applied to the heater was measured to the nearest microvolt with a Wenner standardizing potentiometer. Time was measured with a Standard Electric Time Company master clock and a "second accumulator" that switched current from a dummy heater into the calorimeter heater for a selected integral number of seconds.

All the metal parts that extended into the Dewar flask

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[1] Article not copyrighted.

[2] T. Thorvaldson and W. G. Brown, THIS JOURNAL, **52**, 80 (1930).

[3] E. P. Egan, Jr., Z. T. Wakefield and K. L. Elmore, *ibid.*, **73**, 5579, 5581 (1951).

[4] J. C. Southard, *Ind. Eng. Chem.*, **32**, 442 (1940).

[5] C. G. Maier, *J. Phys. Chem.*, **34**, 2860 (1930).

[6] E. P. Egan, Jr., Z. T. Wakefield and K. L. Elmore, THIS JOURNAL, **72**, 2418 (1950).

were coated with a layer of insulating varnish and a layer of Apiezon vacuum wax that was applied as a solution in carbon tetrachloride.

Samples were weighed into thin-walled glass bulbs about 35 mm. in diameter. Each filled bulb was sealed and fused to the end of a 4-mm. glass rod. In a run, the sample was suspended below the stirrer from a rod through the hollow stirrer shaft. The bulb was broken by thrusting it against the bottom of the Dewar flask.

Since the heater and the thermometer were wound on the same copper tube, a superheat of about 0.05° was produced in the thermometer while the heater was energized. Furthermore, dissolution of the sample was practically complete within 1 minute after the sample bulb was broken. A simplified procedure for correction of the temperature rise therefore was required, and the method of Dickinson[7] was used. The time selected in calculating the corrected temperature rise was 0.60 of the heating or dissolution interval.

Low Temperature Heat Capacity and Entropy.—The observed heat capacities, $\Delta Q/\Delta T$, for the empty calorimeter and for the calorimeter charged with 68.4939 g. (*in vacuo*) or 0.271706 mole of $Ca(H_2PO_4)_2 \cdot H_2O$ were plotted on a large scale, and arbitrary smooth curves were drawn through the experimental points. Values read at 5° intervals from the smooth curves were used in the calculation of curvature corrections from second differences.[8] Equations were fitted to the corrected heat capacities, a deviation plot was made, and values calculated from the equations were corrected from the deviation plot. A table of the observed heat capacities is available.[9] The heat capacities at 5° intervals are given in Table I.

The observed heat capacities showed a small, sharp peak at 273°K. The difference between the peak and a smooth curve through the heat capacities at temperatures near 273°K. was 0.0308 cal., which is the same as the heat of fusion of 0.000022 mole of water. The monocalcium phosphate monohydrate charged to the calorimeter, however, was free of moisture and of anhydrous monocalcium phosphate. A space was left above the charge as a precaution against dehydration of the salt when the cap was soldered on the calorimeter. Also, the heat capacity measurements below room temperature were made before those at higher temperatures. When the calorimeter was opened after the measurements were completed, a microscopic examination of material from the top of the charge showed the presence of nuclei of anhydrous monocalcium phosphate along the edges of the plate crystals of monocalcium phosphate monohydrate. The amount of the anhydrous salt was too small to be estimated. In spite of the precautions, a trace amount of the monohydrate apparently was decomposed during the soldering operation to form the anhydrous salt and free water.

The observed heat capacities in Table I are corrected[10,11] for 0.000022 mole of water, although the corrections were small enough to have been ignored. The precision of the measurements is within ±0.05%. One defined calorie is taken equal to 4.18331 international joules.[12]

Table I

Heat Capacity of Monocalcium Phosphate Monohydrate at 5° Intervals, Calories per Mole per Degree

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
10	0.16	130	31.76	250	54.26
15	0.57	135	32.85	255	55.06
20	1.37	140	33.92	260	55.85
25	2.50	145	34.98	265	56.68
30	3.90	150	36.02	270	57.47
35	5.44	155	37.03	275	58.25
40	7.07	160	38.04	280	59.09
45	8.66	165	39.03	285	59.86
50	10.26	170	40.01	290	60.65
55	11.92	175	40.97	295	61.41
60	13.58	180	41.92	300	62.12
65	15.15	185	42.87	305	62.83
70	16.70	190	43.80	310	63.53
75	18.17	195	44.72	315	64.21
80	19.62	200	45.63	320	64.93
85	21.03	205	46.53	325	65.57
90	22.37	210	47.44	330	66.30
95	23.60	215	48.32	335	67.01
100	24.82	220	49.20	340	67.71
105	26.02	225	50.06	345	68.40
110	27.21	230	50.92		
115	28.37	235	51.76	298.16	61.86
120	29.52	240	52.60		
125	30.65	245	53.44		

