Heats of Solution at 25° C. in the System $CaO-P_2O_5-H_2O$

EDWARD P. EGAN, JR., and BASIL B. LUFF
Division of Chemical Development, Tennessee Valley Authority, Muscle Shoals, Ala.

Measurements were made of the heats of solution at 25° C. of $Ca(H_2PO_4)_2 \cdot H_2O$ in phosphoric acid solutions to form solutions in the system $CaO-P_2O_5-H_2O$. The heats of solution of $Ca(H_2PO_4)_2$, $CaHPO_4 \cdot 2H_2O$, and $CaHPO_4$ were calculated from the results.

IN THE COLLECTION of thermal data on systems of interest in fertilizer technology, measurements were made of the heats of solution at 25° C. in the liquid-phase region of the system $CaO-P_2O_5-H_2O$ (*3*). The heats of solution of $Ca(H_2PO_4)_2 \cdot H_2O$ were measured directly, and those of $Ca(H_2PO_4)_2$, $CaHPO_4 \cdot 2H_2O$, and $CaHPO_4$ were calculated from the results. The heat capacities of the solutions have been reported (*5*).

Since the heats of solution of the commonly occurring solid phases (*9*) in the system are different, and since users of these data are likely to be interested in values for particular salts, the basic system $CaO-P_2O_5-H_2O$ has been expressed in this paper in four ways, as $Ca(H_2PO_4)_2 \cdot H_2O-H_3PO_4-H_2O$, $Ca(H_2PO_4)_2-H_3PO_4-H_2O$, $CaHPO_4-H_3PO_4-H_2O$, and $CaHPO_4 \cdot 2H_2O-H_3PO_4-H_2O$.

Throughout this paper subscript 3 refers to the assumed solute salt, 2 to H_3PO_4, and 1 to H_2O. In accordance with the usual convention, all exothermic heat effects are signed minus and endothermic effects plus.

The compositions of the solutions on the saturation isotherms at 25° C. in the system $CaO-P_2O_5-H_2O$ are listed in Table I. These data were calculated from cubic equations that were derived to represent the combined data of Elmore and Farr (*9*), Bassett (*1*), and Farr (*11*).

Table I. Compositions along Saturation Isotherms in System $CaO-P_2O_5-H_2O$ at 25° C.

Solid Phase, $CaHPO_4$		Solid Phase, $Ca(H_2PO_4)_2 \cdot H_2O$	
P_2O_5, %	CaO, %	P_2O_5, %	CaO, %
1.548	0.547	24.53	5.797[a]
3.219	1.064	25.81	5.508
4.903	1.551	27.19	5.196
6.585	2.009	28.49	4.900
8.254	2.438	29.72	4.617
9.898	2.840	30.89	4.348
11.51	3.216	32.00	4.092
13.08	3.567	33.06	3.849
14.61	3.895	34.06	3.618
16.09	4.202	35.02	3.399
17.52	4.489	36.81	2.995
18.90	4.757	38.44	2.635
20.22	5.008	39.94	2.316
21.48	5.243	41.31	2.038
22.69	5.465	42.58	1.798
23.84	5.673		
24.53	5.797[a]		

[a] Composition at $CaHPO_4-Ca(H_2PO_4)_2 \cdot H_2O$–solution invariant point.

MATERIALS AND APPARATUS

$Ca(H_2PO_4)_2 \cdot H_2O$. A solution of 1400 ml. of reagent (85%) H_3PO_4 in 1650 ml. of H_2O was saturated at 100° C. with reagent $Ca(H_2PO_4)_2 \cdot H_2O$, filtered hot, and cooled in a tap water bath. The crystals were filtered off, dissolved in fresh hot phosphoric acid solution, cooled to room temperature with continuous stirring, then filtered on fritted glass, washed free of acid with redistilled dry acetone, and dried overnight in a desiccator over anhydrous $CaSO_4$ (Drierite). The product contained 22.19% CaO (theory 22.25) and 56.19% P_2O_5 (theory 56.31); spectroscopic examination showed no significant impurities.

$CaHPO_4$. Desirably, heats of solution would be measured with $CaHPO_4$, which has a larger heat of solution than $Ca(H_2PO_4)_2 \cdot H_2O$. $CaHPO_4$, however, is difficult to prepare; the best preparations made in quantity usually contain about 0.2% $Ca_2P_2O_7$, 1% $Ca(H_2PO_4)_2 \cdot H_2O$, and 1% occluded mother liquor, even though the crystals appear to be satisfactory petrographically. Since $Ca(H_2PO_4)_2 \cdot H_2O$ can be obtained in a higher state of purity, this salt was used in the measurements in preference to using $CaHPO_4$ and correcting for its impurities.

A small amount of recrystallized $CaHPO_4$, however, was available, and this material was used in a few measurements as a check on the results calculated from measurements with $Ca(H_2PO_4)_2 \cdot H_2O$. The $CaHPO_4$ was obtained by preparing from reagent grade $CaHPO_4$ and recrystallized $2H_3PO_4 \cdot H_2O$ a solution on the $CaHPO_4$ isotherm near the invariant point of the system $CaO-P_2O_5-H_2O$ at 25° C. (*9*), and heating the solution to boiling to crystallize $CaHPO_4$ which has a negative temperature coefficient of solubility. This preparation was made before the recently reported method (*7*) was developed. The product contained 40.64% CaO and 51.93% P_2O_5 and lost 7.76% on ignition at 1000° C. (theory: CaO 41.21%, P_2O_5 52.17%, ignition loss 6.62%).

H_3PO_4. Reagent (85%) phosphoric acid was thrice recrystallized as the hemihydrate, $2H_3PO_4 \cdot H_2O$ (*4*). The final crystals were diluted to a concentration of exactly 10 molal H_3PO_4, as determined by its density (*2*), and portions of this stock solution were diluted by weight to concentrations of 0.5, 1.0, 1.5, 2.0, 3.0, 4.0, 6.0, and 8.0 molal.

Calorimeter. The solution calorimeter has been described (*4, 5*). Approximately 25-gram samples of $Ca(H_2PO_4)_2 \cdot H_2O$ were enclosed in thin-walled glass bulbs and suspended on 3-mm. glass rods through the hollow stirrer shaft. To start the solution period, the bulbs were crushed against the bottom of the Dewar flask. The energy of breaking the bulbs was detectable, but was much smaller than the reproducibility of the heat of solution measurements and was ignored. Samples as large as practicable were used to minimize the number of steps required to go from a given phosphoric acid solution to saturation with $Ca(H_2PO_4)_2 \cdot H_2O$.

To test the adequacy of stirring, particularly for solutions near saturation, a clear glass tube with the same dimensions was substituted for the calorimeter Dewar flask. A significant portion of the sample remained on the hemispherical bottom of the tube for as much as 20 minutes after breaking the sample bulb. To avoid the disadvantages of a high stirrer speed, the hemispherical bottom was altered to a flat bottom about 3/16 inch below the glass draft tube; with this modification the sample was kept in suspension.

Electrical calibrations of the calorimeter system were made immediately before and after each heat of solution measurement. The starting temperature was adjusted so that the solution process ended within less than 0.05° of 25° C., and no temperature corrections were made to the heats of solution. The unit of thermal energy was the defined calorie, 4.1840 absolute joules; the ice-point temperature was 273.15° K. All weights were corrected to vacuum. The density of $Ca(H_2PO_4)_2 \cdot H_2O(c)$ was taken as 2.22 grams per cc. and the densities of the solutions were taken from published values (*14*).

HEATS OF SOLUTION

System $Ca(H_2PO_4)_2 \cdot H_2O$–H_3PO_4–H_2O. To each concentration of phosphoric acid, successive 25-gram portions of $Ca(H_2PO_4)_2 \cdot H_2O$ were added to near saturation. The successive weights of salt dissolved, and the successive calories per step were added to obtain the total weight of salt dissolved and the total calories developed at the final concentration represented by each addition of $Ca(H_2PO_4)_2 \cdot H_2O$.

The adjustment of the final solution from one measurement to a weighed fixed volume of 850 ml. for the next measurement entailed loss of 1 to 2% of the solution. Linear corrections were made in the sample weights and the heat effects to put the initial and final solutions for each run on the same basis.

The observed heats of solution at the final concentration for each step are listed in Table II. The concentration range between the acid and the saturation isotherm was covered twice with each concentration of initial acid. At each acid concentration, the measured integral heats of solution per mole of $Ca(H_2PO_4)_2 \cdot H_2O$ went through a relatively sharp minimum at low m_3, which made analytical representation of the curves difficult. The plot of total grams of salt dissolved against m_3, however, was a line with little curvature that passed through the origin, and the plot of total calories against total grams dissolved was a smooth curve that passed through the origin. The integral heats of solution of $Ca(H_2PO_4)_2 \cdot H_2O$ in calories per mole were calculated from combination of two equations:

$$\text{Total calories} = \sum_{i=0}^{i=4} A_i x^i \qquad (1)$$

$$\text{Total grams salt} = \sum_{i=0}^{i=3} B_i m_3^i \equiv C \qquad (2)$$

$$\Delta H_{\text{soln.}} = 252.078 \left[\frac{A_0}{C} + \frac{A_1}{100} + \frac{A_2 C}{100^2} + \frac{A_3 C^2}{100^3} + \frac{A_4 C^3}{100^4} \right] \qquad (3)$$

where

A_i and B_i are polynomial coefficients
C = solution of Equation 2
x = (total grams salt dissolved)/100
252.078 = gram formula weight of $Ca(H_2PO_4)_2 \cdot H_2O$

In the use of these equations, Equations 1 and 2 were fitted to the data for each concentration of acid at which measurements were made, and the equations were solved at intervals of 0.05 in m_3. Then at each of these intervals in m_3, the data were fitted to polynomials for the values of m_2 at which the measurements were made, and these equations were solved at intervals of 0.5 in m_2. There was thus obtained a table of total grams of salt dissolved and total calories developed at each interval of 0.05 in m_3 and 0.5 in m_2. The over-all deviation of total grams of salt dissolved was 0.30% and that of total calories developed was 0.60%.

