7. *Thermodynamic Functions of Phosphorus Pentabromide.*

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The enthalpies of (i) the aqueous hydrolysis of phosphorus pentabromide, and (ii) the solution of phosphorus pentabromide in carbon disulphide have been measured. A new value, $-54\cdot6 \pm 1\cdot2$ kcal. mole^{-1}, for the standard enthalpy of formation of phosphorus pentabromide is reported, and estimates of related thermodynamic properties are made.

ALTHOUGH accurate data for thermodynamic functions of phosphorus compounds are important, existing values for several simple halides rely on early and unchecked investigations.[1] In this laboratory, we have been concerned with the measurement of spectroscopic and thermodynamic properties of phosphorus iodides and bromides. We report here a new value for the standard enthalpy of formation of phosphorus pentabromide, based on measurements of its aqueous hydrolysis to phosphoric acid, and reliable supplementary thermodynamic data. The values of several related thermodynamic functions have also been calculated.

EXPERIMENTAL

Calorimeter.—A glass Dewar constant-temperature-environment solution calorimeter, totally immersed in a thermostat maintained at 25 ± 0·01°, was used (it is fully described elsewhere [2]). Temperature differences were measured (to ±0·001°) by use of an F53 thermistor (Standard Telephones & Cables Ltd.). The calorimeter was calibrated electrically, and each determination was monitored by use of a miniature platinum-resistance thermometer coupled to a 6 in. potentiometric recorder (Elliot), the trace also being used to estimate thermal leakages. 100 ml. of calorimetric fluid were used in each run. When carbon disulphide was used, the vapour space above the liquid was flushed with dry nitrogen. Samples were loaded into fragile glass ampoules in a nitrogen-filled dry-box.

Purification of Compounds.—*Phosphorus pentabromide.* A commercial sample (B.D.H.) was crystallised from diethyl ether, and the solvent removed at ambient temperature in a desiccator (Found: Br, 92·3. Calc. for PBr_5: Br, 92·8%).

Carbon disulphide. A commercial sample (B.D.H. AnalaR grade) was successively shaken with aqueous potassium permanganate, calcium chloride, and mercury. Immediately prior to use, it was fractionally distilled followed by passage of dry nitrogen through it for *ca.* 15 min. to remove dissolved oxygen.

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[1] Hartley, Holesm, Jacques, Mole, and McCoubrey, *Quart. Rev.*, 1963, **17**, 204.

[2] Finch and Gardner, *J.*, 1964, 2985.

Units.—Results are expressed in terms of the thermochemical calorie: 1 cal. = 4·1840 abs. joules.

Table 1 lists the observed enthalpies of aqueous hydrolysis ($\Delta H_{obs.}$), which refer to the reaction:

$$PBr_5(cryst.) + (n + 4)\ H_2O(liq.) \longrightarrow [H_3PO_4 + 5HBr]nH_2O\ \Delta H_{obs.}$$

TABLE 1.

Expt.	N	T(°c)	$\Delta H_{obs.}$	$\Delta H_f°$ [PBr_5, cryst.]	
1	2986	26·0°	−125·9	−53·60	Mean value −54·6 ± 1·4 kcal. mole^{-1}
2	3082	25·9	−125·7	−53·80	
3	3185	25·9	−123·5	−56·00	
4	3318	25·9	−124·4	−55·10	

N = Molar ratio of calorimeter fluid to phosphorus pentabromide. T = Mean temperature of reaction period.

The standard enthalpy of formation follows from the equation:

$$\Delta H_f°[PBr_5,\ cryst.] = 5\Delta H_f°[HBr,nH_2O] + \Delta H_f°[H_3PO_4,nH_2O] - 4\Delta H_f°[H_2O,\ liq.] - \Delta H_{obs.}$$

Table 2 lists the numerical values and sources of the standard enthalpy data used in the calculations.

It is assumed that the standard enthalpy of soution of HBr in H_3PO_4(aq.) does not differ significantly from the corresponding value in water.

Values for the enthalpy of solution of phosphorus pentabromide in oxygen-free carbon disulphide are recorded in Table 3.

TABLE 2.

