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Heat Capacities of the Liquid Phase in the System $CaO-P_2O_5-H_2O$

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Measurements were made of the heat capacities at 25°, 50°, and 80° C. of solutions in the system $CaO-P_2O_5-H_2O$, and the measured specific heats were converted to partial molal heat capacities of the calcium phosphates $Ca(H_2PO_4)_2 \cdot H_2O$, $Ca(H_2PO_4)_2$, $CaHPO_4 \cdot 2H_2O$, and $CaHPO_4$.

THERMAL data on the solid and liquid phases in the system $CaO-P_2O_5-H_2O$ are useful in interpretation of the reactions involved in fertilizer manufacturing processes and in the behavior of fertilizers in the soil. Measurements were made of the specific heats of liquid phases in the system at 25°, 50°, and 80° C., and the partial molal quantities were derived from the results. The specific heats, with the heats of solution at the same composition (*2*), may be used to determine the temperature dependence of other physical properties of the solutions, such as vapor pressure and electrochemical potentials. The specific heats of the solution are of direct value in engineering calculations involving calcium phosphate solutions.

The measured specific heats of the solutions were converted to partial molal heat capacities of the calcium phosphates $Ca(H_2PO_4)_2 \cdot H_2O$, $Ca(H_2PO_4)_2$, $CaHPO_4$, and $CaHPO_4 \cdot 2H_2O$. For these conversions, the solution compositions were recalculated to represent each of the four ternary systems comprising a single calcium phosphate, phosphoric acid, and water.

MATERIALS AND APPARATUS

Phosphoric Acid. Phosphoric acid hemihydrate, $2H_3PO_4 \cdot H_2O$, was twice recrystallized from reagent phosphoric acid (*3*). The drained, unwashed crystals were melted to form a stock solution (90% H_3PO_4), the exact composition of which was established by its density (*1*).

Dicalcium Phosphate. A solution (*5*) containing 5% CaO, 21% P_2O_5, and 74% H_2O was prepared from reagent dicalcium phosphate and the stock phosphoric acid. The solution was filtered, then heated to crystallize anhydrous dicalcium phosphate.

Preparation of Solutions. The compositions of the solutions used in the measurements were intersections of "water rays" (*9*) of constant ratios P_2O_5:CaO with tielines between $Ca(H_2PO_4)_2$ and 0.5, 1, 1.5, 2, 3, 4, 6, 8, and 10 molal phosphoric acid solutions. The weight ratios P_2O_5:CaO selected for the water rays were 39.180, 19.081, 12.706, 9.514, 7.596, 6.314, 5.396, 4.705, and 4.161. The most concentrated solution on each water ray was prepared by

Table I. Test Solutions Expressed in Terms of System $Ca(H_2PO_4)_2 \cdot H_2O$–H_3PO_4–H_2O

H_3PO_4 Molality, m_2	Wt. %[a] P_2O_5	Wt. %[a] CaO	$Ca(H_2PO_4)_2 \cdot H_2O$ Molality, m_3
Wt. ratio P_2O_5:CaO = 39.18			
10	36.83	0.94	0.3477
8	33.74	0.86	0.2918
6	28.60	0.73	0.2178
4	21.08	0.54	0.1369
3	17.74	0.45	0.1069
2	12.87	0.33	0.0718
Wt. ratio P_2O_5:CaO = 19.081			
10	37.66	1.97	0.7647
8	33.78	1.77	0.6118
6	28.82	1.51	0.4588
4	22.28	1.17	0.3058
3	18.16	0.95	0.2294
2	13.26	0.69	0.1529
1.5	10.44	0.55	0.1147
1.0	7.32	0.38	0.0765
0.5	3.86	0.20	0.0383
Wt. ratio P_2O_5:CaO = 12.706			
8	34.85	2.74	0.9951
6	29.94	2.36	0.7463
4	23.36	1.84	0.4975
3	19.16	1.51	0.3732
2	14.09	1.11	0.2488
Wt. ratio P_2O_5:CaO = 9.514			
6	31.16	3.28	1.0874
4	24.56	2.58	0.7250
3	20.27	2.13	0.5437
2	15.02	1.58	0.3625
1.5	11.93	1.25	0.2719
1.0	8.46	0.89	0.1813
0.1	0.95	0.10	0.0181

H_3PO_4 Molality, m_2	Wt. %[a] P_2O_5	Wt. %[a] CaO	$Ca(H_2PO_4)_2 \cdot H_2O$ Molality, m_3
Wt. ratio P_2O_5:CaO = 7.596			
4	25.90	3.41	0.9995
3	21.53	2.83	0.7497
2	16.10	2.12	0.4998
0.5	4.93	0.65	0.1249
Wt. ratio P_2O_5:CaO = 6.314			
4	27.40	4.34	1.3382
3	22.97	3.64	1.0037
2	17.36	2.75	0.6691
1.5	13.95	2.21	0.5018
1.0	10.02	1.59	0.3346
Wt. ratio P_2O_5:CaO = 5.396			
3	24.63	4.57	1.3253
2	18.85	3.49	0.8836
1.5	15.26	2.83	0.6626
0.5	6.05	1.12	0.2209
0.1	1.31	0.24	0.0442
Wt. ratio P_2O_5:CaO = 4.705			
2	20.63	4.38	1.1644
1.5	16.86	3.58	0.8733
1.0	12.34	2.62	0.5822
Wt. ratio P_2O_5:CaO = 4.164			
2.0	22.81	5.48	1.5502
1.5	18.85	4.53	1.1626
1.0	13.99	3.36	0.7751
0.5	7.89	1.90	0.3875
0.1	1.76	0.42	0.0775

[a] % H_2O = 100 – (% P_2O_5 + CaO).

weight from the stock phosphoric acid solution, recrystallized dicalcium phosphate, and water, and its composition was checked by chemical analysis. Solutions along each water ray were prepared by weight dilution of the concentrated solution. The compositions of solutions so prepared are listed in Table I.

The authors discovered after the measurements were completed that the dilutions along the 39.180 water ray had been miscalculated, so that the compositions of the solutions along this ray in Table I were displaced slightly from the desired intersections. These departures from the desired compositions, however, did not affect the validity of the subsequent calculations.

The compositions of saturated solutions in the system CaO–P_2O_5–H_2O at 25° C. are listed in Table II. These compositions are from both published results (*5, 6*) and recent unpublished measurements of solutions near the $Ca(H_2PO_4)_2 \cdot H_2O$–$CaHPO_4$ invariant point.

Calorimeter. Only minor modifications were made to the solution calorimeter (*4*). The hollow stirrer shaft was closed with a neoprene plug. At 80° C. there was some difficulty from condensation of water on the calorimeter cover and upper walls during the time that the solution, heated to about 75° C., was placed in the calorimeter, and the assembled calorimeter began to approach temperature equilibrium with the bath. To prevent this condensation, the calorimeter cover was preheated to 90° C. on a formed Calrod unit and, while the weighed charge was being preheated to 75° C., a small copper-jacketed oil bath, heated to 95° C., was inserted into the neck of the calorimeter.

As in previous measurements (*4*), a weighed charge of constant volume (850 ml.) was used. The vapor space in the calorimeter was about 160 ml., and a vaporization correction was made for the water required for saturation of this space, based on vapor pressures at 25° C. (*9*). Vapor pressures at 50° and 80° C. were not available, but the isobars at

Table II. Compositions of Solutions on Saturation Isotherms at 25° C.

$CaHPO_4$ Isotherm % P_2O_5	$CaHPO_4$ Isotherm % CaO	$Ca(H_2PO_4)_2 \cdot H_2O$ Isotherm % P_2O_5	$Ca(H_2PO_4)_2 \cdot H_2O$ Isotherm % CaO
1.55	0.55	24.53	5.80[a]
4.90	1.55	27.19	5.20
8.25	2.44	29.72	4.62
11.51	3.22	32.00	4.09
14.61	3.90	34.06	3.62
17.52	4.49	36.81	3.00
20.22	5.01	39.94	2.32
22.69	5.46	42.58	1.80
24.53	5.80[a]		

[a] Invariant point.

25° C. were almost straight lines with small slopes, and the vapor pressure of each solution was assumed to increase with rising temperature at the same rate as phosphoric acid solutions (*6*). The largest vaporization correction was 0.25% of the energy input, and the correction probably was in error by no more than 10%.