The entire calculation then was repeated on the basis of the calculated values, which resulted in a smoothing operation. The over-all deviation of the total grams of salt dissolved was then 0.38%, and that of the total calories developed was 0.16%. The coefficients for Equations 1 and 2 that resulted from the second set of calculations then were substituted in Equation 3 to calculate the integral heats of solution. The results are listed in Table III; to conserve space, the tabulated intervals in m_3 are 0.1 and those in m_2 are 0.5.

The intercepts of the heats of solutions on the H_3PO_4 axis at each concentration are listed in Table IV. These intercepts are heats of solution at infinite dilution in each concentration of acid, and subtraction of these values from corresponding values in Table III yields ϕ_L, or $-\Delta H_{\text{diln.}}$, for $Ca(H_2PO_4)_2 \cdot H_2O$, at each acid concentration. The values of the intercepts in Table IV were obtained by straight-line extrapolation of plots of $\Delta H_{\text{soln.}}$ against $m_3^{1/2}$ from values of m_3 of 0.10 and 0.15. Because of the curvature of the plots of the heats of solution, only two points could be used for the extrapolations, and those chosen gave more consistent results than from values of m_3 of 0.05 and 0.10.

The intercepts obtained similarly for $Ca(H_2PO_4)_2$, $CaHPO_4 \cdot 2H_2O$, and $CaHPO_4$ also are listed in Table IV.

System $CaHPO_4$–H_3PO_4–H_2O. The heats of solution of $CaHPO_4$(c) were calculated from the observed heats of solution of $Ca(H_2PO_4)_2 \cdot H_2O$ by the scheme

Inf. diln.			soln.
	ΔH_1 (H_3PO_4) →	ΔH_2 [$Ca(H_2PO_4)_2 \cdot H_2O$] (c) →	
	ΔH_3 (H_3PO_4) →	ΔH_4($CaHPO_4$) (c) →	
		($m_2 + \Delta m_2$) (H_3PO_4)	

$$\Delta H_4 = \Delta H_1 + \Delta H_2 - \Delta H_3 \qquad (4)$$

so that the final solution phase was identical for both thermal paths. ΔH_1 and ΔH_3 were calculated from published data on the heat of dilution of H_3PO_4 (*4*); ΔH_2 represents the present measurements on $Ca(H_2PO_4)_2 \cdot H_2O$. To ΔH_4 was added the heat of reaction of

$$CaHPO_4(c) + H_3PO_4(c) + H_2O(l) = Ca(H_2PO_4)_2 \cdot H_2O \qquad (5)$$

$$\Delta H = -7603$$

and the heat of fusion of H_3PO_4(c) (*3*). The heats of formation, calories per mole, used in the derivation of the heat of reaction of Equation 5 were $CaHPO_4$(c) −434,700 (*15*), H_3PO_4(c) −306,200 (*12*), H_2O(l) −68,317 (*12*), and $Ca(H_2PO_4)_2 \cdot H_2O$(c) −816,820 (*8*). The excess H_3PO_4 and H_2O required were assumed to form $(m_2 + \Delta m_2)H_3PO_4$ and were corrected for from the data on the heat of dilution of H_3PO_4 (*4*).

A few of the calculated heats of solution of $CaHPO_4$ were checked by direct measurement with the recrystallized salt. In each measurement, the amount of salt and the initial concentration of acid were selected to give a solution with a composition on a tie line between $Ca(H_2PO_4)_2 \cdot H_2O$ and a selected composition of H_3PO_4, so that the solution process was represented by the diagram shown above. The measured and calculated values for the heat of solution of $CaHPO_4$ are shown in Table V.

The values for the heat of solution of $CaHPO_4$ that were calculated from the measured heats of solution of

Table II. Observed Heats of Solution of $Ca(H_2PO_4)_2 \cdot H_2O$ in H_3PO_4 Solutions

			Solution Composition, %					
			Initial		Final			
Step	Initial Wt. Soln., G.	Weight of Sample, G.	P_2O_5	CaO	P_2O_5	CaO	Corr. Δt, ° C.	Cal./Run
			0.5 molal H_3PO_4					
1	867.92	26.8332	3.38	0	4.97	0.67	0.0918	−84.66
2	886.78	25.1050	4.97	0.67	6.38	1.26	0.0878	−80.17
3	903.59	26.7135	6.38	1.26	7.82	1.86	0.0728	−66.46
4	922.56	27.2128	7.82	1.86	9.21	2.45	0.0464	−42.09
5	940.10	21.9713	9.21	2.45	10.28	2.90	0.0324	−29.49
1	867.65	12.9329	3.38	0	4.16	0.33	0.0417	−38.49
2	872.53	25.7364	4.16	0.33	5.65	0.96	0.0952	−87.25
3	889.61	26.3581	5.65	0.96	7.11	1.57	0.0830	−75.06
4	907.56	29.8739	7.11	1.57	8.68	2.23	0.0661	−59.26
5	928.09	25.2651	8.68	2.23	9.94	2.76	0.0316	−28.00
			1.0 molal H_3PO_4					
1	888.20	31.3120	6.46	0	8.16	0.76	0.0476	−41.17
2	910.42	22.8591	8.16	0.76	9.34	1.28	0.0396	−35.63
3	920.14	22.1413	9.34	1.28	10.44	1.78	0.0273	−24.58
4	933.34	22.8898	10.44	1.78	11.54	2.27	0.0145	−12.70
5	936.64	24.4701	11.54	2.27	12.68	2.78	−0.0017	1.53
6	951.33	26.2342	12.68	2.78	13.85	3.30	−0.0250	21.96
7	967.27	21.1783	13.85	3.30	14.76	3.70	−0.0375	32.37
8	977.92	20.7647	14.76	3.70	15.63	4.09	−0.0504	43.64
1	888.11	23.8511	6.46	0	7.77	0.58	0.0339	−30.57
2	903.72	24.1271	7.77	0.58	9.03	1.15	0.0436	−37.82
3	918.49	26.7724	9.03	1.15	10.37	1.74	0.0369	−33.58
4	936.03	29.0360	10.37	1.74	11.75	2.36	0.0171	−15.15
5	955.20	26.2697	11.75	2.36	12.94	2.89	−0.0072	6.48
6	971.15	26.5732	12.94	2.89	14.10	3.41	−0.0302	27.17
7	987.80	24.3008	14.10	3.41	15.11	3.86	−0.0464	41.53
			1.5 molal H_3PO_4					
1	907.43	22.4204	9.28	0	10.42	0.54	−0.0045	3.28
2	921.24	22.1414	10.42	0.54	11.49	1.05	0.0017	−1.49
3	925.03	24.7868	11.49	1.05	12.66	1.60	−0.0034	2.86
4	936.95	26.9899	12.66	1.60	13.88	2.18	−0.0190	16.89
5	953.92	27.6681	13.88	2.18	15.08	2.74	−0.0395	33.12
6	970.41	23.6192	15.08	2.74	16.06	3.21	−0.0523	45.40
7	965.92	21.1173	16.06	3.21	16.92	3.61	−0.0621	53.58
8	977.64	30.2964	16.92	3.61	18.11	4.17	−0.1170	100.43
9	997.12	22.3942	18.11	4.17	18.94	4.57	−0.1064	91.88
1	907.62	31.4434	9.28	0	10.86	0.74	−0.0032	2.96
2	926.04	25.7907	10.86	0.74	12.09	1.33	0.0022	−1.96
3	942.05	26.2267	12.09	1.33	13.29	1.90	−0.0071	6.20
4	958.64	28.1321	13.29	1.90	14.51	2.48	−0.0259	22.09
5	976.03	24.0330	14.51	2.48	15.52	2.95	−0.0428	37.99
6	989.73	25.4104	15.52	2.95	16.54	3.43	−0.0641	57.74
7	1003.77	26.1585	16.54	3.43	17.55	3.91	−0.0881	78.96
8	1018.90	25.5758	17.55	3.91	18.50	4.36	−0.1053	93.04
9	1034.40	28.2233	18.50	4.36	19.50	4.84	−0.1412	124.71
			2.0 molal H_3PO_4					
1	926.45	25.7667	11.87	0	13.07	0.60	−0.0412	35.27
2	943.60	28.8609	13.07	0.60	14.36	1.24	−0.0412	35.93
3	962.72	20.9143	14.36	1.24	15.25	1.69	−0.0346	30.14
4	973.78	23.6587	15.25	1.69	16.22	2.18	−0.0489	44.13
5	987.72	24.3331	16.22	2.18	17.18	2.66	−0.0631	55.44
6	1001.29	26.1772	17.18	2.66	18.18	3.16	−0.0880	77.66
7	1014.79	23.9933	18.18	3.16	19.06	3.60	−0.0988	86.29
8	1016.34	22.0344	19.06	3.60	19.85	4.00	−0.1054	91.61
9	1027.63	24.4292	19.85	4.00	20.70	4.42	−0.1384	119.72
10	1063.19	24.3266	20.70	4.42	21.50	4.82	−0.1468	129.19
11	1059.04	26.5370	21.50	4.82	22.35	5.25	−0.2103	183.58
1	935.84	22.0798	11.87	0	12.89	0.51	−0.0360	33.96
2	950.21	22.5883	12.89	0.51	13.90	1.02	−0.0324	28.77
3	964.59	21.1383	13.90	1.02	14.81	1.47	−0.0289	25.32
4	976.26	27.2715	14.81	1.47	15.94	2.04	−0.0519	45.65
5	993.33	22.2453	15.94	2.04	16.82	2.48	−0.0540	47.76
6	1004.76	26.1451	16.82	2.48	17.82	2.98	−0.0787	71.25
7	1020.28	24.9317	17.82	2.98	18.74	3.44	−0.0923	81.80
8	1033.64	23.9991	18.74	3.44	19.59	3.87	−0.1096	96.69
9	1034.70	22.6460	19.59	3.87	20.38	4.26	−0.1218	129.07
10	1045.47	24.8287	20.38	4.26	21.21	4.68	−0.1480	129.97
11	1057.80	21.4093	21.21	4.68	21.91	5.03	−0.1360	117.69
12	1066.31	20.3844	21.91	5.03	22.56	5.35	−0.1513	131.20
			3.0 molal H_3PO_4					
1	960.37	28.2117	16.46	0	17.59	0.64	−0.1178	102.87
2	980.63	22.4665	17.59	0.64	18.46	1.12	−0.0937	84.43
3	994.22	25.5265	18.46	1.12	19.41	1.65	−0.1116	96.61
4	1007.14	24.8722	19.41	1.65	20.30	2.14	−0.1197	104.13
5	1023.90	28.8412	20.30	2.14	21.28	2.70	−0.1539	134.01
6	1043.59	25.2839	21.28	2.70	22.11	3.16	−0.1483	127.80

