Complex Phosphorus Thermochemistry. Volume-Based Thermodynamics and the Estimation of Standard Enthalpies of Formation of Gas phase Ions: $\Delta_f H^\circ(PCl_4^+, g)$ and $\Delta_f H^\circ(PCl_6^-, g)^\dagger$

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Energy-resolved collision-induced dissociation in a flowing afterglow-guided ion beam tandem mass spectrometer has recently enabled the accurate determination of the standard enthalpy of formation of the gaseous phosphorus pentachloride cation, $\Delta_f H^\circ([PCl_4^+], g)$, found to be 414 ± 17 kJ mol^{-1} (giving a value of 378 ± 18 kJ mol^{-1} at 0 K). Such e*xperimental* values for the standard enthalpy of formation of gas phase complex are now being incorporated into the NIST standard reference data program. Such results, can, inter alia, provide a benchmark by which to test earlier computationally based methods which were made to estimate such quantities in the absence of any experimental data. The establishment of this value experimentally also affords us with the opportunity to explore the likely success of newer, simpler approaches. Previous large-scale direct minimization computations to estimate this (and other) standard enthalpies of formation match very well these new experimental results. This paper raises the question as to whether the much simpler volume-based thermodynamics (VBT) approach could yield equally satisfactory results and so circumvent, completely, the need for detailed modeling of the lattices involved. The conclusion is that the VBT approach portrays the extremely complex thermodynamics quite adequately. Thus for the purposes of obtaining basic thermodynamic data, complex modeling of the underlying structures involved may no longer be necessary. At least this should be the case for highly symmetrical ions, like PCl_4^+, where detailed packing with counterions is possibly less important than in other cases and where covalent interactions (less easily modeled) with neighboring ions is unlikely to be strongly featured. Other gaseous complex ion enthalpies of formation are also predicted here.

Introduction

Phosphorus chemistry is often extremely complex. The stereochemistry and bonding of P is very varied, with the element exhibiting at least 14 coordination geometries. Phosphorus forms all three series of halides P_2X_4, PX_3, and PX_5 (X = F, Cl, Br, and I) as well as some mixed halides. It is the chloride of these, in the form of PCl_5 that forms the main subject of this paper. Molecular in the gas phase, ionic in the crystalline phase, $[PCl_4^+][PCl_6^-]$ and the pentachloride is molecularly or ionically dissociated once placed in solution (depending on the solvent). PCl_5 exhibits what we have

termed "ionic isomerism"[1] and a (metastable) phase $[PCl_4^+]_2[PCl_6^-]Cl^-$ results. Accordingly, the underlying thermodynamics of these materials is of considerable interest.

Hao, Sharrett, and Sunderlin[2] have recently reported on the gas phase thermochemistry of the PCl_4^+ ion using energy-resolved, collision-induced dissociation (CID) in a flowing afterglow-guided ion beam tandem mass spectrometer. They determined the standard enthalpy of formation of the gas phase tetrachlorophosphate ion to be: $\Delta_f H^\circ(PCl_4^+, g) = 378 \pm 18$ kJ mol^{-1}.

Since, in the absence of such experimental data, this (and other gaseous ion) values had previously been estimated by

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(1) Jenkins, H. D. B.; Thakur, K. P.; Finch, A.; Gates, P. N. *Inorg. Chem.* **1982**, *21*, 423–426.
(2) Hao, C.; Sharrett, S. M.; Sunderlin, L. S. *Int. J. Mass Spectrometr.* **2007**, *267*, 357–362.

