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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Table I. Experimental and Predicted Heats of Mixing for the Methanol–CarbonTetrachloride–Benzene System

1 = methanol   2 = carbon tetrachloride   3 = benzene

			ΔH_{123}				
x_1	x_2	x_3	Exptl.	Method I	Method II	Tsao	Equations 2-5
0.2460	0.3750	0.3790	136	94.9	131.0	137.2	134
0.5198	0.2444	0.2358	97	83.9	99.9	108.5	97.4
0.7494	0.1319	0.1187	47	38.9	45.9	51.4	46.3

Table II. Experimental and Predicted Heats of Mixing for the Sulfuric Acid–Phosphoric Acid–Water System

1 = water
2 = sulfuric acid
3 = phosphoric acid

x_1	x_2	x_3	$-\Delta H_{123}$ Exptl.	$-\Delta H_{123}$ Predicted	% Error
0.900	0.020	0.080	680	675	0.7
0.900	0.079	0.021	1370	1263	7.8
0.800	0.176	0.024	2410	2420	0.4
0.850	0.087	0.063	1588	1665	5.8

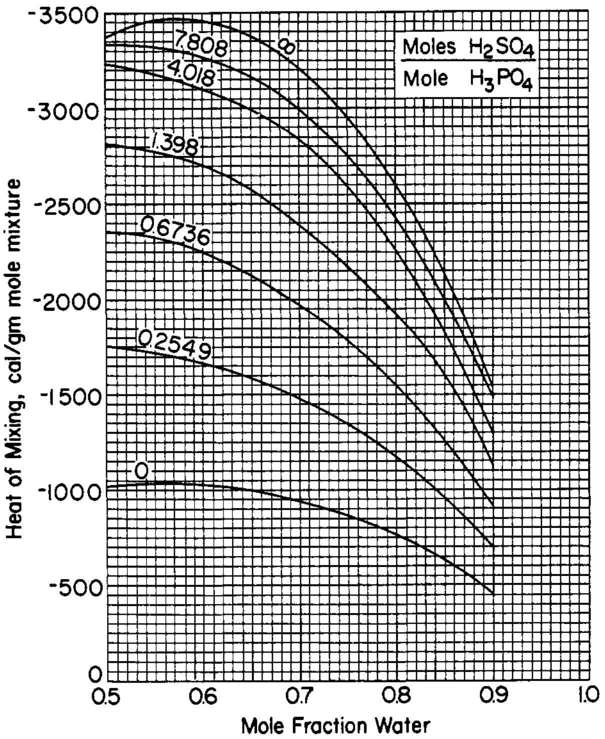
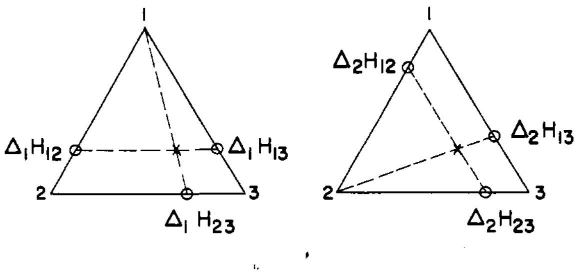


Figure 1. Heats of mixing for the sulfuric acid–phosphoric acid–water system



(a) (b)

Figure 2. Designation of heats of mixing

$$\Delta_1 H_{123} = \frac{x_2}{x_2 + x_3}\,\Delta_1 H_{12} + \frac{x_3}{x_2 + x_3}\,\Delta_1 H_{13} + (1 - x_1)^{1/2}\,\Delta_1 H_{23} \qquad (2)$$

$$\Delta_2 H_{123} = \frac{x_1}{x_1 + x_3}\,\Delta_2 H_{12} + \frac{x_3}{x_1 + x_3}\,\Delta_2 H_{23} + (1 - x_2)^{1/2}\,\Delta_2 H_{13} \qquad (3)$$

$$\Delta_3 H_{123} = \frac{x_1}{x_1 + x_2}\,\Delta_3 H_{13} + \frac{x_2}{x_1 + x_2}\,\Delta_3 H_{23} + (1 - x_3)^{1/2}\,\Delta_3 H_{12} \qquad (4)$$

then the ternary heat of mixing is given by

$$\Delta H_{123} = \frac{\Delta_1 H_{123} + \Delta_2 H_{123} + \Delta_3 H_{123}}{3} \qquad (5)$$

The results obtained with this correlation are compared in Table I with those of Scatchard (*4*) and Tsao (*7*) for the ternary system methanol-carbon tetrachloride-benzene. This system is significant because it contains an associating compound, methanol.

Since the binary system, sulfuric acid-orthophosphoric acid, is a hypothetical one, the correlation was used in reverse to predict the heats of mixing of this hypothetical mixture. Using three of the ternary heats of mixing for sulfuric acid-orthophosphoric acid-water system, the following equation for the binary heats of mixing of the two acids was derived:

$$\Delta H_{23} = x_2 x_3[+1935 - 2641\,(x_2 - x_3) + 510.5(x_2 + x_3)^2] \qquad (6)$$

Using this equation and the general ternary correlation, the results shown in Table II were obtained.

NOMENCLATURE

ΔH_{123} = heat of mixing of ternary system, cal./gm. mole of mixture
ΔH_{12} = heat of mixing of binary system, cal./gm. mole of mixture
ΔH_{23} = heat of mixing of sulfuric and phosphoric acids, cal./mole mixture
x = mole fraction
x_2 = mole fraction sulfuric acid
x_3 = mole fraction phosphoric acid

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