(*Continued on page 523*)

Table II. Observed Heats of Solution of $Ca(H_2PO_4)_2 \cdot H_2O$ in H_3PO_4 Solutions (*Continued*)

Step	Initial Wt. Soln., G.	Weight of Sample, G.	Solution Composition, % Initial P_2O_5	Initial CaO	Final P_2O_5	Final CaO	Corr. Δt, ° C.	Cal./Run
			3.0 molal H_3PO_4 (*Cont.*)					
7	1058.35	25.8199	22.11	3.16	22.93	3.61	−0.1734	151.33
8	1072.57	27.2487	22.93	3.61	23.75	4.08	−0.2025	176.90
9	1087.58	23.9189	23.75	4.08	24.45	4.47	−0.1959	170.42
10	1100.74	23.2641	24.45	4.47	25.11	4.83	−0.2089	182.17
1	960.00	28.1631	16.46	0	17.59	0.63	−0.1193	104.11
2	979.15	24.2219	17.59	0.63	18.53	1.16	−0.1019	85.60
3	994.02	26.2229	18.53	1.16	19.50	1.70	−0.1154	100.55
4	1010.49	24.4839	19.50	1.70	20.37	2.18	−0.1172	102.43
5	1019.16	23.0756	20.37	2.18	21.16	2.63	−0.1231	105.93
6	1032.59	22.8010	21.16	2.63	21.92	3.05	−0.1361	115.48
7	1045.17	25.8436	21.92	3.05	22.75	3.52	−0.1712	147.63
8	1058.87	25.8568	22.75	3.52	23.55	3.96	−0.1884	161.65
9	1072.40	21.6428	23.55	3.96	24.20	4.32	−0.1803	155.87
10	1066.41	25.5215	24.20	4.32	24.95	4.74	−0.2258	191.80
11	1078.59	30.0498	24.95	4.74	25.80	5.22	−0.2824	254.16
			4.0 molal H_3PO_4					
1	991.58	22.6098	20.40	0	21.20	0.50	−0.1503	128.05
2	1004.61	23.8265	21.20	0.50	22.01	1.00	−0.1606	137.29
3	1019.29	21.1703	22.01	1.00	22.71	1.43	−0.1470	125.44
4	1030.18	20.4560	22.71	1.43	23.36	1.84	−0.1439	122.22
5	1040.35	23.7285	23.36	1.84	24.10	2.29	−0.1800	153.75
6	1050.72	21.5588	24.10	2.29	24.75	2.69	−0.1739	147.81
7	1062.19	23.7545	24.75	2.69	25.44	3.12	−0.2043	172.88
8	1074.51	19.6479	25.44	3.12	25.99	3.46	−0.1804	153.31
9	1082.07	22.0971	25.99	3.46	26.60	3.84	−0.2133	180.76
10	1090.40	22.6791	26.60	3.84	27.20	4.22	−0.2358	199.18
11	1099.67	25.7910	27.20	4.22	27.87	4.63	−0.2840	238.94
1	993.86	20.8582	20.40	0	21.13	0.46	−0.1385	119.92
2	1002.26	22.7028	21.13	0.46	21.91	0.94	−0.1534	131.85
3	1015.53	27.5373	21.91	0.94	22.82	1.50	−0.1883	161.72
4	1031.69	23.0718	22.82	1.50	23.55	1.96	−0.1678	143.83
5	1043.38	22.6664	23.55	1.96	24.25	2.39	−0.1751	149.45
6	1054.04	24.9738	24.25	2.39	24.99	2.85	−0.2050	175.48
7	1068.17	24.6606	24.99	2.85	25.70	3.29	−0.2183	186.66
8	1083.06	24.8830	25.70	3.29	26.39	3.71	−0.2353	200.40
9	1097.54	27.3239	26.39	3.71	27.11	4.16	−0.2788	238.26
10	1114.06	24.5785	27.11	4.16	27.74	4.55	−0.2632	224.81
11	1124.70	15.1077	27.74	4.55	28.12	4.79	−0.1387	117.29
			6.0 molal H_3PO_4					
1	1044.68	16.1314	26.82	0	27.27	0.34	−0.3789	154.54
2	1057.14	13.9564	27.27	0.34	27.65	0.62	−0.3068	129.09
3	1067.40	16.9297	27.65	0.62	28.10	0.96	−0.3428	144.92
4	1075.53	18.8858	28.10	0.96	28.59	1.33	−0.4394	186.78
5	1084.65	19.6815	28.59	1.33	29.08	1.70	−0.4689	177.72
6	1086.69	17.2829	29.08	1.70	29.51	2.02	−0.4223	176.96
7	1093.22	19.8719	29.51	2.02	29.99	2.39	−0.4979	208.53
8	1101.06	15.9378	29.99	2.39	30.36	2.67	−0.4120	172.47
9	1098.66	17.5788	30.36	2.67	30.77	2.98	−0.2451	200.01
10	1104.44	18.1369	30.77	2.98	31.19	3.29	−0.2241	183.36
11	1111.08	15.9667	31.19	3.29	31.54	3.56	−0.2299	186.48
12	1115.17	15.1498	31.54	3.56	31.87	3.81	−0.2061	165.33
1	1047.66	16.2292	26.82	0	27.27	0.34	−0.1852	151.53
2	1049.61	17.4866	27.27	0.34	27.74	0.70	−0.2016	165.50
3	1057.34	19.2014	27.74	0.70	28.25	1.08	−0.2252	187.86
4	1065.76	14.7294	28.25	1.08	28.64	1.37	−0.1734	142.36
5	1070.10	20.0281	28.64	1.37	29.14	1.76	−0.2439	201.80
6	1079.69	18.3615	29.14	1.76	29.60	2.10	−0.2234	180.67
7	1061.67	18.5997	29.60	2.10	30.06	2.44	−0.2414	193.08
8	1068.44	18.7069	30.06	2.44	30.51	2.79	−0.2436	195.16
9	1074.71	16.9989	30.51	2.79	30.91	3.09	−0.2363	188.91
10	1064.52	19.6843	30.91	3.09	31.37	3.44	−0.2875	234.01
11	1070.89	20.6182	31.37	3.44	31.84	3.79	−0.3069	244.32
10	1115.86	18.6922	30.91	3.09	31.33	3.40	−0.2625	215.28
11	1121.67	18.4533	31.33	3.40	31.73	3.71	−0.2492	203.86
			8.0 molal H_3PO_4					
1	1090.17	21.1232	31.83	0	32.29	0.42	−0.3255	266.47
2	1099.98	20.8524	32.29	0.42	32.74	0.83	−0.3289	268.17
3	1107.22	19.3989	32.74	0.83	33.14	1.20	−0.3054	247.40
4	1114.42	23.5781	33.14	1.20	33.62	1.63	−0.3805	308.52
5	1124.28	19.6115	33.62	1.63	34.01	1.99	−0.3216	260.44
6	1130.20	22.9790	34.01	1.99	34.46	2.39	−0.3891	314.93
7	1139.87	21.3074	34.46	2.39	34.86	2.76	−0.3627	292.53
8	1147.54	22.9343	34.86	2.76	35.28	3.14	−0.3941	316.22
1	1090.06	23.7207	31.83	0	32.35	0.47	−0.3634	295.98
2	1102.44	19.5104	32.35	0.47	32.76	0.85	−0.3043	247.56
3	1107.47	20.9115	32.76	0.85	33.20	1.25	−0.3328	270.36
4	1114.68	23.9600	33.20	1.25	33.69	1.69	−0.3889	315.34