The entropy of monocalcium phosphate monohydrate at 298.16°K. is 62.10 ± 0.10 e.u., of which 0.05 e.u. represents a Debye extrapolation ($\theta = 133$) between 0 and 10.065°K., and 62.05 e.u. represents graphical integration between 10.065 and 298.16°K. The graphical integration was checked by tabular integration[13] at 5° intervals. On the assumption that the measured solid represents the ideal state, the heat content ($H^0 - H_0^0$) at 298.16°K. is 9950 cal. per mole.

Heats of Formation and Hydration.—In the equation

$$2(H_3PO_4 \cdot 1.0055H_2O)(l) + Ca(OH)_2(c) = Ca(H_2PO_4)_2 \cdot H_2O(c) + H_2O(l) + aq \quad (1)$$

the $Ca(H_2PO_4)_2 \cdot H_2O$ was the only compound whose heat of formation was not known. The heat of reaction was determined by measuring the difference between the sum of the heats of solution of the products and the sum of the heats of solution of the reactants in 4 molal hydrochloric acid at 25° under such conditions that the ionic concentrations of the solutions of products and reactants were identical.

Because of the marked hygroscopicity of H_3PO_4 (l or c), an 84.40% solution of the acid, which is $H_3PO_4 \cdot 1.0055H_2O$, was the reagent in eq. 1. The heat of formation of $H_3PO_4(l)$ is −303,570 cal./mole.[14]

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[7] H. C. Dickinson, *Bull. Natl. Bur. Standards*, **11**, 189 (1914).

[8] R. B. Scott, C. H. Meyers, R. D. Rands, Jr., F. G. Brickwedde and N. Bekkedahl, *J. Research Natl. Bur. Standards*, **35**, 39 (1945).

[9] The observed molal heat capacities and the corresponding temperature intervals have been deposited as Document number 4734 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints or $1.25 for 35 mm. microfilm in advance by check or money order, payable to: Chief, Photoduplication Service, Library of Congress.

[10] W. F. Giauque and J. W. Stout, This Journal, **58**, 1144 (1936).

[11] N. S. Osborne, H. F. Stimson and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **23**, 197 (1939).

[12] F. D. Rossini, F. T. Gucker, H. L. Johnston, L. Pauling and G. W. Vinal, This Journal, **74**, 2699 (1952).

[13] Work Projects Administration, Mathematical Tables Project "Tables of Lagrangian Interpolation Coefficients," Columbia University Press, New York, N. Y., 1944.

[14] T. D. Farr, Tennessee Valley Authority, *Chem. Eng. Rept.*, No. 8 (1950).

The heat of solution, $H_3PO_4(l) + aq = H_3PO_4$ (84.40%), is −1983 cal./mole of H_3PO_4.[15] Thus, the heat of formation of H_3PO_4 (84.40%) is −305,553 cal./mole of H_3PO_4.

Each measurement of a heat of solution was made with 900 g. of 4 molal hydrochloric acid in the solution calorimeter. Electrical calibrations over the same temperature interval were made immediately before and after the measurement of the heat of solution. The after-period of the first calibration thus was the fore-period of the heat of solution, and the after-period of the heat of solution was the fore-period of the second calibration. A starting temperature was chosen that would put the temperature at the end of the dissolution within a few hundredths of a degree of 25°, and temperature corrections were unnecessary. The following heats of solution were obtained. $H_3PO_4 \cdot 1.0055H_2O(l)$, 3 to 7 g.: −1773, −1775, −1784, −1784, or an average of −1779 ± 5 cal./mole of H_3PO_4. $Ca(OH)_2$ (c), 1 to 2 g. in HCl solution to which had been added the stoichiometric amount of $H_3PO_4 \cdot 1.0055H_2O$: −31,462, −31,325, −31,314, −31,186, −31,316, or an average of −31,285 ± 100 cal./mole of $Ca(OH)_2$. $H_2O(l)$, 1 to 10 g.: −64.7, −66.4, −63.7, −64.2, −65.2, or an average of −64.9 ± 1.5 cal./mole of H_2O. In three of the runs, ten times the stoichiometric amount of water was used in an attempt to increase the accuracy of the measurement, but the results were the same as those of the other runs. $Ca(H_2PO_4)_2 \cdot H_2O(c)$, 5 to 9 g. in HCl solution to which had been added the stoichiometric amount of H_2O indicated by eq. 1: 3476, 3455, 3426, 3423, 3444, 3477, or an average of 3450 ± 22 cal./mole of $Ca(H_2PO_4)_2 \cdot H_2O$.

