may result also from such effect as solute adsorption at the gas-liquid interface. Thus, it seems practically impossible to estimate the experimental error.

One can only compare the data presented here with published values (*1, 11, 13, 14*). It was done for binary systems of paraffins (*8*). It appears that the relative deviation among all these values does not exceed 6.5%, and the average relative deviation is 3%. For polar systems, we did not find enough reliable data to compare with our experimental Henry's constants.

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NOMENCLATURE

$f_2(P,T)$ = fugacity of the solute at pressure P and temperature T, atm
$f^0_{2L}(P_0,T)$ = liquid fugacity of the pure solute at pressure P_0 and temperature, atm
H_{21} = Henry's constant of the solute 2 in the solvent 1, atm
j = James-Martin factor
N_1 = number of moles of solvent introduced in the chromatographic column
p_a = atmospheric pressure, atm
p_e = inlet pressure of the column, atm
p_s = outlet pressure of the column, atm
p_{se} = partial pressure of water at temperature T_a, atm
t_m = dead time, sec
t_{R_2} = absolute retention time of the solute, sec
T = temperature in the column, ° K
T_a = ambient temperature, ° K
u_a, u_s = flow rate of the carrier gas in the flow meter, at the outlet of the column, cm^3/sec
x_2 = liquid molar fraction of the solute
z_g = compressibility factor of the gas phase in the column
$\gamma^{*}_{21}(0,T)$ = activity coefficient at infinite dilution of the solute 2 in the solvent 1, when the reference fugacity is chosen as f^0_{2L} $(P_0 = 0,T)$
φ_{2V} = vapor fugacity coefficient of the solute in the gas phase

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Enthalpy of Dilution of Superphosphoric Acids

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Superphosphoric acids in the concentration range 62–85% P_2O_5 (86–117% H_3PO_4) were diluted and hydrolyzed in an acidic solvent in a solution calorimeter to obtain values for their enthalpies of formation and relative apparent molal heat contents. The results join smoothly with data obtained previously for lower concentrations of acid. With the enthalpy of formation of acid containing 62.04% P_2O_5 (85.66% H_3PO_4), taken as −609.14 kcal/mol P_2O_5, the enthalpies of formation ranged from −607.03 kcal/mol P_2O_5 for acid containing 68.76% P_2O_5 (94.94% H_3PO_4) to −591.83 kcal/mol P_2O_5 for acid containing 85.17% P_2O_5 (117.60% H_3PO_4).

Previous studies (*4*) of the enthalpy of dilution of phosphoric acid were extended only to about 90% H_3PO_4, the concentration at which the amount of condensed phosphate species becomes significant. This study extends the thermal data into the concentration range of the superphosphoric acids, a range of increasing importance in fertilizer technology.

To produce a well-defined final state, a solvent and a temperature were chosen that would hydrolyze the condensed phosphates completely to orthophosphate in a length of time suitable for calorimetric measurements. Exploratory tests showed that 10.35*m* HCl effected complete hydrolysis to orthophosphate in less than 30 min at 40° C. All measurements then were made with this solvent at 40° C, and the results were converted to the standard enthalpies of formation at 25° C. The relative apparent molal heat contents, ϕ_L, that were calculated from the enthalpies of formation may be used to calculate the enthalpy of dilution of phosphoric acid between any two concentrations up to 117% H_3PO_4.

MATERIALS AND PROCEDURE

Superphosphoric acid was prepared by dissolving 2.8 kg of reagent P_2O_5 in 1050 ml of reagent H_3PO_4 (85%) at 145° C, and filtering the hot solution through a coarse glass frit into a phosphoric acid reagent bottle for storage. Portions of the stock acid (117.6% H_3PO_4) were diluted with reagent H_3PO_4 to prepare solutions of nominal concentrations—95, 105, 110, and 115% H_3PO_4—and the

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diluted solutions were heated for 6 hr at 100° C to ensure equilibrium distribution of phosphate species. A solution containing 85.66% H_3PO_4 was prepared by diluting twice-recrystallized $2\,H_3PO_4 \cdot H_2O$ with water. Final compositions were determined by the gravimetric quimociac method for phosphorus (*2*). The hydrochloric acid solvent, 10.35*m* HCl, was prepared by dilution of reagent-grade hydrochloric acid; its composition was determined alkalimetrically.