(*Continued on page 524*)

Table II. Observed Heats of Solution of $Ca(H_2PO_4)_2 \cdot H_2O$ in H_3PO_4 Solutions (*Continued*)

Step	Initial Wt. Soln., G.	Weight of Sample, G.	Solution Composition, %, Initial P_2O_5	Initial CaO	Final P_2O_5	Final CaO	Corr. Δt, °C.	Cal./Run
			8.0 molal H_3PO_4 (*Cont.*)					
5	1123.91	21.5088	33.69	1.69	34.11	2.08	−0.3558	287.74
6	1130.36	22.0171	34.11	2.08	34.54	2.46	−0.3726	300.00
7	1137.50	21.4536	34.54	2.46	34.94	2.83	−0.3681	295.46
8	1132.63	17.8089	34.94	2.83	35.27	3.13	−0.3074	243.04
			10.0 molal H_3PO_4					
1	1127.82	20.5759	35.85	0	36.21	0.40	−0.3899	311.06
2	1135.86	18.9049	36.21	0.40	36.54	0.76	−0.3610	287.13
3	1140.32	20.4047	36.54	0.76	36.89	1.14	−0.3942	313.25
4	1147.35	20.2992	36.89	1.14	37.23	1.50	−0.4027	319.39
5	1153.70	22.1679	37.23	1.50	37.59	1.89	−0.4452	352.41
6	1160.64	19.6957	37.59	1.89	37.90	2.23	−0.3961	311.54
1	1129.29	27.3541	35.85	0	36.33	0.53	−0.5195	415.78
2	1144.03	22.9222	36.33	0.53	36.72	0.95	−0.4362	350.32
3	1153.68	20.7203	36.72	0.95	37.07	1.33	−0.3991	319.81
4	1160.66	23.0454	37.07	1.33	37.44	1.74	−0.4522	361.26
5	1169.84	23.2849	37.44	1.74	37.81	2.14	−0.4586	366.75
6	1179.33	19.4301	37.81	2.14	38.11	2.46	−0.3812	303.17

$Ca(H_2PO_4)_2 \cdot H_2O$ were treated in the same manner as those for $Ca(H_2PO_4)_2 \cdot H_2O$ to obtain calculated molar heats of solution at even intervals in m_2 and m_3. The results are shown in Table VI (deposited with ADI), and the heats of solution at infinite dilution in different concentrations of acid are shown in Table IV.

System $CaHPO_4 \cdot 2H_2O$–H_3PO_4–H_2O. The heats of solution for $CaHPO_4 \cdot 2H_2O(c)$ were calculated from the observed heats of solution of $Ca(H_2PO_4)_2 \cdot H_2O$ in the same manner as for $CaHPO_4$ except that the additional correction (*11*)

$$CaHPO_4(c) + 2H_2O(l) = CaHPO_4 \cdot 2H_2O(c) \qquad \Delta H = 4380$$

was added.

The calculated heats of solution are listed in Table VII (deposited with ADI) and the corresponding intercepts in Table IV.

System $Ca(H_2PO_4)_2$–H_3PO_4–H_2O. The heats of solution of $Ca(H_2PO_4)_2(c)$ were calculated from the heats of solution of $Ca(H_2PO_4)_2 \cdot H_2O$ in the same manner as for $CaHPO_4$ except that the correction was based on the reaction (*8*)

$$Ca(H_2PO_4)_2(c) + H_2O(l) = Ca(H_2PO_4)_2 \cdot H_2O(c) \qquad \Delta H = -2463$$

plus the required correction for heat of dilution of the acid (*4*).

The calculated heats of solution are listed in Table VIII (deposited with ADI) and the corresponding intercepts in Table IV.

PARTIAL MOLAL ENTHALPIES

Partial molal enthalpies were calculated for the four systems M–H_3PO_4–H_2O in which M represents the calcium phosphate. The partial molal enthalpies were calculated from relative total enthalpies, L, in which

$$L = m_2\phi_{L(\text{acid})} + m_3\phi_{L(\text{salt})}$$

The relative total enthalpy, L, represents the total heat involved in going from infinite dilution to the solution composition.

The values for $\phi_{L(\text{acid})}$ were taken from the heat of dilution data for H_3PO_4 (*4*). The values for $\phi_{L(\text{salt})}$ were taken from the heats of solution listed in Tables V to VIII and the corresponding heat of solution intercepts listed in Table IV. Partial differentiation of the relative total enthalpies yielded the partial molal enthalpies for the salt and the acid

$$\left(\frac{\partial L}{\partial m_3}\right)_{m_2, m_1, T, P} = \bar{L}_3(\text{salt})$$

$$\left(\frac{\partial L}{\partial m_2}\right)_{m_3, m_1, T, P} = \bar{L}_2(\text{acid})$$

The partial molal enthalpy of water in each system was calculated by difference

$$\bar{L}_1 = (L - m_2\bar{L}_2 - m_3\bar{L}_3)/m_1$$

The curves of the relative total enthalpies could not be represented conveniently by analytical expressions, and the differentiations were made by tabular differentiation through use of 5-point first derivative coefficients (*13*). At each interval of 0.5 in m_2, $\bar{L}_3$ for the salt was calculated at intervals of 0.05 in m_3. Then at each interval of 0.05 in m_3, L was differentiated with respect to m_2 to obtain $\bar{L}_2$, the partial molal enthalpy of H_3PO_4, at intervals of 0.5 in m_2. As shown above $\bar{L}_1$ was obtained by difference. The results are shown in Tables IX to XII.

DISCUSSION

The calculated heats of solution of the four calcium phosphates in phosphoric acid solutions represent the actual heats of solution reasonably well. The calculated heats of solution of $CaHPO_4$ in 1.5 molal H_3PO_4 are not entirely consistent with those calculated for the other acid strengths in the system $CaHPO_4$–H_3PO_4—H_2O. This inconsistency is particularly noticeable in the calculation of $\bar{L}_3$, the partial molal enthalpy of $CaHPO_4$ in the same solution. The reason for this inconsistency is not apparent.

The intercepts of the heats of solution on the H_3PO_4 axis at $m_3 = 0$ for all four salt systems were calculated by

Table III. Integral Heat of Solution of $Ca(H_2PO_4)_2 \cdot H_2O$ in H_3PO_4 Solutions at 25° C., Calories per Mole

H_3PO_4 Molality, m_2	$Ca(H_2PO_4)_2 \cdot H_2O$ Molality, m_3															
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6
0.5	-762.1	-793.7	-774.5	-723.5	-660.5	-603.3										
1.0	-351.5	-372.1	-362.2	-335.3	-296.0	-247.2	-191.4	-130.6	-66.69							
1.5	29.10	3.29	3.97	21.05	50.53	89.62	136.0	187.8	243.2	300.8	359.0	416.8				
2.0	368.1	334.3	334.9	350.0	374.8	407.0	445.2	488.3	535.4	585.7	638.3	692.7	748.3	804.5	860.9	917.0
2.5	676.5	638.3	639.0	653.2	675.3	703.4	736.5	773.8	814.8	859.0	906.0	955.4	1007	1060	1114	1168
3.0	956.4	926.2	925.8	936.8	955.4	980.0	1010	1043	1081	1122	1166	1212	1260	1310	1360	1410
3.5	1214	1201	1198	1204	1219	1240	1268	1300	1337	1377	1419	1463	1507	1552	1596	1640
4.0	1453	1464	1458	1458	1468	1487	1514	1546	1583	1623	1664	1706	1746	1784	1819	1849
4.5	1681	1713	1704	1701	1708	1726	1752	1785	1822	1861	1901	1940	1975	2006	2029	
5.0	1902	1945	1937	1934	1942	1960	1986	2018	2054	2091	2129	2163	2193	2216	2228	
5.5	2128	2145	2150	2160	2175	2196	2221	2250	2280	2312	2343	2373	2401	2427		
6.0	2346	2354	2365	2380	2399	2422	2447	2474	2501	2528	2554	2578	2601			
6.5	2563	2570	2579	2594	2614	2639	2665	2692	2717	2740	2760	2776	2787			
7.0	2779	2785	2789	2802	2822	2848	2876	2904	2928	2948	2961	2966				
7.5	2990	2993	2994	3005	3025	3050	3079	3106	3130	3147	3156	3155				
8.0	3192	3190	3190	3201	3220	3244	3271	3297	3319	3337	3346	3346				
8.5	3380	3374	3377	3389	3406	3427	3450	3473	3494	3512						
9.0	3555	3547	3549	3559	3575	3595	3616	3635	3653	3666						
9.5	3706	3698	3701	3711	3727	3744	3762	3778	3789	3795						
10.0	3823	3818	3825	3838	3854	3871	3885	3895	3899	3894						

