Heat of Formation of Liquid Phosphorus Oxychloride, $POCl_3$

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The heat of formation from the elements in their standard states at 25° C. of liquid $POCl_3$, determined from the heat of its solution in water and published values for the heats of formation of H_3PO_4 and HCl, is 143.4 ± 0.4 kcal./mole.

THE HEAT of formation from the elements at 25° C. of liquid phosphorus oxychloride was measured in a solution calorimeter on the basis of the over-all reaction

$$POCl_3(liq) + 3H_2O(liq) = H_3PO_4(c) + 3HCl(g) \qquad (1)$$

Since it was not practical to use crystalline H_3PO_4 and gaseous HCl as reactants, aqueous solutions of these compounds were used with appropriate thermal corrections. The measured heats of reaction in the solution calorimeter and published heats of formation of the reagents and products were used to calculate the heat of formation of liquid phosphorus oxychloride.

PREPARATION OF REAGENTS

Phosphorus Oxychloride. The phosphorus oxychloride was handled only in an atmosphere of dry nitrogen. Reagent-grade liquid $POCl_3$ (750 ml.) was placed in one leg of a 1-liter borosilicate glass V-tube which was closed and cooled in an ice-salt bath until about 75% of the $POCl_3$ crystallized. The liquid remaining was poured into the empty leg of the V-tube; the crystals were melted and transferred to a vacuum-jacketed still whose column was filled with small glass helices. The still-head temperature was controlled by the flow of cold water through the condenser. The $POCl_3$ was distilled under 5 cm. of Hg pressure, first under total reflux for 2 days to pump off low-boiling contaminants, and then at a reflux ratio of 10 to 1. The middle fraction was transferred in small amounts (about 1.5 grams) to thin-walled 25-cc. glass bulbs and weighed with a precision of 20μg. The density of liquid $POCl_3$ was taken as 1.675 grams per cc. for correction of weights to a vacuum basis.

Phosphoric Acid. Reagent-grade phosphoric acid was twice recrystallized as the hemihydrate, $2H_3PO_4 \cdot H_2O$. The product, not completely free of mother liquor, analyzed 90.66% H_3PO_4. A portion of this acid was diluted by weight with distilled water to a solution containing 80.43% H_3PO_4.

Hydrochloric Acid. Constant-boiling hydrochloric acid prepared from reagent-grade acid contained 20.125% HCl by chemical analysis.

CALORIMETER

The solution calorimeter has been described (*3*, *4*). The calorimeter heater was a 100-ohm constantan heater wound on a thin glass form that served as a draft tube for the stirrer. The heater and form were covered with Apiezon W wax, and the capsule-type platinum resistance thermometer was exposed directly to the solution. A second, all-glass solution calorimeter (*3*), in which the heater was enclosed in a glass spiral, was used for a few measurements, but its mechanical arrangement necessitated the use of an inconveniently small sample bulb.

TEMPERATURE MEASUREMENTS

Temperatures were measured with a capsule-type platinum resistance thermometer with a precision of 0.2 millidegree. Conventional "normal" and "reverse" readings of resistance on a Leeds & Northrup K-2 Mueller bridge, to balance out lead resistance, were made during rating periods (before and after energy introduction periods) to establish heat-leak corrections. Only normal readings were taken during the dissolution of $POCl_3$ and, in addition to the bridge corrections, a term was added for the difference between normal and reverse readings that was established during the rating periods to put corrected