Compound	Process	Datum (kcal. mole^{-1})	Ref.
H_3PO_4(cryst.)	Formation	−305·7	3
H_3PO_4 (cryst.)	Aq. soln.	−3·2 (N = 3000)	4
HBr,nH_2O (500, <N <700)	Formation	−28·775	4
H_2O(liq.)	Formation	−68·32	4
PBr_3(liq.)	Formation	−40·5	1
PBr_3	Vaporisation	9·5	5
Br^+ (g)	Formation	301·3	4
PBr_5	Sublimation	13	4
P (g)	Formation	75·5	1
Br (g)	Formation	26·76	6

TABLE 3.

Expt.	N	T	ΔH_s	
1	568	24·7	+14·25	Mean value = 14·3 ± 0·1 kcal. mole^{-1}
2	898	24·7	+14·37	

DISCUSSION

Comparison with Accepted Data.—The accepted value[4] for the standard enthalpy of formation of phosphorus pentabromide (—66·0 kcal. mole^{-1}) differs considerably from that reported here (—54·6 kcal. mole^{-1}). The former figure is derived from independent determinations: (*a*) the enthalpy of the aqueous hydrolysis of crystalline phosphorus pentabromide (similar to the present investigation); and (*b*) the direct determination of the enthalpy change in the formation reaction:

$$PBr_3(liq.) + Br_2(liq.) \longrightarrow PBr_5\quad \text{(probably in excess of } Br_2\text{)}$$

Correcting the results from method (*b*) with recent data[1] on the standard enthalpy of formation of PBr_3, we derive a value of —60·8 kcal. mole^{-1} for $\Delta H_f°[PBr_5,\ cryst.]$. From method (*a*), utilising the recent data of Holmes[3] for $\Delta H_f°[H_3PO_4,\ cryst.]$, we obtain a

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[3] Holmes, *Trans. Faraday Soc.*, 1962, **58**, 1916.

[4] National Bureau of Standards, Circular 500, Washington, D.C., 1952.

[5] van Driel and Gerding, *Rec. Trav. chim.*, 1941, **60**, 943.

[6] Lewis and Randall, "Thermodynamics," 2nd edn., McGraw-Hill, New York, 1961.

value of 65·4 ± 2 kcal. mole^{-1} (the large error is due to the uncertainty, in the original reference, of the aqueous hydrobromic acid concentration). The sole reference to a determination of $\Delta H_f°[\mathrm{PBr_5}$, cryst] by way of the synthetic reaction:

$$1/4\mathrm{P_4}(\text{white}) + 5/2\ \mathrm{Br_2}(\text{liq.}) \longrightarrow \mathrm{PBr_5}\quad (\text{in excess of } \mathrm{Br_2})$$

is that of Duus [7] who obtained a value of —58·4 kcal. mole^{-1}. In the experimental procedures of both Duus [7] and Ogier,[8] the product, phosphorus pentabromide, was not obtained in its standard state, but was at least partially dissolved in excess of bromine. In view of this, there are two effects which may cause the measured enthalpy changes to differ from those predicted by the equations:

$$\mathrm{PBr_3}(\text{liq.}) + \mathrm{Br_2}(\text{liq.}) = \mathrm{PBr_5}(\text{cryst.})$$
$$1/4\mathrm{P_4}\ (\text{white}) + 5/2\ \mathrm{Br_2}(\text{liq.}) \longrightarrow \mathrm{PBr_2}(\text{cryst.})$$

These effects are (i) the enthalpy change attendant on dissolution of $\mathrm{PBr_5}$ in bromine; this reaction is probably endothermic (cf. $\Delta H_s[\mathrm{PBr_5}]$ in carbon disulphide), and (ii) the partial formation of perbromo-species such as phosphorus heptabromide; this reaction is probably exothermic. The extent to which either or both of these reactions affect the experimental enthalpy data of Duus [7] and of Ogier [8] cannot be estimated from the available data.