In each specific-heat measurement (*4*), the energy input was adjusted to yield a temperature rise of 0.5° C. The energy measurements were based on the defined calorie of 4.1840 absolute joules. The temperature base was 0° C. (273.15° K.). All temperatures were measured to 0.0001° C.; the last two places are significant only in determining small temperature differences, and three decimal places were used for consistency in calculating the variation of the specific heat with temperature.

SPECIFIC HEATS

The measured specific heats at the midpoint of each temperature interval at 25°, 50°, and 80° C. are listed in Tables III, IV, and V. Pairs of measurements at the same tem-

Table III. Observed Specific Heats at 25° C.

H_3PO_4 Molality, m	t, ° C.	Cal./G. Soln.
Wt. ratio P_2O_5:CaO = 39.18		
10	24.742	0.6255
	25.288	0.6264
10	24.742	0.6256
	25.289	0.6261
8	24.613	0.6543
	25.152	0.6547
6	24.667	0.7043
	25.202	0.7035
4	24.749	0.7781
	25.278	0.7788
3	24.727	0.8110
	25.254	0.8111
2	24.729	0.8605
	25.281	0.8607
Wt. ratio P_2O_5:CaO = 19.081		
10	25.130	0.6106
	25.674	0.6123
10	24.795	0.6146
	25.373	0.6176
10	24.733	0.6124
	25.276	0.6130
8	24.679	0.6469
	25.215	0.6474
6	24.768	0.7082
	25.315	0.7111
6	24.753	0.6979
	25.287	0.6986
6	24.747	0.6956
	25.280	0.6966
4	24.727	0.7606
	25.260	0.7607
3	24.749	0.8041
	25.285	0.8064
3	24.729	0.8026
	25.262	0.8023
2	24.727	0.8517
	25.258	0.8500
2	24.734	0.8522
	25.265	0.8519
1.5	24.723	0.8918
	25.253	0.8932
1	24.746	0.9166
	25.272	0.9171
0.5	24.750	0.9536
	25.277	0.9542
Wt. ratio P_2O_5:CaO = 12.706		
8	24.752	0.6306
	25.292	0.6305
6	24.750	0.6780
	25.281	0.6786
4	24.769	0.7468
	25.314	0.7515
4	24.741	0.7454
	25.273	0.7456
3	24.734	0.7891
	25.263	0.7884
2	24.751	0.8419
	25.273	0.8423
Wt. ratio P_2O_5:CaO = 9.514		
6	24.752	0.6619
	25.286	0.6620
4	24.751	0.7282
	25.286	0.7289
3	24.756	0.7729
	25.289	0.7736
Wt. ratio P_2O_5:CaO = 9.514 cont.		
2	24.750	0.8278
	25.276	0.8296
1.5	24.750	0.8611
	25.277	0.8618
1	24.749	0.9001
	25.275	0.9002
0.1	24.750	0.9887
	25.275	0.9889
Wt. ratio P_2O_5:CaO = 7.596		
4	24.747	0.7098
	25.271	0.7101
3	24.752	0.7554
	25.282	0.7557
2	24.750	0.8132
	25.282	0.8137
0.5	24.750	0.9382
	25.278	0.9392
Wt. ratio P_2O_5:CaO = 6.314		
4	24.752	0.6925
	25.287	0.6896
4	24.751	0.6885
	25.285	0.6889
3	24.749	0.7347
	25.280	0.7352
2	24.755	0.7979
	25.288	0.7979
1.5	24.744	0.8337
	25.273	0.8338
1.0	24.746	0.8771
	25.278	0.8780
Wt. ratio P_2O_5:CaO = 5.396		
3	24.750	0.7146
	25.280	0.7145
2	24.736	0.7756
	25.270	0.7759
1.5	24.746	0.8155
	25.277	0.8151
0.5	24.746	0.9238
	25.277	0.9230
0.1	24.753	0.9818
	25.279	0.9812
Wt. ratio P_2O_5:CaO = 4.705		
2	24.753	0.7532
	25.284	0.7532
1.5	24.738	0.7987
	25.270	0.8020
1.5	24.723	0.7937
	25.246	0.7947
1	24.737	0.8505
	25.269	0.8465
1	24.737	0.8461
	25.267	0.8455
Wt. ratio P_2O_5: CaO = 4.164		
2	24.742	0.7243
	25.287	0.7246
1.5	24.718	0.7685
	25.244	0.7692
1	24.720	0.8242
	25.248	0.8240
0.5	24.736	0.8956
	25.263	0.8958
0.1	24.727	0.9745
	25.249	0.9751

perature that differed by more than 0.0010 cal. per ° C. per gram of solution were repeated.

At each measured solution concentration, the specific heats at the observed midpoint temperatures were fitted to a quadratic equation in t, and the specific heats were calculated at integral temperatures of 25.0°, 50.0°, and 80.0° C. The over-all average deviation of the specific heats with respect to temperature was 0.0004 cal. per ° C. per gram of solution.

Table IV. Observed Specific Heats at 50° C.

H_3PO_4 Molality, m	t, ° C.	Cal./G. Soln.
Wt. ratio P_2O_5:CaO = 39.18		
10	49.742	0.6408
	50.269	0.6429
10	49.742	0.6416
	50.269	0.6424
8	49.749	0.6697
	50.282	0.6704
6	49.750	0.7214
	50.272	0.7178
6	49.740	0.7113
	50.267	0.7108
6	49.753	0.7191
	50.290	0.7213
4	49.736	0.7922
	50.257	0.7909
4	49.735	0.7899
	50.271	0.7912
4	49.745	0.7917
	50.286	0.7922
3	49.746	0.8207
	50.279	0.8217
2	49.740	0.8688
	50.268	0.8699
Wt. ratio P_2O_5:CaO = 19.081		
10	49.724	0.6289
	50.252	0.6282
8	49.743	0.6628
	50.277	0.6624
6	49.738	0.7099
	50.269	0.7091
6	49.740	0.7113
	50.267	0.7108
4	49.744	0.7741
	50.276	0.7742
3	49.751	0.8144
	50.282	0.8160
3	49.755	0.8146
	50.283	0.8145
2	49.738	0.8614
	50.270	0.8612
1.5	49.728	0.9001
	50.243	0.9004
1	49.744	0.9232
	50.266	0.9236
0.5	49.756	0.9585
	50.279	0.9579
Wt. ratio P_2O_5:CaO = 12.706		
8	49.713	0.6463
	50.236	0.6468
6	49.797	0.6930
	50.319	0.6934
4	49.733	0.7570
	50.255	0.7563
3	49.734	0.7993
	50.264	0.7992
2	49.730	0.8522
	50.249	0.8504
2	49.740	0.8519
	50.270	0.8518
Wt. ratio P_2O_5:CaO = 9.514		
6	49.761	0.6759
	50.285	0.6768
4	49.975	0.7423
	50.500	0.7408
4	49.734	0.7419
	50.256	0.7424
3	49.758	0.7842
	50.296	0.7846
3	49.740	0.7852
	50.274	0.7848
2	49.749	0.8376
	50.274	0.8383
1.5	49.738	0.8705
	50.265	0.8709
Wt. ratio P_2O_5:CaO = 9.514 cont.		
1	49.727	0.9080
	50.252	0.9081
0.1	49.767	0.9905
	50.290	0.9907
Wt. ratio P_2O_5:CaO = 7.596		
4	49.770	0.7246
	50.321	0.7240
3	49.739	0.7671
	50.268	0.7700
3	49.742	0.7671
	50.274	0.7705
3	49.760	0.7675
	50.310	0.7684
2	49.723	0.8239
	50.254	0.8243
0.5	49.734	0.9438
	50.260	0.9431
Wt. ratio P_2O_5:CaO = 6.314		
4	49.732	0.7023
	50.254	0.7035
4	49.749	0.7006
	50.282	0.7020
3	49.696	0.7475
	50.230	0.7484
2	49.736	0.8069
	50.264	0.8086
2	49.740	0.8080
	50.272	0.8085
1.5	49.737	0.8430
	50.264	0.8444
1.5	49.742	0.8427
	50.278	0.8445
1.5	49.741	0.8447
	50.267	0.8431
1	49.731	0.8849
	50.256	0.8863
1	49.736	0.8857
	50.263	0.8858
Wt. ratio P_2O_5:CaO = 5.396		
3	49.749	0.7258
	50.287	0.7268
2	49.743	0.7889
	50.276	0.7895
1.5	49.734	0.8258
	50.262	0.8265
0.5	49.730	0.9279
	50.253	0.9278
0.1	49.735	0.9835
	50.260	0.9835
Wt. ratio P_2O_5:CaO = 4.705		
2	49.745	0.7671
	50.283	0.7670
1.5	49.720	0.8068
	50.254	0.8066
1	49.739	0.8545
	50.271	0.8543
Wt. ratio P_2O_5:CaO = 4.164		
2	49.765	0.7375
	50.310	0.7383
1.5	49.750	0.7818
	50.280	0.7836
1.5	49.731	0.7805
	50.257	0.7827
1.5	49.747	0.7819
	50.285	0.7826
1	49.745	0.8347
	50.282	0.8356
0.5	49.727	0.9042
	50.249	0.9045
0.1	49.732	0.9777
	50.257	0.9785

Table V. Observed Specific Heats at 80° C.