Table 1. Volumes for Key Compounds Discussed in This Paper Derived from Either Crystal Structure Data or Estimated Using Our New Internally-Consistent Ion Volumes[12]

compound	formula unit volume from crystal structure data V_m /nm³	volumes estimated using internally-consistent volume[a] approach for compounds, V_m /nm³ and for single ions, $V(ion)_{ICV}$/nm³	notes
[PCl₄⁺][Cl⁻](s)	$V_m = 0.6361/4 = 0.1590$ ($a = b = 9.24$ Å, $c = 7.45$ Å, $Z = 4$)[b]	$V(PCl_4^+)_{ICV} = 0.1292$	$V(PCl_4^+)_{ICV} = V_m - V(Cl^-)_{ICV}$ $= 0.1590 - 0.0298^a$
[PCl₄⁺][PCl₆⁻](s)	$V_m = 0.6325/2 = 0.3162$ ($a = b = 9.22$ Å, $c = 7.44$ Å, $Z = 2$)[b]	$V(PCl_6^-)_{ICV} = 0.1870$	$V(PCl_6^-)_{ICV} = V_m - V(PCl_4^+)_{ICV}$ $= 0.3162 - 0.1292$
[Me₄N⁺][Br⁻](s)	$V_m = 0.3266/2 = 0.1633$ ($a = b = 7.708$ Å, $c = 5.498$ Å, $Z = 2$)[c]	$V(Me_3N^+)_{ICV} = 0.1270$	$V(Me_3N^+)_{ICV} = V_m - V(Br^-)_{ICV}$ $= 0.1633 - 0.0363^a$
[Me₄N⁺][PCl₆⁻](s)	stable salt but crystal structure not reported; volume estimated in next column	$V_m = 0.3140$	$V_m = V(Me_3N^+)_{ICV} + V(PCl_6^-)_{ICV}$ $= 0.1270 + 0.1870^d$
[K⁺][PCl₆⁻](s)	unstable salt volume estimated in next column	$V_m = 0.2147$	$V_m = V(K^+)_{ICV} + V(PCl_6^-)_{ICV}$ $= 0.0277^a + 0.1870^d$
[Rb⁺][PCl₆⁻](s)	unstable salt volume estimated in next column	$V_m = 0.2184$	$V_m = V(Rb^+)_{ICV} + V(PCl_6^-)_{ICV}^d$ $= 0.0314^a + 0.1870$
[Cs⁺][PCl₆⁻](s)	stable salt but crystal structure not reported; volume estimated in next column	$V_m = 0.2290$	$V_m = V(Cs^+)_{ICV} + V(PCl_6^-)_{ICV}^d$ $= 0.0420^a + 0.1870$
[PBr₄⁺][Br⁻](s)	$V_m = 0.7954/4 = 0.1988$ ($a = 5.663$ Å, $b = 17.031$ Å, $c = 8.247$ Å, $Z = 4$)[e]	$V(PBr_4^+)_{ICV} = 0.1625$	$V(PBr_4^+)_{ICV} = V_m - V(Br^-)_{ICV}$ $= 0.1988 - 0.0363^a$
[PBr₄⁺][Br₃⁻](s)	$V_m = 1.0906/4 = 0.2726$ ($a = 9.35$ Å, $b = 7.94$ Å, $c = 14.69$ Å, $Z = 4$)[e]	$V(Br_3^-)_{ICV} = 0.1101$	$V(Br_3^-)_{ICV} = V_m - V(PBr_4^+)_{ICV}$ $= 0.2726 - 0.1625$

[a] See ref 12. [b] Refs (13) − (16) in ref 4c. [c] See ref 13. This is a recent redetermination of a previous structure investigation. [d] By volume additivity. [e] See ref 14 based on single crystal X-ray diffraction. N.B. For all compounds listed, the ionic strength, $I = 1$.

Table 2. Lattice Energy, U_{POT}/kJ mol⁻¹ and Standard Entropy, $S°_{298}$/J K⁻¹ mol⁻¹