Estimation of Related Thermodynamic Functions.—It is of interest to calculate the lattice energy (U, at 25°) of crystalline phosphorus pentabromide, which has the constitution $\mathrm{PBr_4^+Br^-}$. Since all the structural parameters are known,[9] it is in principle possible to compute a Madelung constant. Hence a value for the lattice energy may be derived by using a Born–Mayer, or similar, expression. This requires an estimate for the repulsion exponent and implies a wholly ionic force-model. The latter assumption is doubtful, and hence it is reasonable, consistent with the accuracy of the method, to use the simpler Kapustinskii [10] equation in the form:

$$U = \frac{287{\cdot}2}{r_C + r_A}\left[1 - \frac{0{\cdot}345}{r_C + r_A}\right] \text{kcal. mole}^{-1}$$

where r_C and r_A are the Goldschmidt cation and anion radii, respectively. An estimate of r_C was made by combining the P–Br distance in $\mathrm{PBr_4^+}$ (2·2 Å) with the van der Waals radius of bromine (1·95 Å). This gives a value of 89 kcal. mole^{-1} for the lattice energy of phosphorus pentabromide. The value is fairly sensitive to the " radius " chosen for the cation $\mathrm{PBr_4^+}$, a 10% increase in r_C causing a 6% decrease in U. The dimensions of the tetraethyl ammonium ion are approximately equal to those of $\mathrm{PBr_4^+}$, and tetraethyl ammonium bromide has a similar lattice energy to $\mathrm{PBr_4^+Br^-}$ (92 kcal. mole^{-1} at 25°, using Kapustinkii's equation). From this, the lattice enthalpy, $\Delta H_L°$, may be found by using the relationships:

$$\Delta H_L° = (U + 2\boldsymbol{R}T), \text{ and } \Delta H_L° = \Delta H_f°[\mathrm{PBr_4^+}, g] + \Delta H_f°[\mathrm{Br^-}, g] - \Delta H_f°[\mathrm{PBr_5}, \text{cryst.}]$$

whence the absolute enthalpy of formation of the complex-ion is +89 kcal. mole^{-1}. Using van Driel and Gerding's value (+9·5 kcal. mole^{-1}) [5] for the latent heat of vaporisation of $\mathrm{PBr_3}$, the reaction $\mathrm{PBr_3(g) + Br^+(g) \longrightarrow PBr_4^+}$ is exothermic to the extent of 181 kcal. mole^{-1}.

A new value for the P–Br mean bond energy, $\bar{E}$, defined by

$$\Delta H = 5\bar{E} = \Delta H_f°[P, g] + 5\Delta H_f°[\mathrm{Br}, g] - \Delta H_f°[\mathrm{PBr_5}, g]$$

can now be evaluated. Using a value quoted by Hartley *et al.* (see Table 2) for the heat of sublimation of $\mathrm{PBr_5}$, and our value for $\Delta H_f°[\mathrm{PBr_5}$, cryst.], we obtain $\bar{E}$ = 50 kcal. mole^{-1}.

[7] Duus, Ph.D. Thesis, Harvard University, 1924.
[8] Ogier, *Compt. rend.*, 1881, **92**, 83.
[9] van Driel and MacGillavry, *Rec. Trav. chim.*, 1943, **62**, 167.
[10] Kapustinskii, *Quart. Rev.*, 1956, **10**, 283.

Unlike the case of phosphorus pentachloride, the available force-constant data do not permit a division of the total energy, ΔH, between axial and equatorial bonds ($\Delta H = 3E_{\text{equat.}} + 2E_{\text{axial}}$).

An estimate of the order of magnitude of the ionisation potential of the PBr_4 species may be made by using the cycle:

$$\begin{tikzcd}
1/4P_4(\text{white}) + 2Br_2(\text{liq.}) \arrow[r, "\Delta H_f^\circ"] \arrow[d, "\Delta H_f^\circ[P, g] + 4\Delta H_f^\circ[Br, g]"] & PBr_4^+(g) \\
P(g) + 4Br(g) & PBr_4(g) \arrow[l, "\Delta H"'] \arrow[u, "\Delta H\ (\text{ionisation})"']
\end{tikzcd}$$

The P–Br bond-lengths in phosphorus tribromide and in the complex PBr_4^+ are closely similar (2·23 and 2·2 Å, respectively). If we assume a similar value in PBr_4, then it is a reasonable approximation to put ΔH, the enthalpy of the step $PBr_4(g) \longrightarrow P(g) + 4Br(g)$, equal to four times the P–Br bond-dissociation energy in phosphorus tribromide, *i.e.*, 4×62 kcal. mole^{-1}. From the above cycle, and with these assumptions, we derive a value of *ca.* 7 ev for the ionisation potential of the hypothetical species PBr_4.

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