H_3PO_4 Molality, *m*	*t*, ° C.	Cal./G. Soln.
Wt. ratio P_2O_5:CaO = 39.18		
10	80.039	0.6590
	80.564	0.6577
10	79.749	0.6569
	80.229	0.6574
8	79.733	0.6882
	80.265	0.6845
8	79.716	0.6857
	80.251	0.6852
6	79.651	0.7301
	80.188	0.7301
4	79.654	0.8017
	80.182	0.8019
3	79.697	0.8327
	80.222	0.8326
2	79.683	0.8796
	80.205	0.8794
Wt. ratio P_2O_5:CaO = 19.081		
10	79.668	0.6431
	80.202	0.6442
8	79.713	0.6770
	80.248	0.6755
8	79.748	0.6764
	80.280	0.6780
8	79.712	0.6761
	80.245	0.6767
6	79.686	0.7223
	80.217	0.7226
4	79.691	0.7844
	80.223	0.7833
3	79.665	0.8230
	80.197	0.8226
2	79.660	0.8713
	80.188	0.8705
1.5	79.699	0.9083
	80.225	0.9063
1.5	79.710	0.9062
	80.237	0.9072
1	79.684	0.9282
	80.207	0.9278
0.5	79.700	0.9607
	80.224	0.9596
Wt. ratio P_2O_5:CaO = 12.706		
8	79.696	0.6601
	80.235	0.6601
6	79.694	0.7060
	80.227	0.7066
4	79.694	0.7706
	80.223	0.7685
4	79.733	0.7675
	80.255	0.7687
3	79.767	0.8108
	80.292	0.8093
3	80.250	0.8081
	80.777	0.8112
2	79.725	0.8598
	80.248	0.8606
Wt. ratio P_2O_5:CaO = 9.514		
6	79.731	0.6876
	80.260	0.6881
4	79.790	0.7617
	80.319	0.7538
4	79.723	0.7542
	80.257	0.7539
3	79.721	0.7961
	80.246	0.7958
2	79.736	0.8476
	80.272	0.8496
2	79.701	0.8482
	80.228	0.8485
1.5	79.697	0.8801
	80.220	0.8792
1	79.726	0.9117
	80.250	0.9120
0.1	79.709	0.9922
	80.228	0.9913
Wt. ratio P_2O_5:CaO = 7.596		
4	79.725	0.7349
	80.260	0.7344
3	79.744	0.7791
	80.275	0.7779
3	79.745	0.7774
	80.272	0.7775
2	79.725	0.8335
	80.253	0.8342
0.5	79.713	0.9480
	80.230	0.9480
Wt. ratio P_2O_5:CaO = 6.314		
4	79.725	0.7144
	80.253	0.7146
3	79.715	0.7583
	80.242	0.7588
2	79.724	0.8176
	80.250	0.8176
1.5	79.731	0.8523
	80.257	0.8520
1	79.739	0.8935
	80.266	0.8939
Wt. ratio P_2O_5:CaO = 5.396		
3	79.747	0.7379
	80.272	0.7382
2	79.740	0.8009
	80.265	0.7993
2	79.733	0.7979
	80.266	0.7981
1.5	79.739	0.8355
	80.272	0.8369
1.5	79.707	0.8359
	80.227	0.8357
0.5	79.747	0.9338
	80.272	0.9344
0.1	79.733	0.9875
	80.254	0.9858
0.1	79.719	0.9879
	80.236	0.9860
Wt. ratio P_2O_5:CaO = 4.705		
2	79.715	0.7759
	80.241	0.7762
1.5	79.738	0.8162
	80.264	0.8152
1	79.717	0.8698
	80.231	0.8643
1	79.725	0.8651
	80.245	0.8641
Wt. ratio P_2O_5:CaO = 4.164		
2	...	...[a]
	...	...[a]
1.5	...	...[a]
	...	...[a]
1	...	...[a]
	...	...[a]
0.1	79.708	0.9804
	80.225	0.9793

[a]Not determined; partial crystallization of $CaHPO_4$ during measurements.

Table VI. Specific Heats of Solutions, Calories per Gram of Solution

At 25° C.

P_2O_5, %	CaO, % 0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0	5.5	6.0
2	0.9715	0.9691(0.70)[a]										
4	0.9504	0.9450	0.9416(1.31)									
6	0.9294	0.9244	0.9194	0.9158(1.86)								
8	0.9087	0.9040	0.8994	0.8947	0.8912(2.37)							
10	0.8882	0.8838	0.8794	0.8751	0.8707	0.8676(2.85)						
12	0.8678	0.8637	0.8596	0.8555	0.8514	0.8473	0.8448(3.31)					
14	0.8477	0.8438	0.8400	0.8361	0.8322	0.8284	0.8245	0.8226(3.75)				
16	0.8277	0.8240	0.8204	0.8167	0.8131	0.8094	0.8058	0.8022	0.8009(4.17)			
18	0.8078	0.8044	0.8009	0.7974	0.7940	0.7905	0.7870	0.7836	0.7801	0.7795(4.59)		
20	0.7870	0.7839	0.7808	0.7776	0.7745	0.7713	0.7682	0.7650	0.7619	0.7588(4.99)		
22	0.7686	0.7654	0.7622	0.7590	0.7559	0.7527	0.7495	0.7463	0.7431	0.7399	0.7374(5.39)	
24	0.7492	0.7461	0.7430	0.7399	0.7368	0.7337	0.7306	0.7275	0.7244	0.7214	0.7182	0.7165(5.79)
26	0.7296	0.7266	0.7237	0.7208	0.7178	0.7149	0.7120	0.7090	0.7061	0.7032	0.7010(5.36)	
28	0.7122	0.7088	0.7053	0.7018	0.6984	0.6950	0.6915	0.6880	0.6846	0.6817(4.92)		
30	0.6928	0.6896	0.6864	0.6831	0.6799	0.6767	0.6735	0.6703	0.6673(4.47)			
32	0.6738	0.6707	0.6677	0.6646	0.6615	0.6584	0.6554	0.6523	0.6521(4.03)			
34	0.6555	0.6523	0.6491	0.6459	0.6428	0.6396	0.6364	0.6357(3.60)				
36	0.6375	0.6341	0.6308	0.6274	0.6240	0.6207	0.6196(3.16)					
38	0.6182	0.6153	0.6124	0.6094	0.6065	0.6052(2.73)						
40	0.5999	0.5970	0.5941	0.5911	0.5894(2.30)							
42	0.5818	0.5788	0.5759	0.5735(1.90)								
44	0.5637	0.5607	0.5577	0.5576(1.53)								
46	0.5451	0.5424	0.5412(1.21)									
48	0.5277	0.5250(0.94)										
50	0.5105	0.5090(0.72)										

At 50° C.