The solution calorimeter (*4*) was modified in a few details. The heater was replaced with a 4-lead helical Constantan heater mounted in a glass tube that had been shaped into a helix and suspended from the calorimeter cover by the ends of the 5-mm glass tube through which the leads were passed. The head of the platinum resistance thermometer was sealed with Apiezon-W wax to a flared 5-mm glass support tube through which the leads were passed. This assembly was suspended from the calorimeter cover which, when in place, located the thermometer inside the glass helix. The glass draft tube was replaced with a less fragile inert plastic tube fastened inside the glass helix with platinum wire. The technique of temperature and energy measurements has been described (*3*).

CALCULATIONS AND RESULTS

The method of determining the heats of formation of the superphosphoric acids is shown schematically in the following equations in which the solvent is 10.35*m* HCl.

$$P_2O_5 \cdot X\,H_2O + (4.821 - X)\,H_2O = P_2O_5 \cdot 4.821\,H_2O \qquad \Delta H_{R1},\ 40°\,C$$

$$\text{Ampul } (P_2O_5 \cdot X\,H_2O) + \text{solvent} = \text{solution } A_1 \qquad \Delta H_1$$

$$\text{Ampul } (H_2O) + \text{solution } A_1 = \text{solution } A_2 \qquad \Delta H_2$$

$$\text{Ampul } (P_2O_5 \cdot 4.821\,H_2O) + \text{solvent} = \text{solution } B_1 \qquad \Delta H_3$$

$$\text{Solution } A_2 = \text{solution } B_1 \qquad \Delta H_4 = 0$$

$$\Delta H_{R1}\ (40°\,C) = \Delta H_1 + (4.821 - X)\Delta H_2 - \Delta H_3 + \Delta H_4 \tag{1}$$

$$\Delta H_{R2}\ (25°\,C) = \Delta H_{R1}\ (40°\,C) + \int_{40°}^{25°} \Delta C_p dT \tag{2}$$

$$\Delta H_f^0 (P_2O_5 \cdot X\,H_2O) = \Delta H_f^0\,(P_2O_5 \cdot 4.821\,H_2O) - \Delta H_{R2} \tag{3}$$

The measured heats of solution (ΔH_1) of the phosphoric acids in 10.35*m* HCl are listed in Table I. The average of 11 determinations of the heat of solution of 85.66% H_3PO_4 ($P_2O_5 \cdot 4.821\,H_2O$) in 10.35*m* HCl at 40° C (ΔH_3) was −178.29 cal/mol with a standard deviation of 0.82 cal/mol. Small corrections for the heats of vaporization of water and HCl from 10.35*m* HCl solution were calculated from vapor pressure data (*7*).

The enthalpies of solution of the stoichiometric amounts of water in the hydrochloric acid solution in which the superphosphoric acid samples had been dissolved were so low that it was impractical to measure them. Solutions that covered the concentration range of solution A_1, the hydrochloric acid solvent in which the superphosphoric acid samples had been dissolved, were prepared and their enthalpies of dilution with water were measured at 40° C. The results are listed in Table II. An equation expressing the enthalpy of dilution as a function of the ratios of the concentrations of the two acids was derived by the method of least squares.

$$H = -26.72 - 13.17\,R + 13.57\,R^2 \tag{4}$$

where

H = heat of dilution, cal/g H_2O
R = acid ratio, % H_3PO_4/% HCl

The standard deviation of Equation 4 is 0.11 cal/g.

The heats of dilution with the stoichiometric amounts of water were assumed to be the same as with the amounts used in the measurements, approximately five times the stoichiometric amounts. The heat effects of adding the stoichiometric amount of water to the hydrochloric acid solutions in which the superphosphoric acid samples had been dissolved were calculated from Equation 4. The results are listed in Table III.

