

Lattice Energies of Apatites and the Estimation of  $\Delta H_f^\circ(\text{PO}_4^{3-}, \text{g})$ 

Natalie J. Flora and Claude H. Yoder\*

*Department of Chemistry, Franklin and Marshall College, Lancaster, Pennsylvania 17604*

H. Donald Brooke Jenkins\*

*Department of Chemistry, University of Warwick, Coventry CV4 7AL, West Midlands, U.K.*

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Experimentally based lattice energies are calculated for the apatite family of double salts  $\text{M}_5(\text{PO}_4)_3\text{X}$ , where M is a divalent metal cation (Ca, Sr, Ba) and X is hydroxide or a halide. These values are also shown to be estimable, generally to within 4%, using the recently derived Glasser–Jenkins equation,  $U_{\text{POT}} = A/(2V_m)^{1/3}$ , where  $A = 121.39 \text{ kJ mol}^{-1}$ . The apatites exhibiting greater covalent character (e.g.,  $\text{M} = \text{Pb}, \text{Cd}$ , etc.) are less well reproduced but are within 8% of the experimentally based value. The lattice energy for ionic apatites (having identical lattice ionic strengths,  $I$ ) takes the particularly simple form  $U_{\text{POT}}/\text{kJ mol}^{-1} = 26680/(V_m/\text{nm}^3)^{1/3}$ , reproducing cycle values of  $U_{\text{POT}}$  well when  $V_m$  is estimated by ion volume summation and employing a volume for the  $\text{PO}_4^{3-}$  ion (not previously quantified with an associated error) of  $0.063 \pm 0.003 \text{ nm}^3$ . A value for the enthalpy of formation of the gaseous phosphate ion,  $\Delta H_f^\circ(\text{PO}_4^{3-}, \text{g})$ , is absent from current thermochemical tabulations. Examination of solution and solid state thermochemical cycles for apatites, however, leads us to a remarkably consistent value of  $321.8 \pm 1.2 \text{ kJ mol}^{-1}$ . Experimental and estimated lattice energies were used along with other thermodynamic data to determine enthalpies, entropies, and free energies of dissolution for apatites of uncertain stabilities. These dissolution values are compared with the corresponding values for stable apatites and are used to rationalize the relative instability of certain derivatives.

## Introduction

The apatites are a class of compounds with the stoichiometry of  $\text{M}_5(\text{PO}_4)_3\text{X}$ , where M is a divalent metal cation and X is hydroxide or a halide. These compounds are present in nature as the very common fluoroapatite,  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ , as the lead mineral pyromorphite,  $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$ , and in biological systems as the bone and teeth forming hydroxyapatite,  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ . The formation of other apatites, such as  $\text{Cd}_5(\text{PO}_4)_3\text{OH}$  and  $\text{Cu}_5(\text{PO}_4)_3\text{OH}$ , has been invoked as impure phase (solid solution) materials responsible for various bone diseases.<sup>1a,1b</sup> The formation of stable, insoluble apatites is also involved in some methods for the remediation of contamination by metals such as lead.

Approximately 200 crystalline phosphate minerals have been identified, but by far the major amount of phosphorus (eleventh in the order of elemental abundance in the earth's crust) occurs in a single mineral family, the apatites.<sup>2</sup> The

understanding of the relative stabilities of this very important class of compounds is a necessary and desirable step for a number of applications. These include development of logical laboratory syntheses, rationalization of the ion-exchanging characteristics of bone and of teeth, and the understanding of the structural effects that result in stability for the apatites of only a small number of divalent metal cations (primarily Ca, Sr, Ba, Cd, and Pb). Because these double salts are predominantly ionic, the lattice energy is a crucial thermodynamic quantity that, unfortunately, is not easily obtained by the standard Born equation or the more general but less accurate Kapustinskii modification. The principal limitations of the latter equation are, first, that it can be applied to binary materials only and, second, that, in requiring thermochemical radii as input, it effectively confers spherical symmetry on the ions involved.

Fortunately, equations have been developed during the past decade that can be applied to the estimation of the lattice energy of even very complex materials and which avoid the

\* To whom correspondence should be addressed. E-mail: claudie.yoder@fandm.edu (C.H.Y.).

(1) (a) Tsuchiya, K. *Keio J. Med.* **1969**, *18*, 181–94. (b) Pujari, M.; Patel, P. *J. Solid State Chem.* **1989**, *83*, 100–104.