compound	ionic strength, I	volume, V_m/nm³	lattice energy[a], U_{POT} /kJ mol⁻¹	standard entropy[b], $S°_{298}$/J K⁻¹ mol⁻¹	notes
[PCl₄⁺][Cl⁻](s)	1	0.1590	537	231	Latimer's Rules[c] give $S°_{298}$([PCl₄⁺][Cl⁻], s) = 39.5 + (4*34.4) + 36.3 = 213 J K⁻¹ mol⁻¹
[PCl₄⁺][PCl₆⁻](s)	1	0.3162	448	445	Latimer's Rules[c] give $S°_{298}$([PCl₄⁺][PCl₆⁻], s) = 39.5 + (4*34.4) + 39.5 + (6*37.2) = 440 J K⁻¹ mol⁻¹
[PBr₄⁺][Br⁻](s)	1	0.1988	506	285	Latimer's Rules[c] give $S°_{298}$([PBr₄⁺][Br⁻], s) = 39.5 + (4*50.8) + 50.3 = 293 J K⁻¹ mol⁻¹
[PBr₄⁺][Br₃⁻](s)	1	0.2726	466	385	Latimer's Rules[c] give $S°_{298}$([PBr₄⁺][PBr₃⁻], s) = 39.5 + (4*50.8) + 39.5 + (3*44.7) = 416 J K⁻¹ mol⁻¹
[Me₄N⁺][Br⁻](s)	1	0.1633	533	237	not estimable from Latimer's Rules[c]
[Me₄N⁺][PCl₆⁻](s)	1	0.3140	449	442	not estimable from Latimer's Rules[c]
[K⁺][PCl₆⁻](s)	1	0.2147	496	307	Latimer's Rules[c] give $S°_{298}$([K⁺][PCl₆⁻], s) = 46.4 + (6*37.2) = 270 ± 0.8 J K⁻¹ mol⁻¹
[Rb⁺][PCl₆⁻](s)	1	0.2184	493	312	Latimer's Rules[c] give $S°_{298}$([Rb⁺][PCl₆⁻], s) = 59.2 + (6*37.2) = 282 ± 0.5 J K⁻¹ mol⁻¹
[Cs⁺][PCl₆⁻](s)	1	0.2290	487	326	Latimer's Rules[c] give $S°_{298}$([Cs⁺][PCl₆⁻], s) = 67.9 + (6*37.2) = 291 ± 3.7 J K⁻¹ mol⁻¹

[a] Equation 1 with $\alpha = 117.3$ kJ mol⁻¹ nm; $\beta = 51.9$ kJ mol⁻¹. [b] Equation 5 with $k = 1360$ J K⁻¹ mol⁻¹ nm⁻³; $c = 15$ J K⁻¹ mol⁻¹. [c] Using Mill's parameters[15] and Latimer's Rules.[16]

use of Born−Fajans−Haber thermochemical cycles,[3] this new experimental route offers us a means of assessment of the quality of the earlier, computationally based, studies.

Derivation of *gas-phase* energetics from solid state lattice energy calculations offers an "across-phase" comparison of two types of thermochemical data and is therefore particularly testing of the thermodynamics involved.

The history of lattice energy estimation in the field of phosphorus chemistry (and in particular with regard to the above solid-state modifications of phosphorus (V) chloride)[1,4] is an interesting one. It progressed, largely through the medium of this journal, by employing increasingly sophis-

ticated levels[1,4,5] of computation and modeling protocols. The first known example of pressure-induced ionization in solids and the varying phase modifications of PCl₅ were used to estimate thermodynamic data[1] for the gaseous PCl₄⁺ and PCl₆⁻ ions. Values of $\Delta_f H°(PCl_4^+, g) = 462.4$ kJ mol⁻¹ and $\Delta_f H°(PCl_6^-, g) = -880.4$ kJ mol⁻¹ were initially reported. By 1996 it was possible to study extremely complex lattices, and computation of lattice potential energies, U_{POT}, using

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(4) (a) Finch, A.; Gates, P. N.; Jenkins, H. D. B.; Thakur, K. P. *J. Chem. Soc., Chem. Commun.* **1980**, 579−580. (b) Finch, A.; Gates, P. N.; Muir, A. S. *J. Chem. Soc., Chem. Commun.* **1981**, 812. (c) Jenkins, H. D. B.; Sharman, L.; Finch, A.; Gates, P. N. *Inorg. Chem.* **1996**, *35*, 6316−6326.

