Partial Molal Heat Contents and Free Energies in Phosphoric Acid Solutions

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IN AN ARTICLE on the heat capacity of phosphoric acid solutions (*2*) four tables of partial molal quantities for phosphoric acid were presented. Subsequent measurements of the heat of solution of orthophosphoric acid (*1*) yielded better values of $(\bar{H}_2 - \bar{H}_2^\circ)$ and $(\bar{H}_1 - \bar{H}_1^\circ)$. Tables V to VIII supersede Tables V to VIII of the earlier publication (*2*). The earlier data were calculated by tabluar integration, whereas the revised data were calculated analytically on an IBM-610 computer. The revised data extend only through 85% H_3PO_4.

LITERATURE CITED

(1) Egan, E.P., Jr., Luff, B.B., *J. Phys. Chem.* **65**, 523 (1961).
(2) Egan, E.P., Jr., Luff, B.B., Wakefield, Z.T., *Ibid.*, **62**, 1091 (1958).

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Table V. Relative Partial Molal Heat Content of Phosphoric Acid in Phosphoric Acid Solutions, $(\bar{H}_2 - \bar{H}_2^\circ)$

H_3PO_4, Wt. %	15°	25°	40°	60°	70°	80°
5	381	406	437	500	550	644
10	513	590	639	745	798	878
15	688	754	791	943	1036	1111
20	856	931	988	1126	1194	1252
25	1062	1151	1222	1353	1407	1475
30	1295	1392	1462	1580	1644	1741
35	1547	1651	1731	1852	1918	2016
40	1823	1929	2022	2161	2229	2329
45	2114	2229	2337	2490	2561	2652
50	2424	2549	2668	2845	2933	3030
55	2748	2889	3026	3220	3317	3419
60	3088	3247	3408	3626	3726	3842
65	3445	3619	3794	4025	4134	4259
70	3816	3998	4185	4433	4550	4685
75	4185	4374	4573	4841	4968	5108
80	4537	4733	4943	5221	5352	5495
85	4858	5059	5279	5568	5703	5849

Table VI. Relative Partial Molal Heat Content of Water in Phosphoric Acid Solutions, $-(\bar{H}_1 - \bar{H}_1^\circ)$

H_3PO_4, Wt. %	15°	25°	40°	60°	70°	80°
5	1.106	1.314	1.612	1.864	2.100	2.675
10	2.930	4.020	2.495	3.326	3.557	3.817
15	7.627	8.288	8.605	10.88	12.36	12.28
20	13.97	15.35	16.76	18.47	18.49	18.03
25	25.33	27.15	28.78	29.86	29.53	29.87
30	41.54	43.92	45.55	45.37	45.75	47.89
35	64.00	66.91	69.41	69.83	70.38	72.64
40	94.70	97.74	102.0	105.3	106.0	108.4
45	133.1	138.5	144.6	149.4	150.8	152.2
50	185.8	191.9	199.6	208.1	212.0	214.3
55	252.1	261.3	272.8	285.5	290.9	294.4
60	336.5	350.6	368.3	385.8	392.5	399.8
65	446.6	464.9	486.7	508.3	517.4	527.0
70	588.3	610.0	636.6	664.9	677.5	690.1
75	767.7	792.7	824.8	862.6	880.1	896.0
80	991.7	1021	1060	1104	1123	1142
85	1271	1305	1352	1406	1428	1450

Table VII. Relative Partial Molal Free Energy of Phosphoric Acid in Phosphoric Acid Solutions, $(\bar{F}_2 - \bar{F}_2^\circ)$

H_3PO_4, Wt. %	15°	25°	40°	60°	70°	80°
5	−430.1	−458.5	−502.4	−563.4	−595.6	−629.8
10	81.16	64.67	36.70	−4.94	−28.37	−53.94
15	415.6	404.9	386.4	356.7	337.8	316.1
20	693.8	686.6	672.5	647.9	632.1	614.2
25	650.9	945.4	933.2	911.1	897.0	881.1
30	1204	1199	1187	1166	1152	1136
35	1464	1459	1447	1425	1411	1395
40	1741	1736	1724	1701	1686	1669
45	2040	2035	2022	1997	1981	1962
50	2341	2336	2322	2294	2276	2255
55	2669	2663	2648	2617	2597	2575
60	3025	3020	3004	2972	2951	2926
65	3398	3393	3377	3343	3321	3296
70	3785	3780	3764	3730	3707	3680
75	4177	4173	4158	4122	4099	4071
80	4561	4558	4544	4510	4486	4459
85	4933	4932	4920	4888	4865	4839