(2) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon: Oxford, 1984.

assignment of radii. Mallouk et al.<sup>3</sup> modified the Kapustinskii equation by utilizing the cube root of the formula unit volume rather than the cation–anion distance. Glasser<sup>4</sup> extended the Kapustinskii equation to complex ionic solids by substituting the ionic strength-like term  $\sum n_i z_i^2 = 2I$  where  $n_i$  is the number of ions of charge  $z_i$  in the formula unit, for the original quantity  $\nu z_+ z_-$ , where  $\nu$  is the number of moles of ions in the lattice. Recently, Glasser and Jenkins have reported a generalized version, for ionic salts having lattice energies in the range<sup>5d</sup>  $5000 < U_{\text{POT}}/\text{kJ mol}^{-1} < 70000$ , that combines both the ionic strength-like term and the cube root volume dependence

$$U_{\text{POT}} = AI(2I/V_m)^{1/3} \quad (1)$$

where  $A = 121.39 \text{ kJ mol}^{-1} \text{ nm}$  is the standard electrostatic conversion factor (combination of the Madelung constant and the electrostatic factor in the Kapustinskii equation),  $I$  is the lattice ionic strength,  $V_m (=V_{\text{cell}}/Z)$  is the volume of the molecular (formula) unit,  $V_{\text{cell}}$  is the unit cell volume, and  $Z$  is the number of formula units per unit cell.<sup>5</sup> This equation requires no parameters other than the volume (obtainable in most cases directly from crystal structure data) and the easily calculated lattice ionic strength term and, moreover, for a given family of minerals of identical ionic strengths ( $A$  and  $I$  constant), reduces to an inverse cube root dependence on volume alone. Since the definition of  $V_m$  is vital to the use of the equation, we clarify this by means of an example related to the apatites. The crystal structure of fluorapatite,  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ , shows the cell to have a volume of  $0.5233 \text{ nm}^3$  (Table 2), and it contains (since  $Z = 2$ ) two  $\text{Ca}_5(\text{PO}_4)_3\text{F}$  formula units per cell. Hence  $V_m(\text{Ca}_5(\text{PO}_4)_3\text{F}) = 0.2616 \text{ nm}^3$  which, utilized in eq 1 with the value  $I = 1/2(5(2)^2 + 3(-3)^2 + 1(-1)^2) = 24$ , leads to  $U_{\text{POT}}(\text{Ca}_5(\text{PO}_4)_3\text{F}) = 16556 \text{ kJ mol}^{-1}$ . Because thermodynamic and structural data for the apatites are generally reported for the formula unit,  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ , the value for  $U_{\text{POT}}(\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2) = 33112 \text{ kJ mol}^{-1}$ , twice that for  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ , as expected.

We report here a comparison of the “experimental” (i.e., thermochemical cycle based) lattice energies of a variety of apatites with the values obtained from Glasser–Jenkins eq 1. We also calculate the lattice energies for several apatites

(3) Mallouk, T. E.; Rosenthal, G. L.; Muller, G.; Busasco, R.; Bartlett, N. *Inorg. Chem.* **1984**, *23*, 3167.

(4) Glasser, L. *Inorg. Chem.* **1995**, *34*, 4935.

(5) (a) Glasser, L.; Jenkins, H. D. B. *J. Am. Chem. Soc.* **2000**, *122*, 632–638. It should be noted that an incorrect form of eq 1 of the current paper is given in Scheme 1B (as eq 4) in ref 5b. (b) Jenkins, H. D. B.; Glasser, L. *Inorg. Chem.* **2002**, *41*, 4378. (c) Jenkins, H. D. B.; Tudela, D.; Glasser, L. *Inorg. Chem.* **2002**, *41*, 2364. (d) Jenkins and his various co-workers (Passmore, Glasser, Tudela) have developed a suite of simple equations useful for the estimation of lattice energy of ionic materials, requiring only knowledge of the volume or density. These equations fall into two categories: equations for ionic salts with lattice energies  $< 5000 \text{ kJ mol}^{-1}$  (see refs 7a, 5c) and the limiting equation used in this paper for ionic salts having lattice energies  $> 5000 \text{ kJ mol}^{-1}$  and described in ref 5a. Scheme 1 in ref 5b (noting the correction) gives a summary of these various equations. (e) The back substitution of the prescribed value for  $\Delta H_f^\circ(\text{PO}_4^{3-})$ , g) into cycle C when that same cycle has been used to generate the value may be seen by some as a circular argument. Our purpose in doing this is to represent the most appropriate lattice energy from both the hydration (cycle A) and gaseous ion (cycle C) cycles and form an average value with which to judge the values estimated using eq 1.