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Table 3. Estimation of $\Delta_r H(30)$, $\Delta_r S(30)$, and $\Delta_r G(30)$ for Decomposition Reaction 30

M	$\Delta_f H°(M^+, g)^a$ kJ mol^{-1}	$U_{POT}(MPCl_6, s)^b$ kJ mol^{-1}	$\Delta_f H°(MCl, s)^a$ kJ mol^{-1}	$\Delta_r H°(30)$ kJ mol^{-1}	$S°(MCl, s)^a$ J K^{-1} mol^{-1}	$S°(MPCl_6, s)^b$ J K^{-1} mol^{-1}	$\Delta_r S°(30)$ J K^{-1} mol^{-1}	$\Delta_r G°(30)$ kJ mol^{-1}
K	514.3	496	−436.7	−79 ± 5	82.6	307	+7	−81 ± 5
Rb	490.1	493	−435.3	−57 ± 5	95.9	312	+15	−61 ± 5
Cs	458.0	487	−443.0	−37 ± 5	101.2	326	+6	−39 ± 5

^{a} NBS value, ref 24. ^{b} From Table 2.

large mainframe computers was, by then, well-developed[5] especially for species containing complex ions like PCl_4^+ and PCl_6^-. The direct minimization methods derived by Jenkins and Pratt,[5] were tailor-made to study such complex lattices, employing the new strategy of using multiple minimization conditions involving the individual lattice parameters.[5c] Such calculations represented state of the art at that time and yielded[4c] revised values of $\Delta_f H°(PCl_4^+, g) = 384 ± 10$ kJ mol^{-1} and $\Delta_f H°(PCl_6^-, g) = -813 ± 10$ kJ mol^{-1}, which we now find are substantially in agreement with the latest experimental work.[2] Such a result increases our confidence that other calculations made during that era of gas-phase thermochemical data are likely to be satisfactory also.

In the intervening decade, much progress was made. The main result has been vast simplification made to this type of calculation. Based initially on work by Mallouk and Bartlett,[6] a *volume-based* approach to thermodynamics (VBT) has evolved[7] and has given rise to the following equations:

−for materials with lattice energies which are *less than* 5000 kJ mol^{-1}:

$$U_{POT}/\text{kJ mol}^{-1} \approx 2I[\alpha/(V_m/\text{nm}^3)^{1/3} + \beta] \quad (1)$$

where U_{POT} is the lattice energy, I is the ionic strength factor,[8,9] and α and β are stoichiometrically dependent[7a] constants, though α varies only marginally in value.

−U_{POT} can also be related to density, ρ_m, such that the analogous equation is

$$U_{POT}/\text{kJ mol}^{-1} \approx \gamma[(\rho_m/\text{g cm}^{-3})/(M_m/\text{g})]^{1/3} + \delta \quad (2)$$

with related stoichiometrically dependent constants,[8b] γ and δ (in this form, also incorporating the ionic strength factor, I, simply for convenience).

−for ionic materials with lattice energies *greater than* 5000 kJ mol^{-1}, the equation[7e] takes a generalized form, with no fitted constants:

$$U_{POT}/\text{kJ mol}^{-1} \approx AI[2I/(V_m/\text{nm}^3)]^{1/3} \quad (3)$$

where A (= 121.4 kJ mol^{-1}) is a standard electrostatic constant or, in terms of density,

$$U_{POT}/\text{kJ mol}^{-1} \approx B[(I^4\rho_m/\text{g cm}^{-3})/(M_m/\text{g})]^{1/3} \quad (4)$$

where $B = 1291.7$ kJ mol^{-1}. VBT can even encompass the lattice energy of partially covalent materials.[10a] Very recently Tudela[10b] has suggested the use of the relationship 5

$$\frac{U_{POT}(\text{Compound 1})}{U_{POT}(\text{Compound 2})} \approx \frac{[V_m(\text{Compound 2})]^{1/3}}{[V_m(\text{Compound 1})]^{1/3}} \quad (5)$$

for isostructural compounds having a degree of covalency, to predict their lattice energies.