Table I. Observed Heats of Solution in Water

Wt. Sample, Grams	Corr. Temp. Rise, °C.	−Cal./Run	−Cal./Mole
$POCl_3$ (liq), Black-Wax Calorimeter			
1.49003	0.84335	782.5259	80,526
1.44542	0.81127	752.7150	79,849
1.47019	0.82706	767.9654	80,094
1.44976	0.81763	758.3490	80,206
1.56147	0.87917	816.2861	80,157
		Average	80,166 ± 0.20%
$POCl_3$ (liq), All-Glass Calorimeter			
1.57056	0.81710	822.0180	80,253
1.52774	0.87314	798.9236	80,184
1.52503	0.87075	796.9411	80,127
		Average	80,188 ± 0.06%
$(H_3PO_4 \cdot 0.5604H_2O)_{soln}$ (90.66% H_3PO_4)			
27.48926	1.14448	1076.6326	4233.45
26.27942	1.09553	1028.9391	4232.19
26.40725	1.10185	1032.7746	4227.41
26.70872	1.11061	1041.7725	4216.09
20.84224	0.87450	814.8105	4225.76
22.63069	0.95032	885.0737	4227.39
23.21584	0.97352	907.4206	4224.87
24.25902	1.01466	946.2878	4216.38
		Average	4225.44 ± 0.11%
$(H_3PO_4 \cdot 1.3235H_2O)_{soln}$ (80.43% H_3PO_4)			
39.28537	1.07947	1013.6266	3143.65
39.61191	1.08814	1022.6200	3145.42
40.81012	1.11815	1050.8534	3137.35
40.31845	1.10684	1039.1782	3140.32
		Average	3141.68 ± 0.09%
$(HCl \cdot 8.0327H_2O)_{soln}$ (20.125% HCl)			
30.53814	0.24626	233.6471	1386.16
27.21946	0.21982	207.8946	1383.80
24.41019	0.19868	187.3051	1390.23
27.71084	0.22405	211.8791	1385.26
24.98971	0.20387	192.4426	1395.20
24.49623	0.19958	188.1191	1391.34
26.29476	0.21448	202.2666	1393.68
26.70299	0.21663	204.7001	1388.83
		Average	1389.31 ± 0.24%

Table II. Heat of Formation of $POCl_3$

90.66% H_3PO_4 Reagent		
$POCl_3(liq) + 27.6585H_2O(liq) = H_3PO_4\cdot 0.5604H_2O(soln) + 3(HCl\cdot 8.0327H_2O)(soln)$	$\Delta H_1 = -71,774$	
$H_3PO_4(liq) + 0.5604H_2O(liq) = (H_3PO_4\cdot 0.5604H_2O)(soln)$	$\Delta H_2 = -1923$	(*3*)
$H_3PO_4(c) = H_3PO_4(liq)$	$\Delta H_3 = 3100$	(*3*)
$3(HCl\cdot 8.0327H_2O)(soln) = 3HCl(g) + 24.0981H_2O(liq)$	$\Delta H_4 = 48,969$	(*6*)
$POCl_3(liq) + 3H_2O(liq) = 3HCl(g) + H_3PO_4(c)$	$\Delta H_5 = \Delta H_1 - \Delta H_2 - \Delta H_3 + \Delta H_4 = -23,982$	
$X \quad 3(-68,317) \quad 3(-22,063) \quad -306,200$		(*6*)
	$\Delta H^\circ f$ $POCl_3(liq) = -143,460$ cal./mole	
80.43% H_3PO_4 Reagent		
$POCl_3(liq) + 28.4216H_2O(liq) = H_3PO_4\cdot 1.3235H_2O(soln) + 3(HCl\cdot 8.0327H_2O)(soln)$	$\Delta H_6 = -72,857$	
$H_3PO_4(liq) + 1.3235H_2O(liq) = (H_3PO_4\cdot 1.3235H_2O)(soln)$	$\Delta H_7 = -2944$	(*3*)
$POCl_3(liq) + 3H_2O(liq) = 3HCl(g) + H_3PO_4(c)$	$\Delta H_8 = \Delta H_6 - \Delta H_7 - \Delta H_3 + \Delta H_4 = -24,044$	
$X \quad 3(-68,317) \quad 3(-22,063) \quad -306,200$		(*6*)
	$\Delta H^\circ f$ $POCl_3(liq) = -143,390$ cal./mole	

temperature readings during the solution period on the same basis as those taken during the rating periods.

Time was measured on a second-timer driven from a constant-frequency supply. The calorimeter system was calibrated electrically immediately before and after each solution period. The defined thermochemical calorie (1 cal. =4.1840 abs. joules) was used to convert electrical energy to thermal energy.