2	0.9738	0.9715(0.70)										
4	0.9542	0.9491	0.9460(1.31)									
6	0.9346	0.9299	0.9252	0.9218(1.86)								
8	0.9151	0.9107	0.9063	0.9019	0.8986(2.37)							
10	0.8956	0.8915	0.8874	0.8834	0.8792	0.8763(2.85)						
12	0.8762	0.8724	0.8685	0.8646	0.8608	0.8569	0.8545(3.31)					
14	0.8569	0.8532	0.8496	0.8460	0.8423	0.8387	0.8350	0.8332(3.75)				
16	0.8377	0.8342	0.8307	0.8273	0.8238	0.8204	0.8169	0.8134	0.8123(4.17)			
18	0.8186	0.8152	0.8119	0.8086	0.8053	0.8020	0.7987	0.7954	0.7920	0.7914(4.59)		
20	0.7996	0.7964	0.7932	0.7900	0.7868	0.7836	0.7804	0.7772	0.7740	0.7708(4.99)		
22	0.7808	0.7776	0.7745	0.7714	0.7682	0.7651	0.7620	0.7589	0.7557	0.7526	0.7502(5.39)	
24	0.7621	0.7590	0.7559	0.7528	0.7498	0.7467	0.7436	0.7405	0.7374	0.7343	0.7312	0.7294(5.79)
26	0.7436	0.7405	0.7375	0.7344	0.7313	0.7282	0.7252	0.7221	0.7190	0.7160	0.7138(5.36)	
28	0.7255	0.7224	0.7192	0.7160	0.7129	0.7097	0.7066	0.7034	0.7003	0.6976(4.92)		
30	0.7078	0.7045	0.7012	0.6979	0.6947	0.6914	0.6881	0.6848	0.6817(4.47)			
32	0.6893	0.6862	0.6830	0.6799	0.6768	0.6736	0.6705	0.6674	0.6672(4.03)			
34	0.6705	0.6676	0.6648	0.6619	0.6590	0.6562	0.6533	0.6528(3.60)				
36	0.6516	0.6490	0.6465	0.6439	0.6414	0.6388	0.6380(3.16)					
38	0.6326	0.6303	0.6281	0.6258	0.6235	0.6225(2.73)						
40	0.6128	0.6111	0.6094	0.6077	0.6067(2.30)							
42	0.5926	0.5915	0.5905	0.5896(1.90)								
44	0.5719	0.5716	0.5712	0.5712(1.53)								
46	0.5513	0.5514	0.5515(1.21)									
48	0.5299	0.5307(0.94)										
50	0.5080	0.5087(0.72)										

At 80° C.

2	0.9777	0.9751(0.70)										
4	0.9592	0.9537	0.9502(1.31)									
6	0.9406	0.9356	0.9307	0.9271(1.86)								
8	0.9219	0.9174	0.9130	0.9085	0.9052(2.37)							
10	0.9032	0.8991	0.8950	0.8910 -	0.8869	0.8841(2.85)						
12	0.8844	0.8806	0.8769	0.8732	0.8695	0.8658	0.8635(3.31)					
14	0.8656	0.8622	0.8587	0.8553	0.8518	0.8484	0.8449	0.8432(3.75)				
16	0.8470	0.8437	0.8404	0.8372	0.8339	0.8306	0.8274	0.8241	0.8230(4.17)			
18	0.8285	0.8253	0.8221	0.8190	0.8158	0.8126	0.8094	0.8063	0.8031	0.8025(4.59)		
20	0.8102	0.8070	0.8038	0.8007	0.7975	0.7944	0.7912	0.7881	0.7849	0.7818(4.99)		
22	0.7921	0.7889	0.7856	0.7824	0.7792	0.7760	0.7728	0.7695	0.7663	0.7631	0.7606(5.39)	
24	0.7743	0.7710	0.7676	0.7642	0.7608	0.7575	0.7541	0.7507	0.7473	0.7440	0.7406	0.7386(5.79)
26	0.7556	0.7524	0.7491	0.7459	0.7426	0.7394	0.7362	0.7330	0.7297	0.7265	0.7242(5.36)	
28	0.7394	0.7356	0.7317	0.7278	0.7239	0.7201	0.7162	0.7123	0.7084	0.7052(4.92)		
30	0.7216	0.7176	0.7137	0.7097	0.7057	0.7017	0.6977	0.6937	0.6900(4.47)			
32	0.7027	0.6992	0.6958	0.6924	0.6890	0.6856	0.6822	0.6788	0.6786(4.03)			
34	0.6857	0.6820	0.6878	0.6746	0.6709	0.6672	0.6635	0.6628(3.60)				
36	0.6692	0.6651	0.6611	0.6570	0.6529	0.6489	0.6476(3.16)					
38	0.6506	0.6472	0.6438	0.6404	0.6370	0.6354(2.73)						
40	0.6342	0.6305	0.6269	0.6232	0.6210(2.30)							
42	0.6187	0.6145	0.6102	0.6068(1.90)								
44	0.6033	0.5986	0.5939	0.5937(1.53)								
46	0.6015	0.5903	0.5856(1.21)									
48	0.5923	0.5803(0.94)										
50	0.5846	0.5774(0.72)										

[a] Specific heat at saturation; % CaO at saturation at 25° C. in parentheses.

Table VII. Partial Molal Heat Capacities in System $Ca(H_2PO_4)_2 \cdot H_2O-H_3PO_4-H_2O$

$Ca(H_2PO_4)_2 \cdot H_2O$ Molality, m_3	$\bar{C}_{p_1}$ 25°	$\bar{C}_{p_1}$ 50°	$\bar{C}_{p_1}$ 80°	$\bar{C}_{p_2}$ 25°	$\bar{C}_{p_2}$ 50°	$\bar{C}_{p_2}$ 80°	$\bar{C}_{p_3}$ 25°	$\bar{C}_{p_3}$ 50°	$\bar{C}_{p_3}$ 80°
				$m_2 = 0.5 H_3PO_4$					
0.2	17.917	17.964	18.066	25.22	28.90	32.13	53.10	61.90	31.92
0.4	17.797	17.829	18.160	25.98	27.77	37.61	73.78	87.49	5.42
0.6	17.566	17.398	18.427	26.03	26.15	35.50	99.22	136.07	-22.05
(0.643)[a]									
				$m_2 = 1.0 H_3PO_4$					
0.2	17.916	17.962	18.018	25.68	29.30	32.27	54.68	68.00	66.09
0.4	17.870	17.983	17.838	26.47	28.49	36.62	60.19	67.11	84.72
0.6	17.793	18.002	17.665	26.57	27.24	34.77	68.45	67.50	107.42
0.8	17.618	17.950	17.380	28.53	28.88	31.79	79.46	69.18	134.18
(0.992)									
				$m_2 = 2.0 H_3PO_4$					
0.2	17.847	17.918	18.032	26.50	29.97	32.57	66.79	71.30	73.53
0.4	17.817	17.920	17.940	27.33	29.78	35.00	67.18	72.94	74.93
0.6	17.796	17.920	17.965	27.53	29.12	33.63	68.77	75.74	77.60
0.8	17.718	17.833	17.971	28.70	30.13	32.05	71.59	79.70	81.55
1.0	17.642	17.705	17.885	28.97	31.36	32.07	75.62	84.82	86.76
1.2	17.499	17.525	17.888	30.04	32.87	28.40	80.86	91.10	93.25
1.4	17.414	17.491	17.429	28.19	28.99	36.10	87.33	98.53	101.00
(1.556)									
				$m_2 = 3.0 H_3PO_4$					
0.2	17.807	17.901	17.954	27.19	30.48	32.85	69.67	71.85	83.12
0.4	17.759	17.879	17.903	28.02	30.77	33.84	70.27	73.60	81.77
0.6	17.727	17.866	17.952	28.31	30.58	32.92	72.00	76.30	81.67
0.8	17.659	17.790	17.964	28.89	31.13	32.42	74.87	79.96	82.84
1.0	17.608	17.699	17.887	28.64	31.40	33.12	78.87	84.58	85.26
1.2	17.497	17.597	17.862	28.80	31.23	32.23	84.00	90.15	88.94
1.4	17.406	17.418	18.006	27.75	31.72	27.41	90.27	96.68	93.88
1.6	17.428	17.337	17.799	23.64	29.52	28.07	97.67	104.17	100.08
(1.657)									
				$m_2 = 4.0 H_3PO_4$					
0.2	17.744	17.875	17.903	27.75	30.84	33.14	77.34	70.75	86.01
0.4	17.693	17.814	17.902	28.55	31.46	33.15	76.16	73.92	85.66
0.6	17.670	17.764	17.933	28.92	31.63	32.63	75.68	78.18	86.25
0.8	17.654	17.679	17.895	29.11	31.87	32.89	75.88	83.52	87.77
1.0	17.676	17.601	17.779	28.59	31.50	33.94	76.78	89.95	90.22
1.2	17.677	17.533	17.647	28.14	30.37	34.85	78.37	97.46	93.60
1.4	17.600	17.203	17.914	28.47	32.16	29.73	80.64	106.06	97.91
(1.575)									
				$m_2 = 5.0 H_3PO_4$					
0.2	17.698	17.850	17.891	28.18	31.04	33.42	77.74	73.70	86.74
0.4	17.634	17.763	17.950	28.92	31.85	32.94	77.18	76.09	84.38
0.6	17.596	17.692	17.985	29.34	32.28	32.77	77.23	79.53	82.24
0.8	17.585	17.630	17.945	29.36	32.34	33.48	77.89	84.03	80.34
1.0	17.615	17.600	17.875	28.80	31.67	34.55	79.16	89.59	78.67
1.2	17.644	17.592	17.747	28.06	30.30	36.28	81.04	96.21	77.23
1.4	17.380	17.409	17.573	30.35	30.33	38.54	83.53	103.88	76.02
(1.488)									
				$m_2 = 6.0 H_3PO_4$					
0.2	17.655	17.818	17.894	28.48	31.09	33.71	86.27	83.04	77.58
0.4	17.611	17.734	17.929	29.12	31.94	33.19	81.62	81.54	81.33
0.6	17.602	17.682	17.871	29.59	32.51	33.34	77.06	80.44	85.99
0.8	17.653	17.685	17.709	29.63	32.56	34.18	72.60	79.73	91.57
1.0	17.760	17.761	17.523	29.30	31.90	34.93	68.24	79.44	98.07
1.2	17.922	17.855	17.206	28.58	31.01	36.50	63.97	79.54	105.47
1.4	17.500	18.362	15.136	33.39	26.21	53.84	59.80	80.04	113.80
(1.402)									
				$m_2 = 7.0 H_3PO_4$					
0.2	17.622	17.813	17.867	28.64	30.98	33.98	87.26	88.11	73.44
0.4	17.580	17.746	17.823	29.17	31.73	33.92	82.59	82.94	83.00
0.6	17.560	17.717	17.672	29.66	32.33	34.33	77.96	77.78	93.89
0.8	17.584	17.758	17.435	29.92	32.52	34.99	73.36	72.62	106.11
1.0	17.640	17.882	17.201	30.06	32.20	35.10	68.80	67.46	119.66
1.2	17.777	17.945	16.851	29.68	32.51	35.53	64.27	62.31	134.54
(1.317)									
				$m_2 = 8.0 H_3PO_4$					
0.2	17.604	17.828	17.812	28.68	30.71	34.26	88.05	87.76	82.75
0.4	17.572	17.760	17.678	29.05	31.23	35.11	84.21	86.40	84.95
0.6	17.532	17.695	17.560	29.56	31.75	35.75	80.44	85.31	87.73
0.8	17.480	17.638	17.495	30.25	32.22	35.91	76.73	84.48	91.10
1.0	17.416	17.598	17.555	31.10	32.56	35.04	73.10	83.93	95.07
1.2	17.450	17.280	17.707	31.36	34.80	33.36	69.52	83.65	99.62
(1.233)									