−standard entropy, $S°_{298}$, is closely linearly dependent on molar volume, V_m[11a,b]

$$S°_{298}/\text{J K}^{-1}\text{ mol}^{-1} \approx k(V_m/\text{nm}^3\text{ formula unit}^{-1}) + c \quad (6)$$

where k and c are constants.[11c]

−the latter relation can similarly be expressed in terms of density,[7i] ρ,

$$S°_{298}/\text{J K}^{-1}\text{ mol}^{-1} \approx k'[(M/\text{g})/(\rho/\text{g cm}^{-3})] + c \quad (7)$$

where k' is a related constant[11d] and M is the formula mass of the ionic material.

As this paper shows, at one level one is now able to tackle problems relating to the phosphorus halides and to lattice energy and enthalpy of formation estimation in general, in a much more direct and simplified manner which is computationally less intensive. No longer is use of a large mainframe necessary, nor is there need to input atomic coordinates or develop sophisticated structural models or

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(8) (a) I is the ionic strength factor[8] where $I = {}^1\!/_2\Sigma n_i z_i^2$ where n_i is the number of ions in the formula unit having a charge z_i and α and β take the values given in Table 1, ref 7a, for the various stoichiometries listed (1:1, 2:1, 1:2, or the general p:q) while in the case of 2:2 salts the values in ref 7h should be adopted. (b) For values of γ and δ for individual stoichiometries see Table 1, ref 7g.

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(10) (a) Glasser, L.; von Szentpály, L. *J. Am. Chem. Soc.* **2006**, *128*, 12314–12321. (b) Tudela, D. *J. Chem. Educ.* **2008**, *85*, 863–865.

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representations for the complex ions involved, securing convergence in complex lattice sums no longer is an issue—a simple hand-held calculator or spreadsheet is now all that is required. At another level one must not underrate the computationally intensive approach for its ability to give insight into subtleties which are manifest in the energetics of polymorphic inorganic materials and in local energy defects in ways that are clearly not accessible to VBT.

VBT Calculations. Table 1 assembles the crystal structure data available for the various phosphorus salts and related materials at the level required for VBT calculations.

Estimation of Volumes of Salts and Individual Ions Using Our Internally−Consistent Ion Volumes. Recently we have reported some (optimized) single ion volumes, V_{ICV} (see Table 1, ref 11), and using this set we have used the principles of ion volume additivity to obtain the following complex ion volumes (see descriptive notes in Table 1 above):

$$V(PCl_4^+)_{ICV} = 0.1292 \text{ nm}^3 \quad (8)$$

$$V(PCl_6^-)_{ICV} = 0.1870 \text{ nm}^3 \quad (9)$$

$$V(PBr_4^+)_{ICV} = 0.1625 \text{ nm}^3 \quad (10)$$

$$V(Me_3N^+)_{ICV} = 0.1270 \text{ nm}^3 \quad (12)$$

$$V(Br_3^-)_{ICV} = 0.1101 \text{ nm}^3 \quad (13)$$

We are able, using our Isomegethic (volume additivity) rule[7j,l] to reproduce, well, known crystal structure volumes of two extremely complex phosphorus salts: $[PCl_4^+]_2$-$[PCl_6^-][Cl^-]$ ($a = 8.798$ Å, $b = 8.4765$ Å, $c = 12.3683$, $\beta = 92.751°$, $Z = 2$ for which $V_m = V_{cell}/Z = 0.461$ nm^3) and $[PCl_4^+]_2[PCl_6^-][Br^-]$ ($a = b = 8.7472$ Å, $c = 12.3281$, $Z = 2$ for which $V_m = V_{cell}/Z = 0.471$ nm^3, thus

$$V_m\{[PCl_4^+]_2[PCl_6^-][Cl^-]\} \approx 2V(PCl_4^+)_{ICV} + V(PCl_6^-)_{ICV} +$$
$$V(Cl^-)_{ICV} \approx 2(0.1292) + (0.1870) + 0.0298 \approx 0.475 \text{ nm}^3 \quad (14)$$

this prediction being only 3.0% in error and

$$V_m\{[PCl_4^+]_2[PCl_6^-][Br^-]\} \approx 2V(PCl_4^+)_{ICV} + V(PCl_6^-)_{ICV} +$$
$$V(Br^-)_{ICV} \approx 2(0.1292) + (0.1870) + 0.0363 \approx 0.482 \text{ nm}^3 \quad (15)$$

being some 2.3% in error.