**Table 1.** Experimental Lattice Energy ( $\text{kJ mol}^{-1}$ ) from Thermodynamic Cycles (A and C)<sup>a</sup>

apatite	$\Delta H_f^\circ$ (kJ/mol)	$U_{\text{POT}}$ (cycle A)	$U_{\text{POT}}$ (cycle C)	$U_{\text{POT}}^h$ exptl
$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	−13314 <sup>b</sup>	34095	34089	34092 ± 3
$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$	−13558 <sup>b</sup>	34114	34121	34118 ± 4
$\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$	−13180 <sup>b</sup>	33781	33787	33784 ± 3
$\text{Sr}_{10}(\text{PO}_4)_6(\text{OH})_2$	−13373 <sup>c</sup>	33805	32799	32802 ± 3
$\text{Sr}_{10}(\text{PO}_4)_6\text{F}_2$	−13604 <sup>c</sup>	32810	32818	32814 ± 4
$\text{Sr}_{10}(\text{PO}_4)_6\text{Cl}_2$	−13233 <sup>d</sup>	32484	32490	32487 ± 3
$\text{Ba}_{10}(\text{PO}_4)_6\text{Cl}_2$	−13246 <sup>c</sup>	31199	31203	31201 ± 2
$\text{Cd}_{10}(\text{PO}_4)_6(\text{OH})_2$	−8648 <sup>e</sup>	36408	36402	36405 ± 3
$\text{Cd}_{10}(\text{PO}_4)_6\text{F}_2$	−8795 <sup>e</sup>	36330	36337	36334 ± 4
$\text{Cd}_{10}(\text{PO}_4)_6\text{Cl}_2$	−8463 <sup>f</sup>	36043	36048	36046 ± 3
$\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$	−8261 <sup>e</sup>	33520	33517	33518 ± 2
$\text{Pb}_{10}(\text{PO}_4)_6\text{F}_2$	−8529 <sup>e</sup>	33562	33574	33568 ± 6
$\text{Pb}_{10}(\text{PO}_4)_6\text{Cl}_2$	−8220 <sup>g</sup>	33298	33308	33306 ± 5
$\text{Pb}_{10}(\text{PO}_4)_6\text{Br}_2$	−8180 <sup>g</sup>	33287	33296	33291 ± 5

<sup>a</sup> The enthalpy of hydration of the phosphate ion,  $-2879 \text{ kJ/mol}$ , was obtained from: Marcus, Y. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 339–349. From bond energies and electron affinity given by: Dobrotin, R. B.; Novikov, G. V. *Obshch. Prikl. Khim.*, **1974**, *6*, 12; *Chem. Abstr.* **1975**, *83*, 66491f. <sup>b</sup> Chifera, A. B.; Somrani, S.; Jemal, M. *J. Chim. Phys.* **1991**, *88*, 1893–1900. <sup>c</sup> Khattech, I.; Lacout, J. L.; Jemal, M. *Ann. Chim. (Paris)* **1996**, *21*, 251–8. <sup>d</sup> Khattech, I.; Jemal, M. *Thermochim. Acta* **1997**, *298*, 17–21. <sup>e</sup> Jemal, M.; Cherifa, A. B.; Khattech, I.; Ntahomvukiye, I. *Thermochim. Acta* **1995**, *259*, 13–21. <sup>f</sup> Cherifa, A. B.; Jemal, M. *Thermochim. Acta* **2001**, *366* (1), 1–6. <sup>g</sup>  $\Delta H_f^\circ$  and lattice energy calculated from  $K_{\text{sp}}$  value, obtained from: Nriagu, J. O. *Inorg. Chem.* **1972**, *11*, 2499–2500. <sup>h</sup> Average of columns 4 and 5.

