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A PREDICTION RULE FOR THE STANDARD ENTHALPIES OF FORMATION ($-\Delta H_f^{\ominus}$) OF PHOSPHATE ALKALI SALTS $M_{n+2-x}H_xP_nO_{3n+1}$

PHILIP J. POMONIS and ANTONIOS T. SDOUKOS

Department of Chemistry, University of Ioannina 45110 (Greece)

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ABSTRACT

By using the relationship between the standard enthalpies of formation ($-\Delta H_f^{\ominus}$) and the mean Sanderson electronegativity $\bar{S}$ of polyphosphate alkali salts $M_{n+2-x}H_xP_nO_{3n+1}$ for $n = 1$, 2, 3 and 4, it is possible to predict the corresponding values of ($-\Delta H_f^{\ominus}$) for the higher members of the series with $n = 5$, 6, 7, etc. This becomes feasible by exploring the additive regularities observed for each homologous series. Relationships are proposed which can be used to calculate enthalpy values for a particular cation within 1–2% accuracy limits.

INTRODUCTION

The standard enthalpies of formation ($-\Delta H_f^{\ominus}$) of the first members ($n = 1$, 2, 3 and 4) of the alkali substituted polyphosphate salts $M_{n+2-x}H_xP_nO_{3n+1}$, where M = Li, Na, K, Rb, and Cs, have been summarized in a monograph [1]. However, for the higher members of the series ($n > 4$) there is a lack of data, apparently due to the complexity of the molecules. In searching for a way to estimate those unknown values, we observed that, for constant n, substitution of x alkali metals by hydrogen affects the molecular weight W as well as the mean electronegativity $\bar{S}$ of the molecule. This last quantity was introduced by Sanderson [2], and for a polyatomic molecule is given by

$$\bar{S} = \left[\Pi S_i^{v_i}\right]^{1/\Sigma v_i} \qquad (1)$$

where S_i is the electronegativity of element i participating in the compound under a stoichiometric coefficient v_i. Many authors have successfully correlated $\bar{S}$ with different experimental results for aluminosilicates, such as their acidic properties and the shift of frequencies of vibration of species adsorbed on them [3–5]. Regularities in patterns of the form ($-\Delta H_f^{\ominus}$) = f(molecular weight) have been used by Woolf [6] to estimate heats of formation for inorganic fluorine compounds. Both these methods, i.e. based

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on molecular weight or mean electronegativity, appear very promising in describing some fundamental properties of compounds forming homologous series by using a very limited input, namely the atomic weights or elemental electronegativities. As will be seen in the next section, both methods give similar results for $(-\Delta H_f^{\ominus})$ values of compounds of the $M_{n+2-x}H_xP_nO_{3n+1}$ series. Further, the mean electronegativity values, $\bar{S}$, can probably be used in estimating the proton activity of such compounds [7], according to the suggestion of Sanderson [2], via the well-known equation $q_H = (\bar{S} - S_H)/(2.08\ S_H^{1/2})$, which provides an estimate of the average partial charge on hydrogen atoms. This possibility becomes particularly promising in the light of SAPO compounds, i.e. molecular sieves consisting of Si, Al, P and O atoms, prepared recently by the Union Carbide group [8] and used subsequently as catalysts by many workers in the field [9]. We shall not discuss this matter further for the moment, turning our attention instead to the calculation of enthalpies of formation of polyphosphate compounds.

DISCUSSION

Graphs of $(-\Delta H_f^{\ominus})$ versus $\bar{S}$ and versus W for Cs polyphosphates are shown as an example in Fig. 1, although similar graphs can be drawn for any other alkali salt. From this figure it is observed that for a certain n, say 4 or 3, the corresponding members of the series fall on a straight line within a reasonable deviation. Secondly, from the data of ref. 1, as shown in Table 1, it may be seen that the differences $(-\Delta H_f^{\ominus})$ between the acid $H_{n+2}P_nO_{3n+1}$ and the fully substituted form $M_{n+2}P_nO_{3n+1}$ of the phosphates for $n = i$ and $n = i + 1$ tend to the values of $(-\Delta H_f^{\ominus})$ for HPO_3 or MPO_3 shown in the same table. In other words, for the higher members of the phosphate series, it seems that the heat of reaction for the additions