VBT Study of More Complex Lattices. Table 2 gives the results for some lattice potential energies, U_{POT}/kJ mol^{-1} and standard entropies, $S°_{298}$/ J K^{-1} mol^{-1} as estimated for 1:1 lattices, using the VBT approach[6,7]

Complex salts like $[PCl_4^+]_2[PCl_6^-][Cl^-]$ and $[PCl_4^+]_2$-$[PCl_6^-][Br^-]$ are not yet amenable to treatment via the simple lattice energy−volume relationships of VBT developed so far and use of the generalized values given[7a] for α and β are unlikely to be effective either. However, a simple

approach based on Yoder's[17] simple salt approximation (SSA), where lattice enthalpies of complex salts (usually minerals, in the original application) are approximated by their simpler additive counterpart lattice potential energies which are estimated in Table 2, is thus

$$U_{POT}\{[PCl_4^+]_2[PCl_6^-][Cl^-]\} \approx U_{POT}\{[PCl_4^+][PCl_6^-]\} +$$
$$U_{POT}\{[PCl_4^+][Cl^-]\} = 448 + 537 = 985 \text{ kJ mol}^{-1} \quad (16)$$

$$U_{POT}\{[PCl_4^+]_2[PCl_6^-][Br^-]\} \approx U_{POT}\{[PCl_4^+][PCl_6^-]\} +$$
$$U_{POT}\{[PCl_4^+][Br^-]\} = 448 + 506 = 954 \text{ kJ mol}^{-1} \quad (17)$$

Consideration of a Born−Fajans−Haber cycle shows that, provided the enthalpy change for the solid state reactions (X = Cl, Br)

$$[PCl_4^+]_2[PCl_6^-][X^-](s) \rightarrow [PCl_4^+][PCl_6^-](s) +$$
$$[PCl_4^+][Cl^-](s) \quad (18)$$
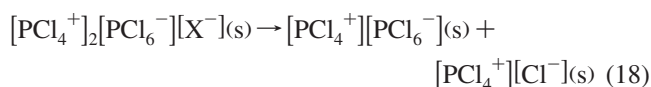
are relatively small, then the SSA approximation should work reasonably well.

Compared to previous estimates of these lattice enthalpies, made using large-scale LATEN[18−20] computations [4d] which estimated that

$$U_{POT}\{[PCl_4^+]_2[PCl_6^-][Cl^-]\} \approx 1038 \pm 5 \text{ kJ mol}^{-1} \quad (19)$$

and

$$U_{POT}\{[PCl_4^+]_2[PCl_6^-][Br^-]\} \approx 1013 \pm 5 \text{ kJ mol}^{-1} \quad (20)$$

the former estimates are some 5.1% and 5.8% different, respectively. Alternatively, estimates made using Glasser's extension[9] of the Kapustinskii equation[21] (designed to handle more complex lattices) leads to estimates

$$U_{POT}\{[PCl_4^+]_2[PCl_6^-][Cl^-]\} \approx 992 \pm 43 \text{ kJ mol}^{-1} \quad (21)$$

and

$$U_{POT}\{[PCl_4^+]_2[PCl_6^-][Br^-]\} \approx 975 \pm 43 \text{ kJ mol}^{-1} \quad (22)$$

and these are some 1.0% and 2.2% different from the large-scale computational results in eqs 19 and 20, respectively.

The entropy *changes*, $\Delta_r S(18)$, for solid state reactions of the type (18) are anticipated to be close to zero and thus simple additive approximations in the form

$$S°_{298}\{[PCl_4^+]_2[PCl_6^-][Cl^-]\} \approx S°_{298}\{(PCl_4^+)(PCl_6^-)\} +$$
$$S°_{298}\{(PCl_4^+)(Cl^-)\} = 445 + 231 = 676 \text{ J K}^{-1} \text{ mol}^{-1} \quad (23)$$

$$S°_{298}\{[PCl_4^+]_2[PCl_6^-][Br^-]\} \approx S°_{298}\{(PCl_4^+)(PCl_6^-)\} +$$
$$S°_{298}\{(PCl_4^+)(Br^-)\} = 445 + 285 = 730 \text{ J K}^{-1} \text{ mol}^{-1} \quad (24)$$

are then appropriate.