Table VIII. Relative Partial Molal Free Energy of Water in Phosphoric Acid Solutions, $-(\bar{F}_1 - \bar{F}_1^\circ)$

H_3PO_4, Wt. %	15°	25°	40°	60°	70°	80°
5	6.15	6.46	6.98	7.79	8.25	8.76
10	13.62	13.79	13.99	14.14	14.10	13.98
15	22.18	22.66	23.36	24.22	24.58	24.92
20	33.15	33.62	34.18	34.66	34.79	34.86
25	46.57	47.44	48.72	50.49	51.45	52.47
30	64.22	65.14	66.49	68.40	69.45	70.53
35	87.35	88.21	89.41	91.02	91.87	92.72
40	117.9	118.8	120.0	121.4	122.2	122.9
45	158.0	158.8	160.0	160.8	161.2	161.6
50	208.7	209.3	209.8	209.9	209.7	209.4
55	275.2	275.6	275.7	274.8	274.0	273.0
60	364.4	365.2	365.7	365.2	364.6	363.9
65	478.1	478.7	478.6	476.8	475.4	473.7
70	627.7	628.5	628.4	626.4	624.7	622.6
75	818.3	819.4	819.6	817.5	815.5	813.0
80	1065	1067	1068	1068	1068	1065
85	1387	1390	1393	1395	1394	1393

Heats of Mixing of Ternary System: Sulfuric Acid–Phosphoric Acid–Water

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TERNARY HEATS of mixing are presently available for only a few systems. A review of the literature indicated that no data were available for the heats of mixing of the sulfuric acid-phosphoric acid-water ternary system. The need for such data is indicated by the large number of industrial processes in which this system occurs.

Several correlations for predicting ternary heats of mixing from the binary data have been proposed (*4*, *5*, *7*). The desirability of such correlations seems obvious. A new correlation is proposed which gives good agreement with the experimental data.

EXPERIMENTAL

The heat of mixing apparatus was designed to permit observation of the temperature rise accompanying an exothermic mixing process in a calorimeter and to compare this with the temperature rise corresponding to a known electrical heat input. Because of lags in system response and temperature measurement, the observed temperature rise was corrected for heat loss occurring in the interval between initial and final temperature measurement. The correction was applied by drift measurement (*2*).

DISCUSSION OF RESULTS

Because orthophosphoric acid is neither soluble nor stable in aqueous solutions having less than 50 mole % water (*6*), no heat of mixing data were obtained in this region.

Heat of mixing data at 25° C. for the ternary system sulfuric acid-orthophosphoric acid-water are presented in Figure 1. These data are estimated to be correct to ±1%. As a further check on the accuracy, the results for the sulfuric acid-water system were compared to the values given by Rossini (*3*). The average, absolute deviation was 0.9%.

Heats of mixing data for the binary, phosphoric acid-water, are those of Farr (*1*).

CORRELATION OF DATA

Tsao and Smith (*7*) have proposed the following equation for correlating ternary heats of mixing with the binary data:

$$\Delta_1 H_{123} = \frac{x_2}{x_2 + x_3}\,\Delta_1 H_{12} + \frac{x_3}{x_2 + x_3}\,\Delta_1 H_{13} + (1 - x_1)\Delta_1 H_{23} \qquad (1)$$

The subscripts between the delta and *H* in the above expression denote that the expression was derived by referring to the vertex represented by component 1 on a triangular plot. For example, $\Delta_1 H_{12}$ is the heat of mixing for the binary $_{12}$ at the composition indicated on Figure 2*a*. If the reference vertex is component 2, then the binary heats of mixing are evaluated at the compositions shown in Figure 2*b*. Unfortunately, the accuracy of the correlation is affected by the choice of reference vertex.

Referring to Equation 1, it obviously is rigorous if the heat of mixing for components 2 and 3 is zero and unaffected by the presence of component 1. The third term on the right side of the equation then represents a contribution for the heat of mixing between components 2 and 3. There is some theoretical basis for suspecting that this contribution is better related with $(1 - x_1)^{1/2}$ rather than $(1 - x_1)$.

These considerations led to the following correlation: If we define $\Delta_1 H_{123}$, $\Delta_2 H_{123}$, and $\Delta_3 H_{123}$ as

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