Table IV. Integral Heats of Solution, Intercepts on H_3PO_4 Axis, Calories per Mole

H_3PO_4 Molality, m_2	$Ca(H_2PO_4)_2 \cdot H_2O$	$Ca(H_2PO_4)_2$	$CaHPO_4$	$CaHPO_4 \cdot 2H_2O$
0.5	-659.6	-3131	-5514	-1169
1.0	-280.0	-2768	-5320	-909.3
1.5	107.5	-2435	-5469	-658.3
2.0	476.6	-2138	-4981	-410.8
2.5	801.5	-1835	-4880	-267.7
3.0	1053	-1525	-4742	-159.0
3.5	1249	-1238	-4581	-68.97
4.0	1401	-981.0	-4403	14.46
4.5	1549	-754.4	-4227	96.36
5.0	1732	-544.6	-4042	181.3
5.5	2070	-433.7	-3879	281.1
6.0	2326	-286.8	-3814	389.6
6.5	2545	-84.32	-3865	501.9
7.0	2756	128.3	-3803	615.3
7.5	2969	307.8	-3694	726.6
8.0	3190	471.7	-3576	837.1
8.5	3398	665.3	-3429	949.4
9.0	3580	832.4	-3346	1037
9.5	3733	1070	-3290	1095
10.0	3841	1290	-3271	1110

Table V. Heats of Solution of $CaHPO_4$(c)

Molality H_3PO_4, m_2	ΔH Soln., Cal./G. Obsd.	Calcd.
3	35.00	34.75
	34.95	35.12
	35.27	34.85
4	33.14	33.37
	33.05	33.15
6	29.17	30.05
	28.94	30.10
	29.19	30.06
8	26.03	26.18

straight-line equations for ΔH *vs.* $m_3^{1/2}$. Plots of all the heats of solution have significant curvature at low values of m_3. Additional measurements at values of m_3 below 0.1 would be required to define adequately the shape of the curves as m_3 approaches 0. A somewhat different type of solution calorimeter would be required in this concentration range.

The relative partial molal enthalpies, $\bar{L}_3$, are somewhat less curved for the monocalcium phosphates than for the dicalcium phosphates. The values of $\bar{L}_3$ for $CaHPO_4$ and $CaHPO_4 \cdot 2H_2O$ go through minima at m_3 of about 0.5 when m_2 is between 2.0 and 5.0.

The plots of $\bar{L}_2$ *vs.* m_2 for all four salts show distinct changes in shape of curve or in slope. These changes occur at m_2 of about 2.5, 4.0 to 6.0, and 8.0 to 10.0. The same changes were observed in the system H_3PO_4–H_2O alone (*6*) and are more pronounced in heat capacity data on this system (*5*). Similar changes in slope have been observed also in the density, conductivity, pH, and activity of phosphoric acid solutions. The introduction of calcium ion with a common phosphate ion into phosphoric acid solutions thus has little effect on the properties of the phosphoric acid. The changes in slope probably are related to changes in the ion species in phosphoric acid solutions or to marked changes in the concentration or activity of particular ion species (*10*). The structure of phosphoric acid solutions is complex and is not well enough defined for correlation of the observed changes with the acid structure.

Table IX. Relative[a] Partial Molal Enthalpies in the System $Ca(H_2PO_4)_2 \cdot H_2O$–H_3PO_4–H_2O at 25° C., Calories per Mole

H_3PO_4 Molality, m_2	$Ca(H_2PO_4)_2 \cdot H_2O$ Molality, m_3															
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6
							$L_3(Ca(H_2PO_4)_2 \cdot H_2O)$									
0.5	−163	−141	0	176	314	349										
1.0	−123	−95	−24	79	206	349	499	651	798							
1.5	−128	−124	−74	9	117	241	374	511	646	774	892	995				
2.0	−185	−162	−114	−45	42	143	254	374	498	625	752	877	1000	1117	1228	1333
2.5	−215	−184	−136	−74	1	86	182	286	398	515	636	759	883	1006	1126	1242
3.0	−164	−146	−108	−55	11	90	170	278	384	495	609	725	841	955	1064	1168
3.5	−53	−64	−54	−3	60	139	230	329	433	539	644	744	839	926	1004	1071
4.0	107	51	45	78	141	225	321	425	530	630	721	798	858	896	910	895
4.5	255	154	132	160	224	311	411	516	619	712	788	840	859	835	755	
5.0	330	208	183	212	277	363	460	560	655	737	798	827	811	731	563	
5.5	107	86	100	140	198	267	341	417	490	556	612	656	686	698		
6.0	32	45	77	124	180	241	303	363	418	467	506	535	554			
6.5	32	37	70	122	184	248	308	358	393	412	411	390	350			
7.0	47	30	58	115	185	256	317	358	374	358	309	226				
7.5	48	17	51	99	173	247	308	345	349	313	232	102				
8.0	14	−8	18	73	141	209	267	304	313	285	212	85				
8.5	−26	−27	2	50	107	165	216	254	274	273						
9.0	−39	−39	−12	34	86	137	179	206	212	194						
9.5	−43	−39	−10	32	79	120	148	156	138	90						
10.0	−32	−18	15	57	97	125	133	112	56	−43						
								$L_2(H_3PO_4)$								
0.5	405	426	440	428	400	395										
1.0	556	559	554	541	523	504	476	453	428							
1.5	680	672	663	652	638	618	596	568	538	543	519	502				
2.0	790	782	775	767	757	743	724	702	677	638	608	580	503	470	441	417
2.5	917	919	919	919	917	913	906	897	887	874	860	844	844	830	815	799
3.0	1058	1073	1084	1092	1099	1105	1110	1115	1120	1124	1126	1126	1125	1119	1110	
3.5	1193	1217	1235	1249	1263	1277	1292	1307	1323	1338	1352	1363	1368	1367	1358	
4.0	1319	1346	1367	1385	1402	1420	1439	1459	1479	1499	1516	1530	1538	1535	1519	
4.5	1436	1458	1475	1490	1506	1522	1538	1555	1571	1586	1599	1607	1608	1598	1554	
5.0	1529	1516	1510	1506	1502	1497	1490	1479	1465	1448	1429	1409	1389			
5.5	1634	1607	1591	1579	1568	1554	1537	1515	1490	1460	1428	1396	1366			
6.0	1758	1754	1751	1750	1749	1749	1748	1744	1738	1728	1712	1690				
6.5	1868	1869	1868	1866	1867	1868	1871	1873	1871	1865	1850	1824				
7.0	1970	1970	1967	1965	1963	1963	1964	1964	1962	1955	1940	1916				
7.5	2066	2062	2058	2054	2049	2045	2040	2034	2029	2022	2012	2002				
8.0	2160	2153	2149	2145	2139	2131	2121	2111	2102	2097	2090	2089				
8.5	2254	2249	2246	2243	2238	2231	2223	2214	2204	2194						
9.0	2345	2343	2342	2340	2338	2334	2328	2320	2308	2292						
9.5	2433	2434	2436	2438	2439	2439	2435	2428	2415	2396						
10.0	2519	2526	2533	2542	2550	2556	2559	2555	2543	2519						

								$-L_1(H_2O)$								
0.5	1.19	1.46	2.23	3.23	4.09	4.36										
1.0	3.27	3.40	3.63	4.06	4.76	5.84	7.09	8.73	10.52							
1.5	6.03	5.84	5.82	6.05	6.54	7.24	8.23	9.32	10.55	12.90	14.46	16.14				
2.0	9.41	9.15	9.13	9.30	9.63	10.12	10.77	11.58	12.58	13.33	14.68	16.24	16.22	17.91	19.77	21.81
2.5	14.53	14.68	14.94	15.32	15.83	16.48	17.31	18.33	19.55	20.99	22.64	24.50	27.29	29.63	32.09	34.63
3.0	21.60	22.44	23.20	23.98	24.89	26.00	27.34	28.95	30.82	32.92	35.22	37.66	40.16	42.63	45.01	47.18
3.5	29.66	31.16	32.38	33.59	34.96	36.62	38.61	40.93	43.53	46.31	49.14	51.89	54.38	56.43	57.86	61.70
4.0	38.48	40.31	41.78	43.28	45.03	47.15	49.65	52.48	55.55	58.68	61.67	64.26	66.14	66.91	66.09	66.00
4.5	47.70	49.21	50.49	51.94	53.72	55.89	58.41	61.17	64.06	66.86	69.33	71.08	71.60	70.17	64.57	
5.0	55.79	54.30	53.60	53.44	53.64	54.04	54.50	54.89	55.10	54.99	54.43	53.21	51.10	52.42	53.74	
5.5	65.32	62.63	61.12	60.21	59.54	58.87	58.04	56.94	55.50	53.70	51.59	49.29	47.06	40.00		
6.0	78.07	77.63	77.49	77.64	78.04	78.60	79.19	79.65	79.82	79.52	78.56	76.79	74.40			
6.5	90.42	90.53	90.53	90.72	91.26	92.11	93.10	93.97	94.36	93.88	92.12	88.67	84.00			
7.0	102.8	102.8	102.6	102.6	103.0	103.7	104.5	105.1	105.0	103.9	101.1	96.29				
7.5	115.4	114.8	114.4	114.2	114.1	114.2	114.3	114.1	113.3	111.8	109.1	104.8				
8.0	128.4	127.5	127.0	126.7	126.3	125.8	125.1	124.2	123.1	121.8	119.3	116.7				
8.5	142.3	141.7	141.3	141.1	140.8	140.3	139.7	138.7	137.5	136.1						
9.0	156.7	156.4	156.3	156.3	156.3	156.2	155.8	154.8	153.0	150.1						
9.5	171.2	171.4	171.9	172.6	173.2	173.5	173.2	172.0	169.6	165.5						
10.0	186.5	187.7	189.2	191.0	192.7	194.2	194.7	193.9	190.8	184.8						

[a]Values for salt are relative to infinite dilution of salt in tabulated concentration of acid; values for acid are relative to infinite dilution of acid in water.