(Continued on page 515)

Table VII. Partial Molal Heat Capacities in System $Ca(H_2PO_4)_2 \cdot H_2O-H_3PO_4-H_2O$ (*Continued*)

$Ca(H_2PO_4)_2 \cdot H_2O$ Molality, m_3	$\bar{C}_{p_1}$			$\bar{C}_{p_2}$			$\bar{C}_{p_3}$		
	25°	50°	80°	25°	50°	80°	25°	50°	80°
				$m_2 = 9.0\ H_3PO_4$					
0.2	17.621	17.893	17.739	28.58	30.28	34.53	89.72	90.98	90.50
0.4	17.607	17.877	17.380	28.76	30.42	36.77	86.98	89.77	89.67
0.6	17.547	17.832	17.252	29.28	30.75	37.59	84.31	88.79	89.10
0.8	17.366	17.694	17.272	30.60	31.66	37.49	81.71	88.04	88.79
1.0	17.111	17.487	17.717	32.42	32.99	34.75	79.19	87.50	88.73
(1.151)									
				$m_2 = 10.0\ H_3PO_4$					
0.2	17.677	18.028	17.659	28.35	29.70	34.80	91.48	92.66	98.52
0.4	17.693	18.125	16.923	28.32	29.32	38.91	89.56	87.26	97.43
0.6	17.619	18.171	16.760	28.82	29.34	39.86	87.72	81.72	96.60
0.8	17.254	17.973	17.089	30.97	30.84	38.07	85.96	76.03	96.05
1.0	16.735	17.594	17.782	34.00	33.47	34.25	84.28	70.20	95.76
(1.070)									

[a] Saturated solution at 25° C.

Table VIII. Partial Molal Heat Capacities in System $Ca(H_2PO_4)_2-H_3PO_4-H_2O$

$Ca(H_2PO_4)_2$ Molality, m_3	$\bar{C}_{p_1}$			$\bar{C}_{p_2}$			$\bar{C}_{p_3}$		
	25°	50°	80°	25°	50°	80°	25°	50°	80°
				$m_2 = 0.5\ H_3PO_4$					
0.2	17.918	17.955	17.948	25.14	29.50	32.67	34.96	46.64	60.16
0.4	17.803	17.893	17.715	25.81	29.88	32.57	55.01	57.26	103.07
0.6	17.582	17.778	17.290	25.75	30.04	29.89	79.37	69.83	152.70
(0.640)[a]									
				$m_2 = 1.0\ H_3PO_4$					
0.2	17.911	17.976	17.947	25.62	29.81	32.66	36.76	43.23	63.40
0.4	17.860	17.962	17.840	26.36	30.18	32.53	43.55	44.05	84.76
0.6	17.776	17.776	18.037	26.40	30.23	30.33	52.76	63.86	68.71
0.8	17.646	17.306	18.671	25.41	28.74	33.44	64.39	102.65	15.24
(0.990)									
				$m_2 = 2.0\ H_3PO_4$					
0.2	17.859	17.898	18.022	26.48	30.32	32.69	49.43	48.22	52.80
0.4	17.828	17.799	17.969	27.33	30.69	32.54	49.41	64.26	63.83
0.6	17.811	17.720	17.958	27.52	30.60	31.18	50.58	73.21	70.32
0.8	17.803	17.737	17.860	26.90	29.53	33.26	52.95	75.07	72.28
1.0	17.802	17.921	17.858	25.32	26.90	36.04	56.52	69.84	69.72
1.2	17.622	18.193	18.017	27.69	26.43	34.13	61.28	57.53	62.62
1.4	17.350	18.625	18.042	31.38	26.80	40.97	67.23	38.12	51.00
(1.542)									
				$m_2 = 3.0\ H_3PO_4$					
0.2	17.806	17.894	17.984	27.20	30.70	32.79	52.22	50.64	66.88
0.4	17.755	17.831	17.935	28.09	31.08	32.66	52.83	58.56	67.23
0.6	17.722	17.795	17.970	28.43	30.94	31.98	54.45	63.38	67.42
0.8	17.704	17.810	17.901	28.13	30.26	33.24	57.10	65.09	67.46
1.0	17.701	17.900	17.831	27.08	29.05	34.57	60.76	63.70	67.35
1.2	17.521	17.943	17.953	28.69	29.96	32.42	65.44	59.21	67.09
1.4	17.520	17.928	17.943	26.23	33.51	32.78	71.15	51.62	66.66
1.6	17.579	19.035		21.77	18.22		77.87	40.92	
(1.602)									
				$m_2 = 4.0\ H_3PO_4$					
0.2	17.742	17.875	17.911	27.77	30.94	32.96	59.09	52.52	71.85
0.4	17.683	17.824	17.936	28.67	31.37	32.88	58.06	56.16	68.28
0.6	17.654	17.794	17.963	29.11	31.27	32.73	57.67	60.24	66.44
0.8	17.652	17.759	17.917	29.09	30.95	33.38	57.93	64.77	66.33
1.0	17.679	17.691	17.866	28.52	30.79	33.71	58.83	69.75	67.96
1.2	17.587	17.467	17.941	29.37	32.42	31.74	60.38	75.17	71.31
1.4	17.669	17.290	18.242	27.50	33.02	25.90	62.58	81.03	76.91
(1.520)									
				$m_2 = 5.0\ H_3PO_4$					
0.2	17.695	17.849	17.906	28.21	31.05	33.20	60.48	59.18	67.04
0.4	17.624	17.812	17.876	29.04	31.54	33.20	59.82	57.71	72.76
0.6	17.577	17.799	17.865	29.56	31.57	33.42	59.71	58.84	71.79
0.8	17.552	17.750	17.940	29.78	31.59	33.67	60.15	62.58	64.12
1.0	17.548	17.598	18.194	29.65	32.12	33.48	61.14	68.93	49.75
1.2	17.511	17.267	18.740	29.72	33.81	32.10	62.68	77.89	28.69
1.4	16.968	17.760	20.471	35.20	25.33	20.33	64.78	89.45	0.94
(1.439)									
				$m_2 = 6.0\ H_3PO_4$					
0.2	17.649	17.830	17.908	28.50	31.03	33.51	67.73	63.11	62.83
0.4	17.582	17.785	17.866	29.23	31.60	33.62	65.47	59.77	68.65
0.6	17.540	17.749	17.799	29.79	31.85	34.07	63.47	60.72	70.61