**Table 2.** Calculated (Equation 5) and Experimental Lattice Energies ( $\text{kJ mol}^{-1}$ )

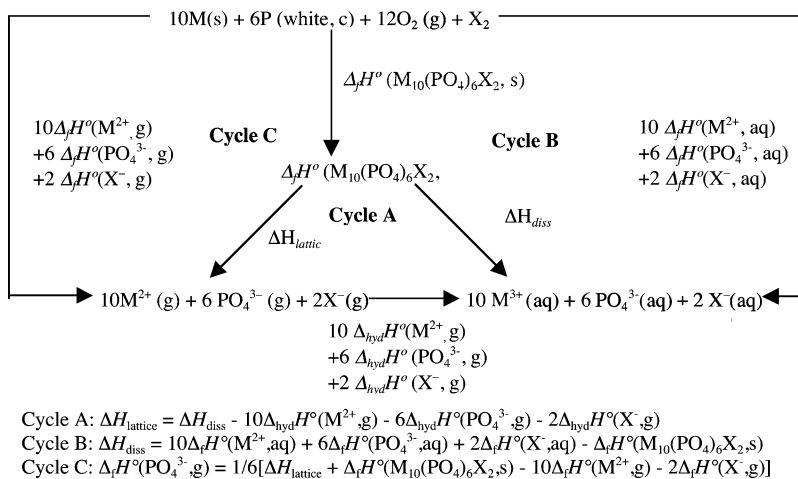
apatite	$V_m \text{ nm}^3$	$U_{\text{POT}}^c$ calcd (eq 5)	$U_{\text{POT}}^d$ exptl	percent difference
$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	0.5288 <sup>a</sup>	32993	34092 ± 3	3.2
$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$	0.5233 <sup>a</sup>	33108	34118 ± 4	3.0
$\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$	0.5450 <sup>a</sup>	32663	33784 ± 3	3.3
$\text{Sr}_{10}(\text{PO}_4)_6(\text{OH})_2$	0.6010 <sup>a</sup>	31615	32802 ± 3	3.6
$\text{Sr}_{10}(\text{PO}_4)_6\text{F}_2$	0.5967 <sup>a</sup>	31691	32814 ± 4	3.4
$\text{Sr}_{10}(\text{PO}_4)_6\text{Cl}_2$	0.6152 <sup>a</sup>	31370	32487 ± 3	3.4
$\text{Ba}_{10}(\text{PO}_4)_6\text{Cl}_2$	0.6951 <sup>a</sup>	30119	31201 ± 2	3.5
$\text{Cd}_{10}(\text{PO}_4)_6(\text{OH})_2$	0.5015 <sup>b</sup>	33581	36405 ± 3	7.8
$\text{Cd}_{10}(\text{PO}_4)_6\text{F}_2$	0.4966 <sup>b</sup>	33691	36334 ± 4	7.3
$\text{Cd}_{10}(\text{PO}_4)_6\text{Cl}_2$	0.5211 <sup>a</sup>	33155	36046 ± 3	8.0
$\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$	0.6274 <sup>b</sup>	31165	33518 ± 2	7.0
$\text{Pb}_{10}(\text{PO}_4)_6\text{F}_2$	0.6010 <sup>a</sup>	31615	33568 ± 6	5.8
$\text{Pb}_{10}(\text{PO}_4)_6\text{Cl}_2$	0.6332 <sup>a</sup>	31070	33306 ± 5	6.7
$\text{Pb}_{10}(\text{PO}_4)_6\text{Br}_2$	0.6548 <sup>a</sup>	30723	33291 ± 5	7.7

<sup>a</sup> Cell volumes obtained from the International Center for Diffraction Data (ICDD), PDF-2 Sets 1-44 Inorganics (includes zeolites and minerals), 1994.  $V_m = V_{\text{cell}}/Z$ . <sup>b</sup> Cell volumes obtained from: *Landolt-Börnstein, New Series*, Hellwege, K.-H., Ed.; Group III: Crystal and Solid State Physics, Vol. 7., *Crystal Data and Inorganic Compounds*; Springer Verlag: Berlin, 1973.  $V_m = V_{\text{cell}}/Z$ . <sup>c</sup> Calculated lattice energy obtained from  $U_{\text{POT}} = AI(2I/V_m)^{1/3}$  in the form of eq 5. <sup>d</sup> The experimental  $U_{\text{POT}}$  is the average of  $U_{\text{POT}}$  from cycle A and the  $U_{\text{POT}}$  from cycle C (Table 1).

whose existence is uncertain and use these values to rationalize their relative stabilities and to explain the observed “instability” of pure phase magnesium, zinc, and iodo apatites.