Table I. Observed Enthalpy of Solution, ΔH_1, of Phosphoric Acids in 10.35 Molal HCl at 40° C

H_3PO_4, %	Mol H_2O/mol P_2O_5	$-\Delta H_1$, cal/mol P_2O_5	No. of detns.
94.94	3.580	1730.1 ± 2.8	5
105.1	2.472	5959.3 ± 7.3	4
110.0	2.014	9324.0 ± 13.0	4
115.1	1.575	13955.0 ± 15.0	6
117.6	1.372	15991.0 ± 9.0	4

The enthalpies of solution measured at 40° C (Equation 1) were converted to those at 25° C by Equation 2 through use of second-degree heat-capacity equations for determining differences in the heat capacities of the products and reactants. The equations were derived from data for water (*9*), and for $P_2O_5 \cdot 4.821\,H_2O$ (85.66% H_3PO_4) (*5*). Heat capacities of the more concentrated acids were estimated by combining the values in the ranges 65-85% H_3PO_4 and 15-80° C (*5*), with unpublished values for liquid H_3PO_4 (27-58° C) and liquid $2\,H_3PO_4 \cdot H_2O$ (24-40° C) obtained in the measurement of the low-temperature heat capacities of these compounds (*6*). Heat capacity values from the low-temperature calorimeter join smoothly with values from the solution calorimeter, and extrapolate smoothly to the value for anhydrous P_2O_5 (*1*). The second-degree equation that expresses the heat capacity in terms of temperature and concentration is

$$C_p = 32.15 + 0.067\,T + 12.82\,n - 0.000774\,T^2 + 0.153\,n^2 + 0.0221\,Tn \tag{5}$$

where

C_p = heat capacity, cal/mol $P_2O_5 \cdot n\,H_2O$
T = temp, ° C
n = mol H_2O/mol P_2O_5

The enthalpy of formation of water is −68,317 cal/mol (*8*) and the enthalpy of formation of $P_2O_5 \cdot 4.821\,H_2O$ is −609,140 cal/mol (*4, 8*).

The enthalpies of dilution of superphosphoric acids to $P_2O_5 \cdot 4.821\,H_2O$ (85.66% H_3PO_4) at 40° C and 25° C, the changes in heat capacity of the components from 40° to

Table II. Enthalpy of Solution of H_2O in HCl–H_3PO_4 Solutions at 40° C

Acid solution				
Composition, wt %				
H_3PO_4	HCl	R[a]	H_2O, g	−Cal/g H_2O
0.489	27.26	0.0179	16.4722	26.88
1.002	27.12	0.0369	15.9571	27.19
1.494	26.98	0.0554	16.7519	27.48
1.996	26.86	0.0743	16.8375	27.72
2.483	26.72	0.0929	15.4187	27.89
2.976	26.58	0.1120	13.6585	27.81
3.481	26.44	0.1317	17.2617	28.20
3.980	26.30	0.1513	15.0975	28.51
4.226	26.20	0.1613	16.3950	28.42
4.974	26.03	0.1911	18.5485	28.77

[a] R = % H_3PO_4/% HCl.

Table III. Calculated Enthalpy of Dilution, ΔH_2, of HCl–H_3PO_4 Solutions at 40° C

	Average values	
H_3PO_4, %	R^a	$-\Delta H_2$, cal/mol H_2O
94.94	0.1209	506.5
105.1	0.0690	496.6
110.0	0.0420	490.9
115.1	0.0365	489.7
117.6	0.0383	490.1

[a] R = % H_3PO_4/% HCl.

Table IV. Enthalpy of Dilution to $P_2O_5 \cdot 4.812\ H_2O$, ΔH_{R2}, and Enthalpy of Formation of Superphosphoric Acids, ΔH_f^0

Mol H_2O/ mol P_2O_5	Cal/mol P_2O_5			
	$-\Delta H_{R1}$	$\Delta H_c{}^a$	$-\Delta H_{R2}$	$-\Delta H_f^0$
3.580	2180.4	68.4	2112.0 ± 3.7	607,030
2.472	6947.5	127.0	6820.5 ± 8.5	602,320
2.014	10523	152.8	10370.0 ± 14	598,770
1.575	15365	178.5	15187.0 ± 16	593,950
1.372	17503	190.6	17312.0 ± 11	591,830