Table X. Relative[a] Partial Molal Enthalpies in the System $CaHPO_4$–H_3PO_4–H_2O at 25° C., Calories per Mole

H_3PO_4 Molality, m_2	$CaHPO_4$ Molality, m_3															
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6
								L_3 ($CaHPO_4$)								
0.5	−419	−571	−555	−467	−399	−436										
1.0	−217	−463	−543	−494	−353	−159	51	246	403							
1.5	633	−56	−331	−302	−84	208	473	624	596	350	−128	−822				
2.0	−72	−271	−358	−381	−361	−309	−233	−141	−34	82	202	319	420	487	490	386
2.5	55	−154	−266	−314	−315	−280	−217	−134	−37	67	173	272	357	416	433	389
3.0	78	−106	−219	−278	−292	−270	−221	−151	−68	23	114	200	275	331	361	358
3.5	31	−110	−206	−261	−281	−271	−236	−183	−117	−43	34	109	178	237	281	309
4.0	−66	−156	−221	−262	−281	−280	−261	−227	−181	−125	−63	2	69	135	197	255
4.5	−171	−212	−243	−266	−280	−284	−279	−263	−237	−201	−156	−100	−36	37	117	
5.0	−303	−288	−283	−287	−294	−304	−311	−313	−308	−292	−262	−215	−150	−64	46	
5.5	−398	−342	−312	−300	−301	−311	−325	−340	−351	−356	−350	−328	−288	−223		
6.0	−31[illegible]	−291	−271	−255	−243	−237	−239	−250	−273	−310	−361	−430	−518			
6.5	−1	−116	−155	−144	−105	−58	−21	−13	−50	−149	−323	−588	−959			
7.0	91	−60	−117	−110	−65	−10	33	41	−4	−121	−325	−630				
7.5	79	−53	−106	−105	−75	−35	−4	−1	−40	−136	−302	−547				
8.0	36	−54	−97	−108	−100	−86	−76	−80	−105	−162	−256	−395				
8.5	−88	−86	−102	−127	−156	−184	−207	−220	−220	−203						
9.0	−84	−73	−86	−115	−154	−197	−237	−271	−294	−301						
9.5	−63	−50	−60	−87	−128	−176	−228	−279	−326	−366						
10.0	−21	−13	−17	−35	−63	−103	−153	−212	−279	−353						

(Continued on page 528)

Table X. Relative[a] Partial Molal Enthalpies in the System $CaHPO_4$–H_3PO_4–H_2O at 25° C., Calories per Mole (*Continued*)

H_3PO_4 Molality,	CaHPO$_4$ Molality, m_3															
m_2	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6
								$\bar{L}_2$ (H_3PO_4)								
0.5	201	−66	−180	−271	−398	−546										
1.0	681	859	935	980	1043	1153	1473	1934	2334							
1.5	692	707	727	744	750	737	318	175	34	−114	−113	−83				
2.0	759	712	707	708	690	643	566	474	386	287	286	317	923	911	900	896
2.5	934	961	980	995	1007	1020	1033	1046	1056	1059	1052	1029	945	929	914	905
3.0	1049	1050	1055	1060	1065	1067	1066	1062	1056	1046	1033	1018	1001	983	966	953
3.5	1169	1159	1156	1157	1158	1157	1156	1149	1140	1126	1109	1090	1069	1049	1031	
4.0	1291	1275	1268	1266	1266	1266	1263	1257	1247	1233	1216	1195	1174	1153	1135	
4.5	1409	1390	1380	1376	1374	1372	1369	1362	1351	1335	1317	1296	1274	1254	1254	
5.0	1525	1506	1493	1487	1483	1480	1474	1466	1455	1439	1420	1398	1374			
5.5	1650	1647	1646	1647	1650	1655	1660	1665	1668	1667	1661	1645	1619			
6.0	1785	1820	1842	1859	1879	1905	1936	1973	2010	2041	2056	2046	3313			
6.5	1891	1925	1946	1962	1980	2003	2031	2063	2096	2123	2136	2127				
7.0	1972	1977	1981	1984	1987	1988	1988	1987	1985	1984	1984	1987				
7.5	2066	2064	2065	2066	2065	2058	2049	2036	2024	2016	2017	2029				
8.0	2155	2145	2143	2142	2137	2123	2103	2080	2057	2044	2070	2110				
8.5	2250	2243	2243	2243	2239	2230	2215	2195	2174	2156						
9.0	2348	2352	2357	2361	2365	2367	2367	2364	2355	2341						
9.5	2435	2440	2445	2452	2460	2468	2475	2480	2481	2478						
10.0	2524	2538	2548	2561	2578	2601	2627	2655	2679	2696						
								$-\bar{L}_1$ (H_2O)								
0.5	−0.79	−3.57	−4.51	−4.77	−5.37	−7.09										
1.0	5.54	8.10	9.13	10.27	12.57	16.48	42.71	53.65	63.26							
1.5	7.14	5.75	5.10	5.78	7.72	10.28	2.04	0.19	−4.06	−39.92	−48.84	−55.04				
2.0	8.42	6.21	5.66	5.56	5.10	3.90	2.04	−0.05	−1.58	11.25	13.49	17.05	26.73	27.93	27.59	24.54
2.5	15.55	16.22	16.60	16.95	17.52	18.45	19.79	21.50	23.43	25.37	27.03	28.08	26.17	26.89	26.65	24.99
3.0	21.32	20.90	20.67	20.61	20.73	21.05	21.60	22.34	23.26	24.29	25.34	26.30	27.04	27.41	27.28	26.52
3.5	28.30	27.29	26.69	26.38	26.30	26.40	26.64	26.98	27.38	27.80	28.20	28.54	28.78	28.90	28.91	
4.0	36.31	34.97	34.18	33.78	33.64	33.62	33.66	33.69	33.68	33.61	33.51	33.42	33.38	33.47	33.76	
4.5	45.18	43.54	42.60	42.11	41.85	41.67	41.43	41.07	40.58	39.97	39.33	38.78	38.46	38.58	40.72	
5.0	54.88	53.10	52.09	51.51	51.10	50.67	50.11	49.35	48.38	47.26	46.09	45.06	44.40	42.00	40.52	
5.5	66.52	66.37	66.41	66.60	66.90	67.26	67.62	67.91	68.03	67.88	67.34	66.27	64.53			
6.0	80.71	84.57	86.98	88.97	91.21	94.03	97.46	101.2	104.9	107.6	108.3	105.7				
6.5	93.09	96.86	99.13	101.1	103.5	106.6	110.4	114.2	117.5	118.9	117.2	110.7				
7.0	103.2	103.4	103.7	104.1	104.8	105.5	106.0	106.0	105.1	102.9	99.1	93.1				
7.5	115.4	114.8	114.7	114.9	114.9	114.5	113.5	111.9	109.7	106.9	103.7	100.4				
8.0	127.8	126.0	125.6	125.4	124.7	122.9	120.2	116.7	113.1	110.2	112.6	115.0				
8.5	141.8	140.6	140.5	140.3	139.5	137.8	135.2	132.1	128.9	126.4						
9.0	157.2	157.8	158.5	159.0	159.2	159.2	158.7	157.7	156.1	153.5						
9.5	171.6	172.5	173.4	174.4	175.4	176.3	176.8	177.0	176.6	175.4						
10.0	187.4	189.8	191.7	193.9	196.8	200.4	204.6	208.7	212.2	214.0						

[a] See footnote in Table IX.