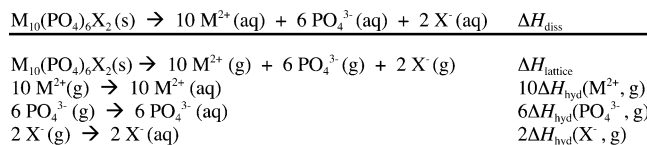
## Results

The experimental lattice energies of the apatites were obtained from their reported enthalpies of formation by the use of the suite of thermochemical cycles illustrated in Figure 1.



**Figure 1.** Thermodynamic cycles.

Cycle A involves the following thermodynamic steps in the dissolution of the apatite,

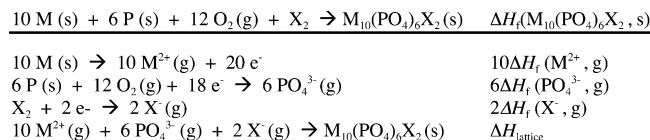


and hence, the following equation holds:

$$\Delta H_{diss} = \Delta H_{lattice} + [10 \Delta_{hyd} H^\circ(M^{2+}, g) + 6 \Delta_{hyd} H^\circ(PO_4^{3-}, g) + 2 \Delta_{hyd} H^\circ(X^-, g)] \quad (2)$$

The enthalpy of dissolution,  $\Delta H_{diss}$ , was obtained (using cycle B) from published values of the enthalpies of formation of aqueous ions<sup>6</sup> combined with literature values of the enthalpies of formation of the apatites (see Table 1). Cycle A has the advantage over cycle C in that cycle A does not require the enthalpy of formation of the gaseous phosphate ion (the magnitude of which is not currently reported in the literature). The enthalpies of hydration (cycle A) were obtained from the compilation of Marcus.<sup>7</sup> The lattice energies, listed in Table 1 as  $U_{POT}$ , were obtained from  $\Delta H_{lattice}$  by correction for the difference between enthalpy and energy.<sup>8</sup>

The values of  $\Delta H_{lattice}$  were then used in the traditional Born–Haber cycle C, as shown for a halide (X), to establish a consistent value for the enthalpy of formation for the gaseous phosphate ion,  $\Delta H_f^\circ(PO_4^{3-}, g)$ .



(6) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumann, R. H.; Harlow, I.; Bailey, S. M.; Churney, K. L.; Nutall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. 2.

(7) (a) Marcus, Y. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 339–349. The value for  $\Delta H_{hyd}(Pb^{2+})$  should be  $-1508.6 \text{ kJ mol}^{-1}$  (private communication, Marcus, Y., 2003). (b) Marcus, Y. *Ion Solvation*; Wiley: Chichester, U.K., 1985. (c) Marcus, Y. *Ion Properties*; Marcel Dekker Inc.: New York, 1997. (d) Marcus, Y.; Jenkins, H. D. B.; Glasser, L. *J. Chem. Soc., Dalton Trans.* **2002**, 3795.

Hence, the following holds:

$$\Delta H_f^\circ(PO_4^{3-}, g) = \{\Delta H_f^\circ(M_{10}(PO_4)_6X_2, s) - [10 \Delta H_f^\circ(M^{2+}, g) + 2 \Delta H_f^\circ(X^-, g) + \Delta H_{lattice}]\}/6 \quad (3)$$

The enthalpies of formation of the gaseous phosphate ion as obtained from the alkaline earth apatites are remarkably consistent, ranging from 320.5 to 323.8 kJ/mol, with an average of

$$\Delta H_f^\circ(PO_4^{3-}, g) = 321.8 \pm 1.2 \text{ kJ/mol} \quad (4)$$

This assigned value of the enthalpy of formation of the phosphate ion was then back substituted into Born–Haber cycle C to regenerate  $\Delta H_{lattice}$ , and, after correction,  $U_{POT}$ . The values obtained in this way are shown in Table 1 as  $U_{POT}$  (cycle C).<sup>5c</sup> As expected, the two values of  $U_{POT}$  are similar and correlate well with one another (correlation coefficient = 0.999). The two values of  $U_{POT}$  are averaged (final column in Table 1) to produce an “experimental”  $U_{POT}$ .