The corrected temperature rise during the dissolution of $POCl_3$ was determined by an established method (*7*). The temperature rise during the dissolution of the phosphoric acid and hydrochloric acid solution was essentially complete in 1 minute, and a simplified method (*2*) was used for the calculation of the corrected temperature rise.

HEATS OF SOLUTION

Exploratory measurements of the heat of solution of liquid $POCl_3$ in 4 *m* hydrochloric acid and in water showed that about 35 minutes was required for complete evolution of heat; dissolution was slightly faster in water than in hydrochloric acid solution. In one run, the solution at 10 minutes after the introduction of $POCl_3$ showed no nonorthophosphoric acid by paper chromatography, and in several runs the solution at 30 minutes after the introduction of $POCl_3$ showed no nonorthophosphoric acid by a differential spectrophotometric method (*5*). The temperature rise continued for at least 35 minutes, however, indicating that the reaction of the $POCl_3$ was not complete in the 30 minutes indicated by the chemical analyses. A solution period of 40 minutes was used in the calculation of the corrected temperature rise to ensure the inclusion of all reaction heat effects.

A fixed volume of 850 ml. of water was used as solvent in all measurements of heats of solution. To balance Equation 1, the stoichiometric quantity of water required by the equation was added before each dissolution of $POCl_3$, thus correcting for the small heat of dilution that would have appeared if the $POCl_3$ was dissolved in the standard 850 ml. of water and the water for hydrolysis was then added. The measured heats of solution of 1.5-gram samples of liquid $POCl_3$ in water to which the stoichiometric quantity of water had been added are given in Table I.

There was some indication that the $POCl_3$ was attacking the Apiezon W wax coating on the stirrer draft tube, and the wax was found to be soluble in liquid $POCl_3$. Results (listed in Table I) of three dissolutions of liquid $POCl_3$ in water in the all-glass calorimeter showed, however, that the attack on the wax had no significant effect on the measurements.

The heats of solution of phosphoric acid and of the constant boiling hydrochloric acid to which the stoichiometric amount of H_3PO_4 had been added are listed in Table I. The measured heats of solution from Table I were combined with published heats of reaction and heats of formation (*3,6*) to arrive at the heat of formation of $POCl_3$ as shown schematically in Table II.

The calculated values for the heat of formation from the elements in the standard states at 25° C. of $POCl_3$ were −143,460 and −143,390 cal. per mole, or an average of −143.4 kcal. per mole. The uncertainty is estimated to be ± 0.4 kcal. per mole. The fact that essentially identical values for the heat of formation of $POCl_3(liq)$ were obtained through use of two calorimeter systems and two strengths of phosphoric acid increases the significance of the calculated results.

The reported heats of solution (*1*) of $POCl_3(liq)$ are:

Thomsen	−72.2 kcal. per mole
Berthelot	−74.6
Neale and Williams	−79.9
Charnley and Skinner	−80.4 ± 0.4
This work	−80.2 ± 0.2

The heat of formation reported by Charnley and Skinner (*1*) was −143.8 kcal. per mole.

LITERATURE CITED

(1) Charnley, T., Skinner, H. A., *J. Chem. Soc.* **1953,** p. 450.
(2) Dickinson, H. C., *Bull. Natl. Bur. Std. U. S.* **11,** 257 (1914).
(3) Egan, E. P., Jr., Luff, B. B., *J. Phys. Chem.* **65,** 523 (1961).
(4) Egan, E. P., Jr., Wakefield, Z. T., Elmore, K. L., *J. Am. Chem. Soc.* **78,** 1811 (1956).
(5) Gee, A., Deitz, V. R., *Ibid.* **77,** 2961 (1955).
(6) *Natl. Bur. of Std. U. S. Circ.* **500,** U. S. Government Printing Office, 1952.
(7) Rossini, F. D., "Experimental Thermochemistry," Vol. **I.**, Chap. 5, Interscience, New York, 1956.

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