(*Continued on page 516*)

Table VIII. Partial Molal Heat Capacities in System $Ca(H_2PO_4)_2$–H_3PO_4–H_2O (*Continued*)

$Ca(H_2PO_4)_2$, Molality, m_3	$\bar{C}_{p_1}$ 25°	$\bar{C}_{p_1}$ 50°	$\bar{C}_{p_1}$ 80°	$\bar{C}_{p_2}$ 25°	$\bar{C}_{p_2}$ 50°	$\bar{C}_{p_2}$ 80°	$\bar{C}_{p_3}$ 25°	$\bar{C}_{p_3}$ 50°	$\bar{C}_{p_3}$ 80°
					m_2 = 5.0 H_3PO_4 (*cont.*)				
0.8	17.516	17.646	17.818	30.21	32.19	34.12	61.76	65.96	68.72
1.0	17.512	17.396	17.942	30.46	33.05	33.86	60.31	75.49	62.96
1.2	17.611	17.003	18.175	29.76	34.13	33.49	59.14	89.31	53.34
(1.356)									
					m_2 = 7.0 H_3PO_4				
0.2	17.622	17.837	17.864	28.65	30.88	33.89	69.09	67.58	58.94
0.4	17.575	17.796	17.761	29.21	31.54	34.15	64.65	59.36	72.33
0.6	17.541	17.714	17.666	29.79	32.11	34.66	60.25	60.51	75.73
0.8	17.523	17.501	17.743	30.37	32.73	34.73	55.89	71.04	69.14
1.0	17.519	17.068	18.001	30.96	33.57	34.86	51.56	90.94	52.55
1.2	17.791	16.507	18.400	29.48	33.37	35.91	47.26	120.22	25.97
(1.274)									
					m_2 = 8.0 H_3PO_4				
0.2	17.605	17.850	17.802	28.66	30.59	34.33	69.07	69.24	65.92
0.4	17.567	17.751	17.725	29.01	31.38	34.78	66.75	66.38	68.06
0.6	17.506	17.608	17.648	29.57	32.35	35.20	64.58	66.70	69.96
0.8	17.431	17.436	17.584	30.27	33.23	35.50	62.54	70.19	71.61
1.0	17.336	17.262	17.420	31.14	33.68	36.48	60.64	76.84	73.01
(1.193)									
					m_2 = 9.0 H_3PO_4				
0.2	17.631	17.911	17.682	28.53	30.17	34.85	73.79	73.13	73.41
0.4	17.641	17.766	17.568	28.60	31.10	35.52	69.96	72.11	74.55
0.6	17.590	17.532	17.548	29.12	32.57	35.69	66.15	71.55	73.61
0.8	17.511	17.354	17.469	29.90	33.68	36.42	62.34	71.44	70.57
1.0	17.392	17.397	17.181	31.01	33.38	38.71	58.55	71.78	65.45
(1.113)									
					m_2 = 10.0 H_3PO_4				
0.2	17.688	18.029	17.539	28.26	29.62	35.43	74.41	75.94	77.55
0.4	17.726	17.821	17.355	28.01	30.70	36.36	75.61	78.35	80.57
0.6	17.635	17.424	17.365	28.44	32.76	36.13	77.11	81.17	84.02
0.8	17.463	17.146	17.069	29.27	34.08	37.50	78.91	84.38	87.91
1.0	17.194	17.341	16.266	30.57	32.67	41.57	81.03	87.99	92.22
(1.034)									

[a] Saturated solution at 25° C.

Table IX. Partial Molal Heat Capacities in the System $CaHPO_4$-H_3PO_4–H_2O

$CaHPO_4$ Molality, m_3	$\bar{C}_{p_1}$ 25°	$\bar{C}_{p_1}$ 50°	$\bar{C}_{p_1}$ 80°	$\bar{C}_{p_2}$ 25°	$\bar{C}_{p_2}$ 50°	$\bar{C}_{p_2}$ 80°	$\bar{C}_{p_3}$ 25°	$\bar{C}_{p_3}$ 50°	$\bar{C}_{p_3}$ 80°
					m_2 = 0.5 H_3PO_4				
0.2	17.958	17.766	18.148	25.11	28.49	34.60	2.72	69.68	−21.13
(0.327)[a]									
					m_2 = 1.0 H_3PO_4				
0.2	17.909	18.034	17.947	25.54	29.02	33.97	11.83	−0.76	28.95
0.4	17.893	17.665	18.069	26.57	29.19	32.47	12.57	58.12	16.63
(0.567)									
					m_2 = 2.0 H_3PO_4				
0.2	17.864	17.909	17.998	26.31	29.92	32.97	19.03	27.58	20.67
0.4	17.813	17.931	17.940	27.28	30.06	32.99	21.93	21.80	31.61
0.6	17.768	17.874	17.901	28.19	30.23	32.13	23.41	27.07	39.42
(0.991)									
					m_2 = 3.0 H_3PO_4				
0.2	17.810	17.870	18.007	26.96	30.60	32.32	25.24	25.09	27.40
0.4	17.749	17.838	17.924	27.90	30.77	33.39	27.34	29.46	32.10
0.6	17.706	17.810	17.907	28.49	30.76	33.18	28.59	32.65	35.37
0.8	17.658	17.894	17.899	29.29	28.74	32.91	28.98	34.67	37.22
1.0	17.645	17.826	17.994	29.68	29.74	31.02	28.51	35.52	37.64
1.2	17.716	17.876	18.052	28.94	28.94	30.33	27.19	35.19	36.63
(1.356)									
					m_2 = 4.0 H_3PO_4				
0.2	17.784	17.858	18.050	27.50	31.07	32.03	24.21	20.44	23.58
0.4	17.696	17.801	17.884	28.41	31.31	33.70	28.47	27.93	32.23
0.6	17.642	17.759	17.822	28.78	31.22	33.93	31.46	33.43	37.46
0.8	17.607	17.781	17.838	28.98	30.30	33.39	33.18	36.94	39.29
1.0	17.597	17.745	17.977	29.02	30.48	31.84	33.64	38.46	37.70
1.2	17.617	17.736	18.181	28.97	30.74	30.40	32.83	37.99	32.70
1.4	17.716	17.747	18.326	28.27	31.39	31.13	30.76	35.52	24.29
1.6	17.883	17.739	18.733	27.22	33.18	29.93	27.42	31.07	12.46
(1.653)									

(*Continued on page 517*)

Table IX. Partial Molal Heat Capacities in the System $CaHPO_4$–H_3PO_4–H_2O (*Continued*)