The Glasser–Jenkins equation<sup>5a,d</sup> was used to estimate the lattice energies of the apatites. For these compounds, the unit cell is generally taken as  $M_{10}(PO_4)_6X_2$ , and therefore,  $I = 48$ , and the equation then simplifies to the form

$$U_{POT}/\text{kJ mol}^{-1} = 26680/(V_m/\text{nm}^3)^{1/3} \quad (5)$$

The values of  $V_m$  were obtained from published X-ray diffraction data. The estimated lattice energies are given in Table 2 and for the alkaline earth apatites are generally within 4% of the “experimental” lattice energies. The greater discrepancy in the cadmium and lead apatites can be

(8) (a) Jenkins, H. D. B.; Roobottom, H. K.; Passmore, J.; Glasser, L. *Inorg. Chem.* **1999**, *38*, 3609–3620. (b) For hydroxyapatites:  $\Delta H_{latt} = U_{POT} + 2RT$ . For fluoro- and chloroapatites:  $\Delta H_{latt} = U_{POT}$  using an extension of eq 2 in ref 8a. (c) It should be noted that eq 6 contains a term involving the cube of the inverse of the lattice energy thus making the calculated volume quite sensitive to error, although somewhat mitigated by division by 6. (d) See also: Jenkins, H. D. B. *J. Chem. Educ.*, submitted. (e) In a recent study<sup>8f</sup> of ion hydration enthalpies, the value of  $V(PO_4^{3-})$  given in eq 7 accords more satisfactorily with the known hydration enthalpy of the  $PO_4^{3-}$  ion than does the earlier value of  $0.090 \text{ nm}^3$ . (f) Jenkins, H. D. B. Manuscript in preparation.

**Table 3.** Ion Volumes/nm<sup>3a</sup>

ion	V, nm <sup>3</sup>	ion	V, nm <sup>3</sup>
Mg <sup>2+</sup>	0.00199 <sup>a</sup>	OH <sup>-</sup>	0.032 <sup>b</sup>
Ca <sup>2+</sup>	0.00499 <sup>a</sup>	F <sup>-</sup>	0.025 <sup>b</sup>
Sr <sup>2+</sup>	0.00858 <sup>a</sup>	Cl <sup>-</sup>	0.047 <sup>b</sup>
Ba <sup>2+</sup>	0.01225 <sup>a</sup>	Br <sup>-</sup>	0.056 <sup>b</sup>
Zn <sup>2+</sup>	0.00240 <sup>a</sup>	I <sup>-</sup>	0.072 <sup>b</sup>
Cd <sup>2+</sup>	0.00458 <sup>a</sup>	PO <sub>4</sub> <sup>3-</sup>	0.090 <sup>b</sup>
Pb <sup>2+</sup>	0.00963 <sup>a</sup>	PO <sub>4</sub> <sup>3-</sup>	0.0635 <sup>c</sup>

<sup>a</sup> Cation volumes calculated from Goldschmidt radii in: Dasent, W. E. *Inorganic Energetics*, 2nd ed.; Cambridge University Press: Cambridge, U.K., 1982. <sup>b</sup> Anion volumes obtained from Table 5 in: Jenkins, H. D.B.; Roobottom, H. K.; Passmore, J.; Glasser, L. *Inorg. Chem.* **1999**, *38*, 3609–3620. <sup>c</sup> Note that the value for PO<sub>4</sub><sup>3-</sup> derived in table 5 of ref 7a (and listed here) was estimated from crystal structure data on a single salt, and no error bars could therefore be provided; the revised value here was determined as discussed in text, is based on 7 salts, and has a standard deviation of 0.003 nm<sup>3</sup>.

attributed to the larger polarizability of these ions and a greater degree of covalent character in their apatites.<sup>9</sup>

The volume used in the Glasser–Jenkins equation can also be obtained, albeit more approximately, from the volume sum of the constituent ions. Individual single volumes for over 400 ions have been reported in a database.<sup>8a</sup> This database (a subset is shown in Table 3) includes a volume (0.090 nm<sup>3</sup>) for the phosphate ion derived from crystal structure data based on a single salt.<sup>8a</sup> We have calculated a phosphate ion volume,  $V(\text{PO}_4^{3-})/\text{nm}^3$ , that should be most appropriate to use (in combination with volumes of other ions present in the lattice) for the estimation of volumes for both apatites whose crystal structures have not been reported or for hypothetical apatites whose existence is doubtful. Rearranging eq 5 explicitly for  $V(\text{PO}_4^{3-})$  produces the following equation after incorporating single ion additivity in place of  $V_m$ :

$$V(\text{PO}_4^{3-}) \approx \{[26680/U_{\text{POT}}]^3 - 10V(\text{M}^{2+}) - 2V(\text{X}^-)\}/6 \quad (6)$$