Table XI. Relative[a] Partial Molal Enthalpies in the System $CaHPO_4 \cdot 2H_2O$–H_3PO_4–H_2O at 25° C., Calories per Mole

H_3PO_4 Molality, m_2	$CaHPO_4 \cdot 2H_2O$ Molality, m_3															
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6
	$\bar{L}_3$ ($CaHPO_4 \cdot 2H_2O$)															
0.5	−400	−538	−524	−446	−385	−411										
1.0	−370	−465	−505	−503	−473	−428	−379	−335	−303							
1.5	−375	−446	−496	−524	−528	−504	−456	−384	−295	−195	−95	−3				
2.0	−391	−485	−542	−566	−564	−544	−509	−461	−402	−333	−252	−161	−59	53	173	298
2.5	−324	−421	−483	−516	−524	−514	−488	−449	−400	−341	−274	−200	−121	−36	52	141
3.0	−247	−343	−409	−448	−464	−462	−444	−413	−371	−320	−263	−200	−134	−67	1	69
3.5	−174	−266	−332	−375	−397	−401	−390	−365	−330	−286	−235	−180	−122	−63	−5	51
4.0	−115	−198	−261	−305	−331	−341	−336	−318	−289	−251	−206	−156	−101	−45	12	68
4.5	−70	−143	−200	−243	−271	−285	−286	−275	−254	−222	−182	−135	−82	−24	38	
5.0	−39	−101	−152	−191	−220	−237	−244	−240	−226	−202	−169	−127	−75	−15	54	
5.5	−37	−83	−124	−159	−187	−209	−222	−226	−221	−205	−178	−139	−87	−21		
6.0	−50	−79	−110	−141	−170	−195	−214	−225	−227	−219	−200	−169	−124			
6.5	−63	−82	−107	−135	−163	−189	−212	−229	−238	−240	−234	−218	−194			
7.0	−70	−90	−113	−138	−163	−188	−211	−232	−251	−266	−277	−285				
7.5	−66	−99	−125	−147	−167	−186	−208	−232	−260	−293	−329	−369				
8.0	−64	−111	−141	−161	−175	−189	−207	−234	−270	−318	−378	−448				
8.5	−85	−125	−154	−175	−192	−207	−224	−245	−273	−308						
9.0	−76	−122	−153	−174	−188	−200	−215	−234	−260	−295						
9.5	−52	−98	−128	−147	−160	−171	−184	−200	−224	−255						
10.0	−9	−41	−65	−82	−95	−107	−119	−134	−152	−176						
	$\bar{L}_2$ (H_3PO_4)															
0.5	403	416	418	399	371	360										
1.0	558	567	578	580	572	558	626	625	651							
1.5	682	678	673	667	658	646	605	587	566	535	480	426				
2.0	798	801	802	802	802	802	800	795	785	805	794	779	791	769	739	701
2.5	926	941	957	971	983	994	1002	1009	1014	1018	1020	1020	1005	997	983	964
3.0	1058	1074	1090	1105	1119	1131	1142	1151	1160	1166	1172	1175	1177	1176	1173	1166
3.5	1185	1199	1214	1229	1243	1256	1268	1278	1287	1295	1301	1307	1311	1314	1317	1320
4.0	1308	1319	1332	1345	1359	1371	1382	1392	1400	1407	1413	1418	1423	1427	1432	1440
4.5	1427	1436	1446	1458	1469	1480	1490	1499	1507	1512	1517	1521	1524	1527	1529	
5.0	1541	1546	1553	1561	1569	1577	1585	1590	1595	1597	1598	1598	1598	1601	1607	
5.5	1651	1652	1655	1660	1664	1669	1672	1674	1675	1674	1671	1667	1663	1660		
6.0	1760	1759	1759	1761	1764	1766	1767	1767	1766	1763	1759	1752	1730			
6.5	1866	1864	1863	1863	1864	1864	1865	1864	1863	1859	1853	1843	1830			
7.0	1969	1968	1966	1964	1963	1963	1964	1964	1963	1959	1951	1939				
7.5	2068	2068	2065	2062	2060	2060	2060	2061	2060	2056	2048	2035				
8.0	2163	2160	2157	2154	2151	2148	2145	2144	2142	2140	2136	2127				
8.5	2255	2254	2252	2251	2249	2247	2246	2245	2245	2246						
9.0	2348	2351	2353	2355	2358	2361	2365	2369	2373	2378						
9.5	2436	2443	2451	2460	2468	2477	2486	2495	2505	2516						
10.0	2524	2538	2554	2572	2590	2608	2626	2644	2662	2681						

(Continued on page 530)

Table XI. Relative[a] Partial Molal Enthalpies in the System $CaHPO_4 \cdot 2H_2O$–H_3PO_4–H_2O at 25° C., Calories per Mole (Continued)

H_3PO_4 Molality, m_2	$CaHPO_4 \cdot 2H_2O$ Molality, m_3															
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6
	L_1 (H_2O)															
0.5	1.04	0.81	0.91	1.23	1.46	1.09										
1.0	3.16	3.07	3.09	3.15	3.25	3.44	5.25	5.82	5.78							
1.5	5.93	5.63	5.27	4.93	4.68	4.60	4.04	4.52	5.32	5.49	5.93	6.34				
2.0	9.58	9.43	9.20	9.06	9.09	9.29	9.64	10.10	10.64	12.55	13.65	15.02				
2.5	14.87	15.33	15.75	16.19	16.67	17.23	17.91	18.74	19.75	20.94	22.30	23.80	17.76	19.69	21.76	23.86
3.0	21.57	22.17	22.73	23.30	23.91	24.61	25.41	26.35	27.44	28.67	30.04	31.53	24.96	26.62	28.30	29.94
3.5	29.13	29.78	30.42	31.09	31.80	32.58	33.45	34.44	35.55	36.80	38.17	39.65	33.09	34.70	36.30	37.83
4.0	37.52	38.13	38.77	39.46	40.19	40.98	41.84	42.79	43.84	45.00	46.29	47.70	41.23	42.86	44.52	46.20
4.5	46.72	47.25	47.84	48.50	49.21	49.97	50.78	51.64	52.56	53.58	54.70	55.97	49.25	50.94	52.76	54.50
5.0	56.54	56.79	57.19	57.68	58.22	58.78	59.34	59.91	60.50	61.14	61.87	62.76	57.41	59.08	60.92	
5.5	66.98	66.90	67.03	67.26	67.52	67.75	67.94	68.08	68.21	68.36	68.62	69.05	63.89	65.90	67.97	
6.0	78.20	77.97	77.92	77.94	77.96	77.94	77.87	77.74	77.57	77.40	77.27	77.19	69.77	70.30		
6.5	90.09	89.84	89.62	89.44	89.26	89.08	88.86	88.59	88.25	87.81	87.22	86.43	77.10			
7.0	102.6	102.4	102.1	101.7	101.4	101.1	100.9	100.6	100.2	99.49	98.34	96.60	85.50			
7.5	115.6	115.4	115.0	114.4	114.0	113.8	113.6	113.3	112.8	111.7	109.8	107.3				
8.0	128.8	128.2	127.7	127.1	126.5	126.0	125.4	124.8	124.0	123.0	122.1	118.5				
8.5	142.5	142.2	141.8	141.4	141.0	140.6	140.2	139.7	139.3	138.9						
9.0	157.1	157.4	157.7	157.9	158.2	158.6	159.0	159.5	159.8	159.9						
9.5	171.9	172.9	174.2	175.5	176.9	178.3	179.6	180.9	182.2	183.6						
10.0	187.3	189.7	192.6	195.7	198.9	202.0	205.1	208.1	211.1	214.2						

[a] See footnote in Table IX.

Table XII. Relative[a] Partial Molal Enthalpies in the System $Ca(H_2PO_4)_2$–H_3PO_4–H_2O at 25° C., Calories per Mole

H_3PO_4 Molality, m_2	$Ca(H_2PO_4)_2$ Molality, m_3															
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6
	L_3 ($CaH_2PO_4)_2$															
0.5	−122	−97	29	196	352	450										
1.0	−62	−99	−33	103	279	469	649	798	902							
1.5	−36	−59	−17	72	196	343	501	662	816	957	1077	1172				
2.0	19	0	24	84	174	288	420	565	716	871	1025	1174				
2.5	35	23	42	90	163	258	370	496	632	773	917	1059	1315	1445	1562	1664
3.0	2	13	43	90	155	234	327	432	547	670	800	934	1198	1330	1452	1564
3.5	−30	5	48	100	160	230	309	397	493	599	712	834	1070	1206	1339	1467
4.0	−45	7	61	119	180	246	317	394	477	567	665	771	962	1096	1235	1378
4.5	−41	20	81	143	207	274	343	415	491	571	656	747	885	1010	1145	1291
5.0	−40	29	96	162	229	297	366	436	509	585	664	748	845	952	1067	
5.5	117	125	167	231	309	394	481	564	640	703	751	779	837	931	1031	
6.0	179	167	198	259	339	429	522	610	689	752	795	815	784	761		
6.5	107	139	184	240	306	379	457	540	625	712	800	888	808			
7.0	4	91	155	206	252	301	357	426	512	619	749	906	976			
7.5	−16	68	131	180	221	261	303	352	410	482	570	678				
8.0	25	57	105	158	211	257	292	310	306	276	211	105				
8.5	−12	45	95	138	175	205	229	246	257	261						
9.0	−8	47	94	133	167	194	217	234	248	257						
9.5	21	72	116	155	192	226	259	294	329	367						
10.0	87	132	175	219	266	320	382	454	539	638						

(Continued on page 531)

Table XII. Relative[a] Partial Molal Enthalpies in the System $Ca(H_2PO_4)_2$–H_3PO_4–H_2O at 25° C., Calories per Mole (*Continued*)

L_2 (H_3PO_4)