$$M_{n+1}P_{n-1}O_{3n-2} + MPO_3 \rightarrow M_{n+2}P_nO_{3n+1} \tag{2}$$

$$H_{n+1}P_{n-1}O_{3n-2} + HPO_3 \rightarrow H_{n+2}P_nO_{3n+1} \tag{3}$$

tends to zero. Therefore the enthalpy of the compounds $M_{n+2}P_nO_{3n+1}$ and $H_{n+2}P_nO_{3n+1}$ can easily be found by successive additions of $(-\Delta H_f^{\ominus})_{MPO_3}$ and $(-\Delta H_f^{\ominus})_{HPO_3}$ to $(-\Delta H_f^{\ominus})_{M_6P_4O_{13}}$ and $(-\Delta H_f^{\ominus})_{H_6P_4O_{13}}$, correspondingly, which are the highest experimentally known values for the series. In other words

$$(-\Delta H_f^{\ominus})_M = (-\Delta H_f^{\ominus})_{M_3PO_4} + (n-1)(-\Delta H_f^{\ominus})_{MPO_3} \tag{4}$$

and

$$(-\Delta H_f^{\ominus})_H = (-\Delta H_f^{\ominus})_{H_3PO_4} + (n-1)(-\Delta H_f^{\ominus})_{HPO_3} \tag{5}$$

This result is actually not strange, as similar behaviour has been observed in other series-forming compounds, such as n-alkanes, for which $(-\Delta H_f^{\ominus})_{C_nH_{2n+2}} = (-\Delta H_f^{\ominus})_{CH_4} + 20.5\ (n-1)$.