The results indicated that no correction was required for the effect of the size of the charge. In five tests, the energy of breaking the glass sample bulb was within the limits of error of the measurements.

Substitution of the molal heats of solution in eq. 1 leads to a value of −38,228 ± 103 cal. for the heat of reaction at 25°. Heats of formation at 25°, in cal./mole, are: $H_3PO_4 \cdot 1.0055H_2O(l)$, −305,553; $Ca(OH)_2(c)$,[16] −235,800; $H_2O(l)$, −68,317. The heat of formation of $Ca(H_2PO_4)_2 \cdot H_2O(c)$ at 25° then is −816,820 cal./mole.

The heat of the reaction

$$2(H_3PO_4 \cdot 1.0055H_2O)(l) + Ca(OH)_2(c) = Ca(H_2PO_4)_2(c) + 2H_2O(l) + aq \quad (2)$$

was determined similarly. The heat of solution of 4 to 9 g. of $Ca(H_2PO_4)_2(c)$ in 4 molal HCl containing the stoichiometric amount of water indicated by eq. 2 was −1104, −1012, −1024, −1104, −1052, −1054, or an average of −1059 ± 31 cal./mole. The heat of reaction (eq. 2) at 25° then is −35,770 cal., and the heat of formation at 25° of $Ca(H_2PO_4)_2$ (c) is −746,040 cal./mole. The heat of hydration

$$Ca(H_2PO_4)_2(c) + H_2O(l) = Ca(H_2PO_4)_2 \cdot H_2O(c) \quad (3)$$

then is −2460 cal./mole at 25°.

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[15] Unpublished TVA data.

[16] National Bureau of Standards Circular 500, U. S. Govt. Printing Office, Washington, D. C., 1952.

[CONTRIBUTION FROM THE PYROTECHNICS CHEMICAL RESEARCH LABORATORY, PICATINNY ARSENAL]

The Reaction between Mercury and Nitrogen Dioxide

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The reaction between mercury and nitrogen dioxide has been investigated in the presence of nitric oxide and oxygen. The nitric oxide to oxygen ratios studied were: (A) greater than 2, (B) 2 to 1.33, (C) 1.33 to 1.00 and (D) less than 1.00. The reaction for (A) appears to be $4Hg + 6NO_2 = Hg_2(NO_3)_2 + Hg_2(NO_2)_2 + 2NO$. In the presence of excess oxygen, in (B), (C) and (D) the nitric oxide formed is reconverted into nitrogen dioxide. The total amount of nitric oxide which may react in this manner is expressed by the relationship $[NO] = [NO_i] + \sum_{1}^{1} \frac{[NO_i]}{3n}$ where $[NO_i]$ is the initial quantity. For nitric oxide to oxygen ratios of 1.33 to 1.00 the net reaction is $4Hg + 4NO_2 + O_2 = Hg_2(NO_3)_2 + Hg_2(NO_2)_2$.

Introduction

In 1928, Pierce and Noyes[1] postulated that mercuric and/or mercurous nitrite were formed during the initial stages of the reaction between mercury and nitrogen dioxide, followed by the formation of nitric oxide and nitrogen. They did not, however, present experimental evidence to verify the hypothesis. In the course of a study of the kinetics of the decomposition of various inorganic nitrates, the reaction between mercury and nitrogen dioxide became of interest, since the gaseous decomposition products were collected by mercury displacement. The reaction also presented a potential method for the analysis of mixtures of nitrogen dioxide, nitric oxide and oxygen.

Experimental

The following reagents were used: mercury, pyrogallol, sodium sulfate, potassium hydroxide, sulfuric acid (Fisher Scientific Company), nitric acid, acetic acid (J. T. Baker Chemical Company), ferric ammonium sulfate, ferrous ammonium sulfate and potassium thiocyanate (Mallinckrodt Chemical Works). All the chemicals were of C.P. grade. The alkaline pyrogallol and mixed acids (nitric and sulfuric) were prepared as described by Johnson.[2] The gases, nitric oxide, oxygen and nitrogen dioxide, were purchased from the Matheson Company, Inc., and were 98.0, 99.6 and 98.0% pure, respectively. Gas sampling bulbs having a 100-ml. capacity were made of Pyrex glass with a three-way stop-

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[1] W. C. Pierce and W. A. Noyes, Jr., THIS JOURNAL, **50**, 2179 (1928).

[2] C. L. Johnson, *Anal. Chem.*, **24**, 1572 (1952).