	Ca(H₂PO₄)₂ Molality, m_3															
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6
0.5	406	416	401	375	359	378										
1.0	557	562	563	556	539	518	440	404	381							
1.5	690	700	710	714	708	692	686	664	641	633	624	634				
2.0	802	810	818	823	823	818	809	795	777	755	737	720	722	702	682	661
2.5	916	915	916	917	917	913	906	894	879	860	838	812	780	754	731	709
3.0	1045	1040	1039	1040	1040	1039	1034	1025	1013	997	977	954	930	906	883	863
3.5	1175	1172	1172	1176	1178	1180	1180	1178	1173	1164	1152	1137	1119	1100	1080	1060
4.0	1301	1302	1305	1309	1314	1318	1323	1326	1327	1326	1323	1316	1306	1293	1277	1260
4.5	1421	1421	1423	1426	1430	1434	1438	1441	1443	1445	1445	1443	1440	1436	1445	
5.0	1548	1562	1572	1581	1591	1603	1617	1633	1649	1665	1678	1685	1684	1620	1557	
5.5	1666	1687	1700	1712	1724	1738	1756	1776	1797	1818	1836	1847	1848	1850		
6.0	1761	1760	1761	1762	1762	1761	1758	1755	1752	1752	1754	1763	1780			
6.5	1857	1842	1836	1830	1822	1810	1793	1773	1752	1735	1726	1730	1745			
7.0	1962	1952	1946	1940	1932	1921	1907	1888	1867	1844	1822	1803				
7.5	2070	2070	2066	2061	2057	2054	2050	2043	2027	1998	1955	1899				
8.0	2164	2163	2160	2156	2151	2146	2140	2130	2117	2098	2023	1894				
8.5	2254	2251	2250	2248	2244	2237	2229	2219	2211	2373	2373					
9.0	2348	2350	2352	2354	2355	2356	2359	2362	2367	2569						
9.5	2437	2446	2454	2462	2470	2480	2494	2512	2536	2805						
10.0	2526	2544	2560	2576	2596	2620	2651	2691	2742							

L_1 (H_2O)

	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6
0.5	1.22	1.40	1.84	2.66	3.78	4.91										
1.0	3.36	3.36	3.69	4.42	5.56	7.06	7.75	9.11	10.29							
1.5	6.38	6.61	7.07	7.74	8.60	9.62	11.31	12.87	14.63	16.82	18.84	21.06				
2.0	9.96	10.25	10.65	11.20	11.94	12.90	14.09	15.54	17.24	19.09	21.34	23.81	27.05	29.49	31.81	33.94
2.5	14.65	14.60	14.75	15.10	15.67	16.45	17.43	18.63	20.01	21.57	23.28	25.11	26.75	28.82	30.95	33.10
3.0	21.02	20.79	20.87	21.20	21.74	22.43	23.27	24.23	25.33	26.56	27.95	29.52	31.29	33.28	35.51	37.98
3.5	28.54	28.46	28.69	29.17	29.84	30.67	31.61	32.67	33.82	35.08	36.47	38.02	39.79	41.82	44.21	46.60
4.0	37.06	37.24	37.68	38.34	39.19	40.20	41.35	42.62	44.00	45.46	47.04	48.74	50.60	52.68	55.05	58.40
4.5	46.24	46.39	46.81	47.46	48.29	49.28	50.40	51.64	52.98	54.46	56.07	57.85	59.83	62.08	65.85	
5.0	57.11	58.55	59.75	61.00	62.44	64.19	66.26	68.64	71.24	73.94	76.60	79.00	80.86	77.61	74.37	
5.5	68.50	70.60	72.16	73.69	75.51	77.79	80.52	83.65	86.94	90.11	92.76	94.44	94.61	94.50		
6.0	78.43	78.36	78.63	79.13	79.77	80.51	81.31	82.17	83.08	84.06	85.17	86.48	88.00			
6.5	89.13	87.54	86.97	86.70	86.30	85.56	84.48	83.22	82.10	81.57	82.18	84.57	87.50			
7.0	101.8	100.7	100.2	99.81	99.22	98.32	97.12	95.74	94.38	93.35	93.03	93.89				
7.5	115.8	116.0	115.7	115.4	115.2	115.2	115.2	114.8	113.6	110.9	106.9	101.5				
8.0	129.0	128.9	128.7	128.5	128.2	128.0	127.4	126.3	124.4	121.0	108.9	88.24				
8.5	142.4	142.1	142.1	142.1	141.7	141.0	140.0	138.8	137.7	137.2						
9.0	157.1	157.7	158.2	158.7	159.2	159.7	160.3	161.0	162.0	163.3						
9.5	172.1	173.7	175.2	176.8	178.6	180.7	183.4	186.9	191.6	197.8						
10.0	187.9	191.9	194.2	197.5	201.4	206.3	212.6	220.7	231.2	244.3						

[a] See footnote in Table IX.

LITERATURE CITED

(1) Bassett, H., *Z. Anorg. Chem.* **53**, 34 (1907).
(2) Christensen, J.H., Reed, R.B., *Ind. Eng. Chem.* **47**, 1277 (1955).
(3) Egan, E.P., Jr., Luff, B.B., *J. Phys. Chem.* **61**, 1500 (1957).
(4) *Ibid.*, **65**, 523 (1961).
(5) Egan, E.P., Jr., Luff, B.B., J. CHEM. ENG. DATA 11, 509 (1966).
(6) Egan, E.P., Jr., Luff, B.B., Wakefield, Z.T., *J. Phys. Chem.* **62**, 1091 (1958).
(7) Egan, E.P., Jr., Wakefield, Z.T., J. CHEM. ENG. DATA **9**, 541 (1964).
(8) Egan, E.P., Jr., Wakefield, Z.T., Elmore, K.L., *J. Am. Chem. Soc.* **78**, 1811 (1956).
(9) Elmore, K.L., Farr, T.D., *Ind. Eng. Chem.* **32**, 580 (1940).
(10) Elmore, K.L., Hatfield, J.D., Dunn, R.L., Jones, A.D., *J. Phys. Chem.* **69**, 3520 (1965).
(11) Farr, T.D., Tennessee Valley Authority, *Chem. Eng. Rept.*, No. 8 (1950).
(12) Natl. Bur. Std., Circ. **500**, (1952).
(13) Salzer, H.E., "Tables of Coefficients for Obtaining the First Derivative without Differences," Natl. Bur. Std., Applied Math. Series 1948, 2.
(14) Smith, A.J., Huffman, E.O., CHEM. ENG. DATA SER. 1, 99 (1956).
(15) TVA, unpublished data.

RECEIVED for review April 1, 1966. Accepted June 3, 1966. Material supplementary to this article has been deposited as Document No. 8994 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 $2.50 for photoprints or $1.75 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to Chief, Photoduplication Service, Library of Congress.

Solid-Liquid Equilibrium in the Benzene-Pyridine System

FRANCIS J. CIOFFI[1] and CHARLES E. MESSER
Chemistry Department, Tufts University, Medford, Mass.

The complete solid-liquid equilibrium phase diagram has been determined for the benzene-pyridine system by a method of warming curve thermoelectric thermometry. The system is of the eutectic type with large regions of solid solution formation. The solidus curves and the curves representing the limits of mutual solid solubility below the eutectic temperature have been located.

LITERATURE on solid-liquid equilibrium in cyclic organic systems, especially those containing hetero atoms, is relatively rare. Wright (*12*) and Murray (*6*) have shown, in their investigation of the benzene-thiophene system, that pairs of organic substances form solid solutions because of fairly close similarity in the sizes, shapes, and electrical force fields of the molecules. The fact that thiophene forms a continuous series of solid solutions with benzene would seem to indicate that pyridine, being more similar to benzene in molecular structure, most certainly would, also. However, Pickering (*7*), Hatcher and Skirrow (*4*), and Kravchenko (*5*) have shown that the benzene-pyridine system is not of the continuous solid solution type but rather of the eutectic type.

This paper extends the work of the above authors and presents the complete solid-liquid phase diagram for the benzene-pyridine system.

EXPERIMENTAL

Materials. Baker's C.P. benzene, thiophene-free, was further purified by two fractional crystallizations followed by a fractional distillation from P_2O_5 through a 15-theoretical plate fractionating column. The center cut, collected over a 0.06° C. range, had a purity of 99.98 mole %, as determined by the warming curve method of Schwab and Wichers (*9*), and later described in greater detail by Glasgow, Streiff, and Rossini (*3*).

[1] Present address: The M.W. Kellogg Co., Piscataway, N. J.

Fisher reagent grade pyridine was refluxed over BaO for 2 days and then distilled through the above fractionating column. The center cut, collected over a 0.04° C. range, had a purity of 99.68 mole %.

Apparatus. The apparatus, which combined the features of the melting point calorimeter of Skau (*10*) and the semimicro heat conduction calorimeters of Andrews (*1*), Stull (*11*), and Ziegler and Messer (*13*), was a radiation-type calorimeter in which the sample was contained in a gold-plated copper can in the center of a hollow copper block which was wound with a heater coil. Thus, the sample was heated by radiation from the copper block. The whole block assembly was supported in an unevacuated, unsilvered Dewar flask immersed in an eutectic mixture of carbon tetrachloride and chloroform maintained at dry ice temperature. Temperatures were measured by a system of calibrated copper-constantan thermocouples.

Procedure. The various benzene-pyridine mixtures, each weighing 7 to 8 grams, were prepared in advance and sealed in glass capsules. The day before a run, the appropriate sample ampoule was broken and its contents were weighed quickly into the sample can to prevent exposure to atmospheric moisture. The can and contents then were placed in the calorimeter, slowly brought to dry ice temperature, and allowed to equilibrate overnight. The next morning the cooling bath was recharged with dry ice and the thermal head (defined as the temperature difference between the sample can and the surrounding copper shield) was slowly brought to approximately 140 μv. (about 4.2° C.) by adjusting the heaters manually while