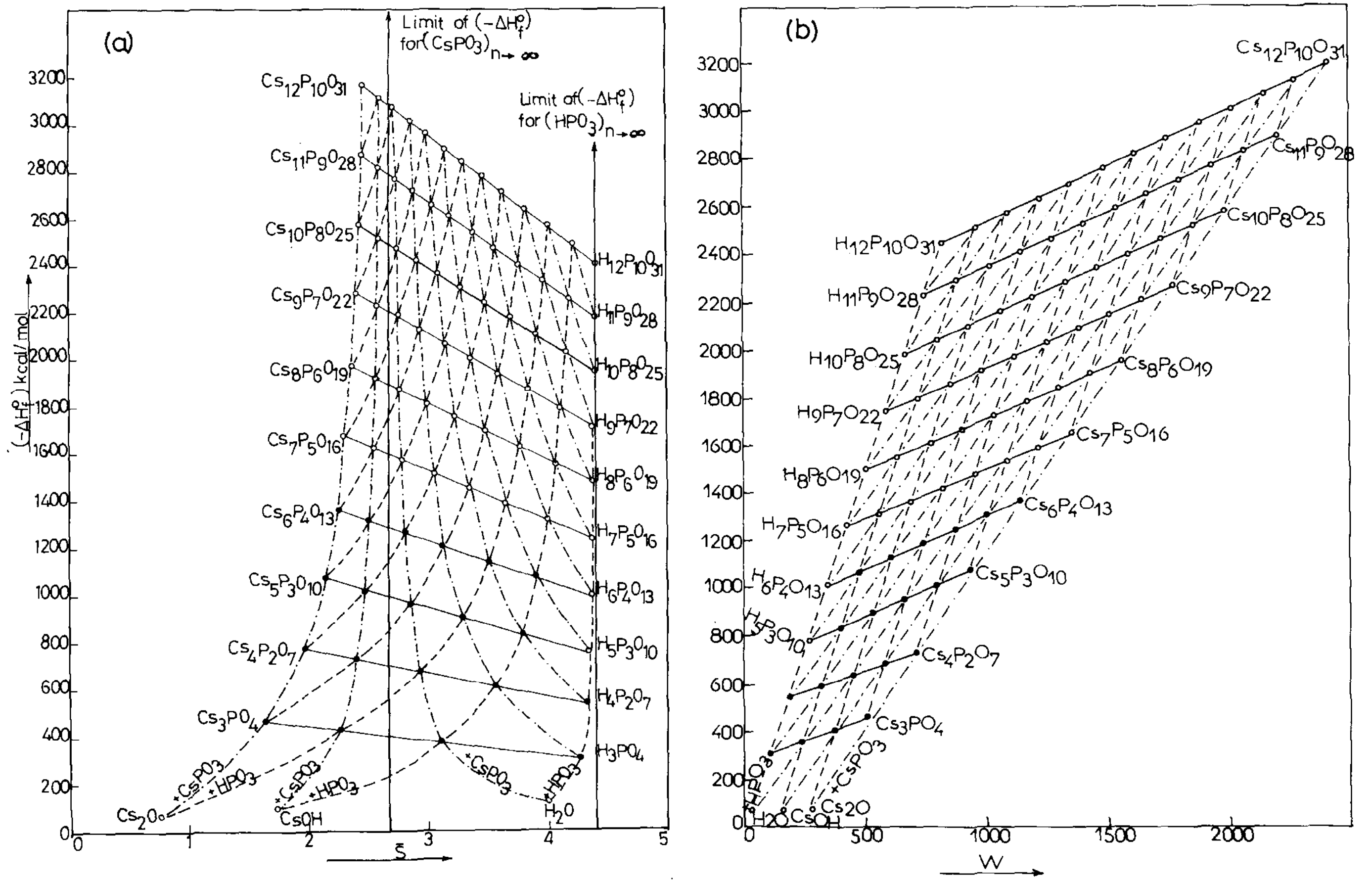

Fig. 1. Graphs of standard enthalpies of formation $(-\Delta H_f^{\ominus})$ of phosphoric acid salts of Cs versus (a) the mean electronegativity $\bar{S}$ and (b) the molecular weight W of the corresponding compound. Filled circles are experimental values. Open circles are values calculated by the method described in the text. (------) and (·–·–·) connect members of the family made up from the previous compound by addition of the HPO_3 or $CsPO_3$ group, respectively.

TABLE 1

Differences $\delta(-\Delta H_f^\ominus)$, between the standard enthalpies of formation of two successive members of the series of phosphate salts: $(-\Delta H_f^\ominus)_{M_{n+3}P_{n+1}O_{3n+4}} - (-\Delta H_f^\ominus)_{M_{n+2}P_nO_{3n+1}}$

Substances	δ value					
	Na	K	Li	Rb	Cs	H
$M_4P_2O_7 - M_3PO_4$	300.8	304	316	305	305	230
$M_5P_3O_{10} - M_4P_2O_7$	297	299	310	300	299	220 [a]
$M_6P_4O_{13} - M_5P_3O_{10}$	286	294	301	290	289	240 [a]
$(-\Delta H_f^\ominus)$ for MPO_3	286.6	297 [b]; 294	302	298	300	233

[a] Estimated.

[b] Two values calculated from different sources.

In this way it is possible to define the two extreme lines of the graphs, i.e. for the free acid and the fully substituted form. Then the intermediate members for any particular n fall on the straight line joining the two extreme forms. As a result, the corresponding $(-\Delta H_f^\ominus)$ values can be defined as the points of intersection of those straight lines with the corresponding values of $\bar{S}$ or W, which are easily found. In this way we obtain the 'trees' shown in Fig. 1 for Cs-substituted phosphoric salts. Similar 'trees' are easily obtained for the other alkalis, Rb, K, Na and Li.

Now, every point shown in the tree of any particular alkali metal can be described by an algebraic equation, which can be easily derived by using the above noted regularities exploited for its development. These regularities in algebraic form, and for the electronegativity-based calculation, are

$$(-\Delta H_f^\ominus)_{M-H} = (-\Delta H_f^\ominus)_H + A(S_H - S_{M-H}) \tag{6}$$

$$A = \frac{(-\Delta H_f^\ominus)_M - (-\Delta H_f^\ominus)_H}{\bar{S}_H - \bar{S}_M} \tag{7}$$

where the subscripts H, M and M − H correspond to the acid and to the fully and partially substituted form of the phosphoric salts.