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VBT Calculations of Standard Enthalpies of Formation of Gaseous Ions. [Me₄N⁺][PCl₆⁻](s). Consideration of the salt $[Me_4N^+][PCl_6^-]$ together with a knowledge of its experimental[22] standard enthalpy of formation, $\Delta_fH°([Me_4N^+][PCl_6^-], s) = -736 \pm 5$ kJ mol⁻¹, leads, in the context of a Born−Fajans−Haber cycle (see Figure 3 in ref 4d), to the relationship

$$[\Delta_fH°([Me_4N^+], g) + \Delta_fH°([PCl_6^-], g)]$$

$$= U_{POT}([Me_4N^+][PCl_6^-]) + 2RT +$$
$$\Delta_fH°([Me_4N^+][PCl_6^-], s)$$

$$= 449 + 4.9 - 736$$

$$= -282.1 \pm 5 \text{ kJ mol}^{-1} \qquad (25)$$

whereupon, since experimentally[23] it has been established that

$$\Delta_fH°([Me_4N^+], g) = 536 \text{ kJ mol}^{-1} \qquad (26)$$

using the lattice potential energy of $[Me_4N^+][PCl_6^-]$ estimated via VBT (Table 2) provides us with the estimate that:

$$\Delta_fH°([PCl_6^-], g) = -818 \pm 5 \text{ kJ mol}^{-1} \qquad (27)$$

This compares well to the value, $\Delta_fH°([PCl_6^-], g) = -813 \pm 10$ kJ mol⁻¹ obtained, previously, using our direct minimization protocol.[4d]

[PCl₄⁺][PCl₆⁻](s). Consideration of the salt $[PCl_4^+][PCl_6^-]$ and knowledge of its experimental[24] standard enthalpy of formation, $\Delta_fH° [PCl_4^+][PCl_6^-] = 2\Delta_fH°(PCl_5, s) = -887$ kJ mol⁻¹, leads, in the context of a Born−Fajans−Haber cycle (see Figure 2 of ref 4d), to the relationship

$$[\Delta_fH°([PCl_4^+], g) + \Delta_fH°([PCl_6^-], g)]$$

$$= U_{POT}([PCl_4^+][PCl_6^-]) +$$
$$2RT + \Delta_fH°([PCl_4^+][PCl_6^-], s)$$

$$= 448 + 4.9 - 887$$
$$= -434.1 \text{ kJ mol}^{-1} \qquad (28)$$

Using the value determined above for $\Delta_fH°([PCl_6^-], g)$ and using the lattice potential energy of $[PCl_4^+][PCl_6^-]$ estimated using VBT (Table 2), we conclude that

$$\Delta_fH°([PCl_4^+], g) = 384 \pm 5 \text{ kJ mol}^{-1} \qquad (29)$$

This is exactly the value estimated in our previous extended study[4d] also agreeing well with the new experimental value reported, at 0 K, by Hao, Sharrett, and

Sunderlin[2] of $\Delta_fH°([PCl_4^+], g) = 378 \pm 17$ kJ mol⁻¹. A previously estimated value made by Jolly and Gin,[25] based on comparisons made with the isoelectronic $SiCl_4$ molecule, led to a higher value of $\Delta_fH°([PCl_4^+], g) = 430 \pm 40$ kJ mol⁻¹.