[a] $\Delta H_c = \int_{40^\circ}^{25^\circ} \Delta C_p dT$

Table V. Enthalpy of Formation of Superphosphoric Acids, ΔH_f^0, Kcal/Mol P_2O_5[a]

P_2O_5, %	$-\Delta H_f^0$	P_2O_5, %	$-\Delta H_f^0$
62	609.08	74	603.94
63	608.97	75	603.13
64	608.80	76	602.27
65	608.57	77	601.35
66	608.29	78	600.38
67	607.95	79	599.34
68	607.55	80	598.25
69	607.09	81	597.10
70	606.57	82	595.89
71	606.00	83	594.63
72	605.37	84	593.31
73	604.68	85	591.93

[a] Calculated from Equation 7.

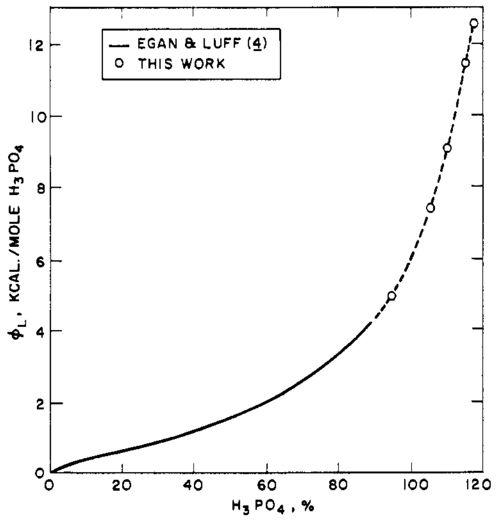

Figure 1. Relative apparent molal heat content of phosphoric acid

Table VI. Relative Apparent Molal Heat Content, ϕ_L, Cal/Mol H_3PO_4, of Superphosphoric Acids

H_3PO_4, %	ϕ_L	H_3PO_4, %	ϕ_L	H_3PO_4, %	ϕ_L
86	3910	97	5220	108	8360
87	3960	98	5430	109	8740
88	4020	99	5660	110	9130
89	4090	100	5900	111	9530
90	4180	101	6150	112	9950
91	4280	102	6420	113	10390
92	4400	103	6710	114	10840
93	4540	104	7010	115	11310
94	4690	105	7320	116	11790
95	4850	106	7650	117	12290
96	5030	107	8000		

25° C, and the enthalpies of formation of the superphosphoric acids are listed in Table IV.

The equation that gives the best least-squares fit (av dev = 0.09 kcal/mol P_2O_5) for the enthalpy of formation as a function of the concentration of phosphoric acid is

$$-\Delta H_f^0 = 565.94 + 25.064\ n - 5.0953\ n^2 + 0.36402\ n^3 \qquad (6)$$

where n = mol H_2O/mol P_2O_5.

ΔH_f^0 may also be represented as a function of the P_2O_5 content by the equation

$$-\Delta H_f^0 = 503.33 + 3.49371\ w - 0.028840\ w^2 \qquad (7)$$

where w = wt % P_2O_5, and the standard deviation is 0.21 kcal/mol P_2O_5. Values calculated from Equation 7 are given in Table V.

Uncertainty intervals for the enthalpies of formation are not given, but they may be calculated readily when uncertainty intervals for the enthalpy of formation of H_3PO_4 are available.

The values for the relative apparent molal heat content, ϕ_L, up to the concentration of 117% H_3PO_4 (Figure 1, Table VI), calculated from the heats of reaction and the relative apparent molal heat content of 85.66% H_3PO_4 *4*. Equation 8, calculated by the method of least-squares, fits the data with a standard deviation of 109 cal/mol:

$$\phi_L = 56628 - 1261.95\ W + 7.5466\ W^2 \qquad (8)$$

where W = wt % H_3PO_4.

The values for ϕ_L are applicable to engineering calculations of heats of dilution of phosphoric acids because they are the sums of the effects of dilution per se, and the effects of the rearrangement of phosphate species to their equilibrium distributions at the new concentration. The consistency of the present values of ϕ_L with those reported previously (*4*) is shown in Figure 1.

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