Similarly, for the molecular weight-based calculations we have

$$(-\Delta H_f^\ominus)_{M-H} = (-\Delta H_f^\ominus)_H + A(W_{M-H} - W_H) \tag{8}$$

$$A = \frac{(-\Delta H_f^\ominus)_M - (-\Delta H_f^\ominus)_H}{W_M - W_H} \tag{9}$$

Now, according to eqn. (1), the value of $\bar{S}$ for any salt of the form $M_{n+2-x}H_xP_nO_{3n+1}$ is given by the equation

$$\bar{S} = \left(S_M^{n+2-x} S_H^x S_P^n S_O^{3n+1}\right)^{1/(5n+3)} \tag{10}$$

TABLE 2

Standard enthalpies of formation ($-\Delta H_f^{\ominus}$) of alkali phosphate salts calculated from eqns. (14) and (15) (first and third column for each cation, respectively). In parentheses (second column for each cation) are the experimental values where they are known

Formula	($-\Delta H_f^{\ominus}$) (kcal mol^{-1})				
	Li	Na	K	Rb	Cs
H_3PO_4	310(310)310	310(310)310	310(310)310	310(310)310	310(310)310
MH_2PO_4	378(386)366	370(369)360	378(378)363	380(379)363	382(381)363
M_2HPO_4	435(430)424	420(417)410	430(427)416	432(430)416	433(432)417
M_3PO_4	481(482)481	460(460)460	470(470)470	471(471)471	472(473)472
$H_4P_2O_7$	543(540)543	543(540)543	543(540)543	543(540)543	543(540)543
$MH_3P_2O_7$	614(632)603	604(603)594	613(614)599	615(616)599	618(618)600
$M_2H_2P_2O_7$	677(696)663	657(663)644	672(676)654	676(678)656	680(678)657
$M_3HP_2O_7$	733(746)723	704(711)695	723(724)710	726(726)712	730(728)715
$M_4P_2O_7$	783(798)783	746(761)746	766(774)766	769(776)769	772(778)772
$H_5P_3O_{10}$	776(–)776	776(–)776	776(–)776	776(–)776	776(–)776
$MH_4P_3O_{10}$	849(868)838	837(828)827	847(838)833	850(844)834	853(845)835
$M_2H_3P_3O_{10}$	910(933)900	892(899)878	911(906)890	915(907)892	920(908)894
$M_3H_2P_3O_{10}$	977(993)961	943(947)930	967(967)948	972(965)951	978(966)954
$M_4HP_3O_{10}$	1033(1050)1023	990(1001)981	1018(1021)1005	1023(1020)1009	1028(1020)1013
$M_5P_3O_{10}$	1085(1108)1085	1032(1056)1032	1062(1073)1062	1067(1976)1067	1072(1077)1072
$H_6P_4O_{13}$	1009(–)1009	1009(–)1009	1009(–)1009	1009(–)1009	1009(–)1009
$MH_5P_4O_{13}$	1083(1105)1072	1070(1053)1060	1081(1064)11067	1084(1073)1068	1087(1074)1069
$M_2H_4P_4O_{13}$	1153(1173)1135	1127(1118)1112	1147(1135)1125	1152(1138)1128	1157(1139)1130
$M_3H_3P_4O_{13}$	1217(1236)1198	1180(1178)1163	1208(1200)1183	1213(1200)1187	1220(1200)1198
$M_4H_2P_4O_{13}$	1278(1297)1261	1229(1236)1215	1262(1261)1242	1269(1258)1246	1277(1258)1251
$M_5HP_4O_{13}$	1334(1354)1324	1275(1290)1266	1312(1215)1300	1319(1313)1306	1327(1313)1311
$M_6P_4O_{13}$	1387(1409)1387	1318(1342)1318	1358(1367)1358	1365(1366)1365	1372(1366)1372

whereas the molecular weight W of the same compound will be

$$W = (n+2-x)w_{\mathrm{M}} + xw_{\mathrm{H}} + nw_{\mathrm{P}} + (3n+1)w_{\mathrm{O}} \tag{11}$$

where w_i is the atomic weight of the element i. Then from eqns. (6), (7) and (10) we obtain