Stability of Alkali Metal Phosphates. In previous excursions[4d] into phosphorus chemistry we identified the decomposition route for unstable alkali metal hexachlorophosphates as being most likely

$$MPCl_6(s) \xrightarrow{\Delta_rG(30)} MCl(s) + PCl_5(s) \qquad (30)$$
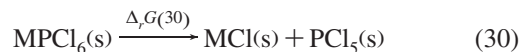
This conclusion is based on the observed diffraction pattern for the alkali metal chloride, MCl, as identified in the residue from the decomposition of known unstable hexachlorophosphate materials. We further predicted that the only salt likely to be stable (although borderline) would be $CsPCl_6$. An abortive attempt, reported in ref 4c, at the synthesis of $CsPCl_6$ was later followed by some successful synthetic work by Muir[26]—the stable cesium salt we had predicted[4c] was indeed prepared and characterized. The equations needed for the estimation of $\Delta_rG(30)$ are established, progressively, below using VBT data and are

$$\Delta_rG(30) = \Delta_rH(30) - T\Delta_rS(30) \qquad (31)$$

$$\Delta_rH(30) = U_{POT}(MPCl_6) + {}^{1}\!/_2RT - \Delta_fH°(M^+, g) -$$
$$\Delta_fH°(PCl_6^-, g) + \Delta_fH°(MCl, s) + \Delta_fH°(PCl_5, s) \quad (32)$$

Substituting data for $\Delta_fH°(PCl_6^-, g)$, $\Delta_fH°(PCl_5, s)$, and the RT term we have

$$\Delta_rH(30)/\text{kJ mol}^{-1} = (376 \pm 5) + U_{POT}(MPCl_6) -$$
$$\Delta_fH°(M^+, g) + \Delta_fH°(MCl, s) \quad (33)$$

A decomposition of an hexachlorophosphate resulting from reaction 30 will be enthalpy, rather than entropy, driven. In fact, $\Delta_rS(30)$, is anticipated to be small by consideration of the nature of this solid state reaction.

$$\Delta_rS(30) = S°(PCl_5, s) + S°(MCl, s) - S°(MPCl_6, s) \quad (34)$$

and substituting data for $S°(PCl_5, s)$

$$\Delta_rS(30)/\text{J K}^{-1} \text{ mol}^{-1} = 231 + S°(MCl, s) - S°(MPCl_6, s) \quad (35)$$

Table 3 shows the evaluation of $\Delta_rH(30)$, $\Delta_rS(30)$, and $\Delta_rG(30)$ for the cases where M = K, Rb, and Cs.

From these estimates we see that: Thermodynamically, $CsPCl_6$ has a much lesser tendency ($\Delta_rG(30)/\text{kJ mol}^{-1} = -39$) to decompose than have either $RbPCl_6$ ($\Delta_rG(30)/\text{kJ mol}^{-1} = -61$) or $KPCl_6$ ($\Delta_rG(30)/\text{kJ mol}^{-1} = -81$) which are clearly unstable.

In our original paper[7a] the anticipated error in the lattice energy calculation of salts like $KAsF_6$ was about 3% (see Table 7, ref 7a); this would suggest an error in $U_{POT}(CsPCl_6)$ of some 15 kJ mol⁻¹. The NBS tables[24] state that their values

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have an overall uncertainty of "between 2 and 20 units of the last figure". Thus, $\Delta_f H°(Cs^+, g)$ and $\Delta_f H°(CsCl, s)$ could both be reasonably assumed to have errors of between 0.2 and 2 kJ mol^{-1}, so that $\Delta_r G(30)$ for the cesium salt could thus have an error amounting to approximately 25 kJ mol^{-1}. We conclude therefore that (on the basis of VBT considerations) the stability of $CsPCl_6$ is, at very least, extremely borderline (which may explain the difficulty we had making the compound).

Conclusions

VBT appears, as judged from these results, to provide a satisfactory account of the key thermodynamics involved in this complex area of phosphorus chemistry when compared to the more sophisticated procedures. The anticipation is that VBT can now offer an alternative approach to the extended protocols involving more computationally intensive methods. It delivers comparable results and conclusions with considerable simplicity and within a fraction of the time, although it does not permit the evaluation of the different components which make up the lattice energy (ionic, covalent, dispersion, etc.). VBT will be particularly appealing to non-specialists (as well as offering a new pedogogical perspective) and it offers us a straightforward means of estimating thermodynamic data for both hypothetical (e.g., $KPCl_6$ and $RbPCl_6$) as well as for established materials.