$CaHPO_4$ Molality, m_3	$\bar{C}_{p_1}$			$\bar{C}_{p_2}$			$\bar{C}_{p_3}$		
	25°	50°	80°	25°	50°	80°	25°	50°	80°
				m_2 = 5.0 H_3PO_4					
0.2	17.721	17.825	18.009	27.93	31.33	32.08	32.31	25.42	36.00
0.4	17.644	17.784	17.846	28.82	31.68	33.89	31.85	27.11	36.26
0.6	17.630	17.769	17.813	29.08	31.62	34.38	30.87	29.38	35.03
0.8	17.664	17.744	17.902	28.91	31.50	33.78	29.38	32.22	32.31
1.0	17.714	17.720	18.071	28.71	31.14	32.67	27.37	35.63	28.11
1.2	17.737	17.570	18.331	29.01	31.94	31.04	24.85	39.60	22.42
1.4	18.288	17.917	18.460	23.68	26.90	31.48	21.82	44.15	15.24
(1.566)									
				m_2 = 6.0 H_3PO_4					
0.2	17.699	17.884	17.828	28.24	31.37	32.50	31.79	12.21	71.57
0.4	17.594	17.754	17.816	29.12	31.89	33.98	33.54	26.05	43.50
0.6	17.570	17.675	17.917	29.37	31.94	34.53	33.26	34.44	25.39
0.8	17.633	17.599	18.065	29.07	32.31	34.08	30.94	37.40	17.29
1.0	17.740	17.703	18.095	28.74	31.74	33.50	26.59	34.91	19.08
1.2	17.842	17.776	17.995	28.97	32.53	32.24	20.21	26.97	30.88
1.4	17.598	18.157	17.398	33.06	31.92	33.02	11.79	13.60	52.65
(1.477)									
				m_2 = 7.0 H_3PO_4					
0.2	17.652	17.889	17.822	28.44	31.20	33.26	39.02	18.02	51.55
0.4	17.557	17.747	17.762	29.33	31.93	33.97	35.83	27.35	46.35
0.6	17.541	17.660	17.782	29.67	32.19	34.39	32.71	33.48	38.29
0.8	17.606	17.554	17.932	29.46	32.75	34.30	29.65	36.42	27.36
1.0	17.700	17.619	18.150	29.10	32.27	34.35	26.66	36.16	13.57
1.2	17.793	17.656	18.525	28.83	32.52	34.00	23.73	32.70	−3.09
(1.389)									
				m_2 = 8.0 H_3PO_4					
0.2	17.529	17.791	17.536	28.52	30.81	34.38	63.92	51.47	78.66
0.4	17.511	17.737	17.755	29.43	31.80	33.84	42.50	34.59	52.17
0.6	17.552	17.719	17.905	29.98	32.38	33.95	29.00	27.10	33.43
0.8	17.604	17.630	17.974	30.09	32.81	34.42	23.41	29.02	22.42
1.0	17.604	17.455	17.912	29.81	32.73	35.21	25.74	40.34	19.16
1.2	17.572	17.158	17.659	28.60	31.91	36.33	35.98	61.05	23.65
(1.299)									
				m_2 = 9.0 H_3PO_4					
0.2	17.573	17.930	17.418	28.50	30.21	35.86	56.10	41.61	53.48
0.4	17.474	17.737	17.819	29.44	31.50	33.62	46.12	38.83	46.40
0.6	17.427	17.602	17.947	30.28	32.49	33.22	36.13	36.05	39.31
0.8	17.444	17.636	17.835	30.95	32.49	34.46	26.14	33.27	32.23
1.0	17.621	17.580	17.690	30.86	33.12	36.07	16.15	30.49	25.14
1.2	18.236	18.026	17.319	28.29	30.70	39.22	6.16	27.71	18.06
(1.210)									
				m_2 = 10.0 H_3PO_4					
0.2	17.600	18.066	17.198	28.35	29.40	37.68	57.44	44.27	32.83
0.4	17.472	17.781	17.983	29.34	31.04	33.29	48.39	42.55	34.20
0.6	17.328	17.526	18.168	30.59	32.53	32.19	39.35	40.84	35.58
0.8	17.179	17.680	17.750	32.05	31.80	34.42	30.30	39.12	36.95
1.0	17.290	17.413	17.272	32.25	33.44	36.94	21.26	37.41	38.32
(1.123)									

[a] Saturated solution at 25° C.

Table X. Partial Molal Heat Capacities in the System $CaHPO_4 \cdot 2H_2O$–H_3PO_4–H_2O

$CaHPO_4 \cdot 2H_2O$ Molality, m_3	$\bar{C}_{p_1}$			$\bar{C}_{p_2}$			$\bar{C}_{p_3}$		
	25°	50°	80°	25°	50°	80°	25°	50°	80°
				m_2 = 0.5 H_3PO_4					
0.2	17.958	17.765	18.150	25.08	28.50	34.57	38.66	105.79	14.44
(0.329)[a]									
				m_2 = 1.0 H_3PO_4					
0.2	17.909	18.035	17.946	25.51	29.02	33.97	47.59	34.90	65.02
0.4	17.895	17.664	18.075	26.53	29.18	32.39	48.06	94.08	51.82
(0.578)									
				m_2 = 2.0 H_3PO_4					
0.2	17.865	17.910	17.997	26.28	29.91	33.02	54.57	63.43	56.43
0.4	17.816	17.936	17.945	27.24	30.05	32.85	57.35	56.99	67.41
0.6	17.771	17.877	17.904	28.18	30.24	32.08	58.64	62.31	75.13
0.8	17.713	17.785	17.821	29.87	26.73	32.85	58.43	79.41	79.59
(0.999)									
				m_2 = 3.0 H_3PO_4					
0.2	17.811	17.870	18.002	26.94	30.58	32.39	60.99	61.24	63.84
0.4	17.753	17.842	17.937	27.85	30.75	33.23	62.64	64.90	67.64
0.6	17.713	17.817	17.918	28.45	30.74	33.08	63.59	67.73	70.65

(*Continued on page 518*)

Table X. Partial Molal Heat Capacities in the System $CaHPO_4 \cdot 2H_2O$–H_3PO_4–H_2O (*Continued*)

$CaHPO_4 \cdot 2H_2O$ Molality, m_3	$\bar{C}_{p_1}$			$\bar{C}_{p_2}$			$\bar{C}_{p_3}$		
	25°	50°	80°	25°	50°	80°	25°	50°	80°
				m_2 = 3.0 H_3PO_4 (*cont.*)					
0.8	17.665	17.905	17.882	29.29	28.65	33.22	63.83	69.73	72.89
1.0	17.646	17.828	17.927	29.78	29.72	31.97	63.38	70.89	74.33
1.2	17.710	17.863	17.972	29.01	28.96	30.88	62.22	71.23	75.00
(1.368)									
				m_2 = 4.0 H_3PO_4					
0.2	17.780	17.859	18.035	27.48	31.05	32.09	60.94	56.36	62.18
0.4	17.699	17.803	17.898	28.36	31.29	33.53	64.20	63.53	68.51
0.6	17.653	17.764	17.843	28.72	31.18	33.81	66.48	68.82	72.42
0.8	17.621	17.792	17.845	28.94	30.21	33.54	67.76	72.22	73.92
1.0	17.608	17.755	17.942	29.06	30.39	32.41	68.06	73.75	72.99
1.2	17.615	17.737	18.073	29.16	30.74	31.53	67.37	73.39	69.64
1.4	17.686	17.745	18.286	28.72	31.36	30.45	65.69	71.15	63.88
1.6	17.823	17.765	18.529	27.83	32.64	30.15	63.02	67.03	55.69
(1.718)									
				m_2 = 5.0 H_3PO_4					
0.2	17.725	17.834	18.000	27.91	31.31	32.11	67.11	59.22	73.66
0.4	17.648	17.784	17.858	28.77	31.67	33.77	66.98	62.44	72.20
0.6	17.633	17.765	17.830	29.01	31.57	34.28	66.35	65.57	70.25
0.8	17.662	17.742	17.904	28.85	31.40	33.80	65.23	68.60	67.80
1.0	17.702	17.730	18.034	28.69	31.01	32.89	63.60	71.55	64.84
1.2	17.702	17.594	18.169	29.16	31.88	32.15	61.48	74.40	61.39
1.4	18.154	17.918	18.274	24.83	27.57	32.02	58.86	77.16	57.44
1.6	17.968	17.389	18.563	27.83	32.64	30.15	55.74	79.83	52.99
(1.686)									
				m_2 = 6.0 H_3PO_4					
0.2	17.697	17.883	18.068	28.22	31.35	32.45	67.85	48.36	51.71
0.4	17.600	17.758	17.800	29.09	31.88	33.93	68.74	61.23	72.22
0.6	17.581	17.686	17.637	29.31	31.89	34.49	68.17	69.26	83.86
0.8	17.641	17.611	17.656	28.99	32.23	34.01	66.13	72.47	86.63
1.0	17.733	17.709	17.823	28.68	31.58	33.41	62.63	70.84	80.52
1.2	17.794	17.751	18.192	29.03	32.38	32.77	57.67	64.38	65.55
1.4	17.647	18.076	16.776	31.78	31.84	51.06	51.25	53.08	41.70
(1.591)									
				m_2 = 7.0 H_3PO_4					
0.2	17.658	17.886	17.839	28.42	31.19	33.11	73.27	54.63	87.66
0.4	17.562	17.751	17.758	29.30	31.93	34.01	70.71	62.49	81.77
0.6	17.544	17.673	17.777	29.62	32.17	34.44	68.09	67.91	73.82
0.8	17.608	17.571	17.938	29.39	32.68	34.17	65.42	70.88	63.82
1.0	17.700	17.636	18.159	29.01	32.10	33.97	62.68	71.40	51.76
1.2	17.789	17.660	18.515	28.74	32.22	33.37	59.89	69.47	37.63
(1.505)									
				m_2 = 8.0 H_3PO_4					
0.2	17.530	17.787	17.553	28.50	30.82	34.10	99.54	87.87	119.25
0.4	17.516	17.738	17.727	29.41	31.82	34.02	77.43	69.75	88.54
0.6	17.559	17.728	17.896	29.94	32.38	34.12	63.80	61.53	67.89
0.8	17.610	17.648	18.005	30.03	32.77	34.27	58.65	63.19	57.30
1.0	17.602	17.485	17.969	29.69	32.58	34.56	61.97	74.74	56.77
1.2	17.563	17.224	17.864	28.32	31.42	33.96	73.77	96.17	66.30
(1.402)									
				m_2 = 9.0 H_3PO_4					
0.2	17.578	17.925	17.470	28.47	30.24	35.42	90.97	77.59	92.29
0.4	17.477	17.734	17.753	29.42	31.54	33.96	81.03	74.10	83.73
0.6	17.428	17.602	17.896	30.28	32.54	33.55	71.08	70.61	75.17
0.8	17.450	17.654	17.880	30.91	32.50	34.31	61.13	67.12	66.60
1.0	17.642	17.627	17.878	30.72	33.01	35.18	51.19	63.63	58.04
1.2	18.322	18.188	18.154	27.75	29.98	34.53	41.24	60.13	49.48
(1.302)									
				m_2 = 10.0 H_3PO_4					
0.2	17.606	18.055	17.282	28.32	29.45	37.05	92.58	80.48	73.12
0.4	17.471	17.773	17.866	29.34	31.10	33.82	83.46	77.95	72.64
0.6	17.323	17.515	18.070	30.62	32.65	32.71	74.33	75.41	72.16
0.8	17.181	17.691	17.789	32.05	31.85	34.30	65.21	72.87	71.67
1.0	17.318	17.455	17.519	32.11	33.39	35.85	56.09	70.33	71.19
(1.208)									