$$\begin{aligned}(-\Delta H_{\mathrm{f}}^{\ominus})_{\mathrm{M-H}} &= (-\Delta H_{\mathrm{f}}^{\ominus})_{\mathrm{H}} + \left[(-\Delta H_{\mathrm{f}}^{\ominus})_{\mathrm{M}} - (-\Delta H_{\mathrm{f}}^{\ominus})_{\mathrm{H}}\right] \\ &\quad\times \frac{S_{\mathrm{H}}^{(n+2)/(5n+3)} - S_{\mathrm{M}}^{(n+2x)/(5n+3)} S_{\mathrm{H}}^{x/(5n+3)}}{S_{\mathrm{H}}^{(n+2)/(5n+3)} - S_{\mathrm{M}}^{(n+2)/(5n+3)}}\end{aligned} \tag{12}$$

and eqns. (8), (9) and (11) yield

$$(-\Delta H_{\mathrm{f}}^{\ominus})_{\mathrm{M-H}} = (-\Delta H_{\mathrm{f}}^{\ominus})_{\mathrm{H}} + \left[(-\Delta H_{\mathrm{f}}^{\ominus})_{\mathrm{M}} - (-\Delta H_{\mathrm{f}}^{\ominus})_{\mathrm{H}}\right] \frac{W_{\mathrm{M-H}} - W_{\mathrm{H}}}{W_{\mathrm{M}} - W_{\mathrm{H}}} \tag{13}$$

Equation (12), with the help of eqns. (4) and (5), as well as the $(-\Delta H_{\mathrm{f}}^{\ominus})$ values for $\mathrm{HPO_3}$ and $\mathrm{MPO_3}$ shown in Table 1 and the relevant Sanderson electronegativities [2] ($S_{\mathrm{H}} = 3.55$, $S_{\mathrm{P}} = 3.43$, $S_{\mathrm{O}} = 5.21$, $S_{\mathrm{Li}} = 0.74$, $S_{\mathrm{Na}} = 0.70$, $S_{\mathrm{K}} = 0.42$, $S_{\mathrm{Rb}} = 0.36$ and $S_{\mathrm{Cs}} = 0.28$), can be obtained in the following form

$$(-\Delta H_{\mathrm{f}}^{\ominus}) = 310 + (n-1)233 + [A + (n-1)B]\,\frac{1 - C^{(n+2-x)/(5n+3)}}{1 - C^{(n+2)/(5n+3)}} \tag{14}$$

where the constants A, B and C have the following values for the particular alkalis. For Li: $A = 171$, $B = 69$, $C = 0.208$; for Na: $A = 150$, $B = 53$, $C = 0.197$; for K: $A = 160$, $B = 63$, $C = 0.118$; for Rb: $A = 161$, $B = 65$, $C = 0.101$; for Cs: $A = 162$, $B = 67$, $C = 0.079$.

In a similar fashion, from eqn. (13), by using eqns. (4) and (5) and the values of Table 1 for $(-\Delta H_{\mathrm{f}}^{\ominus})_{\mathrm{HPO_3}}$ and $(-\Delta H_{\mathrm{f}}^{\ominus})_{\mathrm{MPO_3}}$, one obtains

$$(-\Delta H_{\mathrm{f}}^{\ominus}) = 310 + (n-1)233 + [A + (n-1)B]\,\frac{(n+2-x)}{(n+2)} \tag{15}$$

where the values of A and B are as above.

The values of $(-\Delta H_{\mathrm{f}}^{\ominus})$ calculated from eqns. (14) and (15) are given in Table 2 for $n = 1$ to 4. In the same table the experimental values of $(-\Delta H_{\mathrm{f}}^{\ominus})$, when known, are given in parentheses for comparison.

It seems that the error which may be introduced by this method in the calculation of the enthalpies of formation of phosphate salts, especially the higher homologues, should be less than 1–2%, which is within the usual experimental error. In comparing the two sets of results, we observe that the second approach, based on the molecular weights, underestimates the experimental results slightly as compared with the calculation based on electronegativities. This underestimation is of the order of ~ 1%; it appears quite systematically, but in any case is within the experimental error.

Finally, both such methodologies seem promising in calculating similar properties for other compounds which form homologous series.

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