[a] Saturated solution at 25° C.

The specific heats at each integral temperature and along each water ray were then fitted to cubic equations in per cent P_2O_5 at the compositions listed in Table I. The equations were solved for values of specific heats at even per cent P_2O_5 and irregular per cent CaO. At each even per cent P_2O_5 the specific heats were fitted to least-squares straight lines in per cent CaO, and the equations were solved at even intervals in per cent CaO. The resulting values of specific heat at 25°, 50°, and 80° C. at intervals of 2 in per cent P_2O_5 and at intervals of 0.5 in per cent CaO are listed in Table VI.

The solutions whose specific heats were measured covered the liquid-phase region at 25° C. (*2*). The same compositions were used at 50° and 80° C. and, in spite of the negative coefficient of solubility of $CaHPO_4$ (*5*), there was no difficulty in handling solutions supersaturated with respect to $CaHPO_4$ except for a few compositions at 80° C. nearest the 25° C. $CaHPO_4$ isotherm. The additional area of the liquid phase resulting from the higher solubility of $Ca(H_2PO_4)_2 \cdot H_2O$ at 50° and 80° C. was not covered because of the mechanical difficulty in preparing and handling at room temperature solutions supersaturated with respect to $Ca(H_2PO_4)_2 \cdot H_2O$.

PARTIAL MOLAL QUANTITIES

In the calculations of partial molal quantities, the data for each temperature were treated separately. Four sets of calculations were made, in each of which the solutions were considered to be composed of aqueous solutions of H_3PO_4 as the solvent and a calcium phosphate—$Ca(H_2PO_4)_2 \cdot H_2O$, $Ca(H_2PO_4)_2$, $CaHPO_4 \cdot 2H_2O$, or $CaHPO_4$—as the solute. In these calculations, subscript 1 refers to water (1000 grams), subscript 2 to H_3PO_4, and subscript 3 to the calcium salt.

System $Ca(H_2PO_4)_2 \cdot H_2O$–H_3PO_4–H_2O. Equations were derived to express the specific heat as a function of the total P_2O_5 content along each water ray, and each equation was solved for the compositions corresponding to intervals of 0.5 in the molality, m_2, of the solvent H_3PO_4. Thus, there was solved for the compositions corresponding to intervals of 0.5 in the molality, m_2, of the solvent H_3PO_4. There was thus obtained a table of specific heats at constant values of m_2 and odd values of m_3. These specific heats at each molality of H_3PO_4 were fitted to a cubic equation in m_3 and solved at intervals of 0.05 in m_3. Deviation curves were not used in these calculations, so that the calculations represent a smoothing process.

The total heat capacity at each composition was calculated from the relation

$$C = (1000 + m_2M_2 + m_3M_3)s \qquad (1)$$

where

- C = total heat capacity, cal.
- m_2 = molality of solvent H_3PO_4
- M_2 = gram formula weight of H_3PO_4
- m_3 = molality of solute, in this system $Ca(H_2PO_4)_2 \cdot H_2O$
- M_3 = gram formula weight of solute
- s = specific heat of solution, cal./deg./g.

Then at each value of m_2 the values of C were fitted to a least-squares cubic equation in m_3 which, since both m_1 and m_2 were fixed, was differentiated with respect to m_3 to obtain $\bar{C}_{p_3}$, the partial molal heat capacity of $Ca(H_2PO_4)_2 \cdot H_2O$ in H_3PO_4 solutions. The derivative equation then was solved at intervals of 0.05 in m_3.

A cubic equation in m_2 then was fitted to the values of C at each interval of 0.05 in m_3, and each equation for a constant value of m_3 was differentiated with respect to m_2. The derivative equation was solved at intervals of 0.5 in m_2 to yield $\bar{C}_{p_2}$, the partial molal heat capacity of the solvent H_3PO_4 in the solutions.

The over-all average deviation of the total heat capacities from the cubic equations was less than 0.1% with an occasional maximum deviation of 0.3%.

The partial molal heat capacities of water were calculated from the equation

$$\bar{C}_{p_1} = (C - m_2\bar{C}_{p_2} - m_3\bar{C}_{p_3})/m_1 \qquad (2)$$

where $m_1 = 55.5062$ moles of H_2O.

It would be desirable to convert the partial molal heat capacities to relative values, but the usually accepted method (*8*) of extrapolating plots of $\bar{C}_{p_i}$ *vs.* $m_i^{1/2}$ is not applicable to the present data because of the decided curvature of $\bar{C}_{p_i}$ at low molalities. The most straightforward method of determining $\bar{C}^\circ_{p_i}$ for other than near-ideal solutions appears to be that of Giauque (*7*), in which $\bar{C}_{p_i}$ is plotted as a function of A, moles of water per mole of substance, and extrapolated to infinite dilution. The $\bar{C}^\circ_{p_i}$ thus obtained is used only in the region in which the plot is a straight line, but with the present data the straight-line section is too short to be of use. Relative partial molal heats could be obtained for water, and reasonable values of $\bar{C}^\circ_{p_2}$ could be obtained from the present data and the previous data (*4*) on H_3PO_4, but any value of $\bar{C}^{\circ\prime}_{p_3}$ obtained from the present data would be a pure number with little physical significance in calcium phosphate solutions.

Systems M–H_3PO_4–H_2O. The data for three systems M–H_3PO_4–H_2O, in which M represents $Ca(H_2PO_4)_2$, $CaHPO_4$, and $CaHPO_4 \cdot 2H_2O$, respectively, were treated as for the system $Ca(H_2PO_4)_2 \cdot H_2O$–H_3PO_4–H_2O. The results are listed in Tables VII, VIII, IX, and X. All values of $\bar{C}_p$ were calculated at intervals of 0.05 in m_3 and of 0.5 in m_2, but to conserve space the tabulated intervals are 0.2 in m_3 and 1.0 m_2.

In making the calculations, really satisfactory determinations of partial molal quantities would require specific heats accurate to five decimal places, and to six places in the dilute range, but these are almost impossible to obtain. The equations were "forced" to five decimal places in specific heat for consistency in the calculations.

Plots of $\bar{C}_{p_2}$ against m_2 and of $\bar{C}_{p_3}$ against m_3 showed several significant trends in the data. The curves for $\bar{C}_{p_2}$ showed rather abrupt changes in slope that corresponded to similar changes observed in data for the system H_3PO_4–H_2O (*4*). This correspondence indicates that the addition of calcium to H_3PO_4 solutions has little effect on the types of the acid ion species. Almost all the values for $\bar{C}_{p_3}$ were minimum or maximum at m_3 about 0.6, but the significance of these changes in slope in the curves is not apparent.

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