The phosphate volumes obtained from the alkaline earth apatites using eq 6 ranged from 0.05810 to 0.06812 nm<sup>3</sup>, and the average was determined to be

$$V(\text{PO}_4^{3-}) \approx 0.063 \pm 0.003 \text{ nm}^3 \quad (7)$$

This thermochemical volume,<sup>8c,e</sup> although clearly smaller than the value of 0.090 nm<sup>3</sup> obtained from a single phosphate salt,<sup>8a</sup> is more in agreement (being smaller rather than larger) with anticipated group 15 periodic trends when compared to the value  $V(\text{AsO}_4^{3-}) = 0.088 \pm 0.010 \text{ nm}^3$  estimated from study of two salts (Table 5, ref 8a). However, the volume  $V(\text{SbO}_4^{3-}) = 0.071 \text{ nm}^3$  from the same reference source and reliant like the phosphate volume on data for a single antimonate salt remains, as before,<sup>8a</sup> counter to expected trends. In the absence of other data relating to the volume of the phosphate ion,<sup>7d</sup> we conclude that the value assigned in this work is appropriate for apatite lattices and is used in the remainder of our calculations.

**Table 4.** Lattice Energies Based on Sum of Ion Volumes Compared to Established Value from Thermochemical Cycles

apatite	V <sub>m</sub> , nm <sup>3</sup>	U <sub>POT</sub> , calcd	U <sub>POT</sub> , exptl	percent difference
Mg <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub>	0.4647	34446		
Mg <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	0.4507	34799		
Mg <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> Cl <sub>2</sub>	0.4947	33735		
Mg <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> Br <sub>2</sub>	0.5127	33336		
Mg <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> I <sub>2</sub>	0.5447	32670		
Ca <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub>	0.4947	33735	34092 ± 3	1.05
Ca <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	0.4807	34060	34118 ± 4	0.17
Ca <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> Cl <sub>2</sub>	0.5247	33080	33784 ± 3	2.08
Ca <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> Br <sub>2</sub>	0.5427	32710		
Ca <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> I <sub>2</sub>	0.5747	32091		
Sr <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub>	0.5306	32956	32802 ± 3	0.47
Sr <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	0.5166	33252	32814 ± 4	1.33
Sr <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> Cl <sub>2</sub>	0.5606	32358	32487 ± 3	0.40
Sr <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> Br <sub>2</sub>	0.5786	32019		
Sr <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> I <sub>2</sub>	0.6106	31449		
Ba <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub>	0.5673	32230		
Ba <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	0.5533	32499		
Ba <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> Cl <sub>2</sub>	0.5973	31681	31201 ± 2	1.54
Ba <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> Br <sub>2</sub>	0.6153	31369		
Ba <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> I <sub>2</sub>	0.6473	30843		
Zn <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub>	0.4617	34519		
Zn <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	0.4477	34875		
Zn <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> Cl <sub>2</sub>	0.4917	33802		
Zn <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> Br <sub>2</sub>	0.5097	33399		
Zn <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> I <sub>2</sub>	0.5417	32728		
Cd <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub>	0.4807	34060	36405 ± 3	6.88
Cd <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	0.4667	34397	36334 ± 4	5.33
Cd <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> Cl <sub>2</sub>	0.5107	33379	36046 ± 3	7.40
Cd <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> Br <sub>2</sub>	0.5287	32996		
Cd <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> I <sub>2</sub>	0.5607	32356		
Pb <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub>	0.5154	33277	33518 ± 2	0.72
Pb <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	0.5014	33584	33568 ± 6	0.05
Pb <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> Cl <sub>2</sub>	0.5454	32656	33306 ± 5	1.95
Pb <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> Br <sub>2</sub>	0.5634	32304	33291 ± 5	2.96
Pb <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> I <sub>2</sub>	0.5954	31715		

Using the parameters we have now established, we can calculate lattice energies for apatites that are unknown or whose existence is uncertain. Such values can then be employed with other thermodynamic parameters to rationalize relative stabilities.

Table 4 compares the values of  $U_{\text{POT}}$  calculated from summation of the individual ion volumes (using the newly derived phosphate volume) with the values established from the cycles. Not surprisingly, good agreement (within 3.0%) is obtained for the alkaline earth and lead apatites, while larger deviations are found (some 7% lower) for the cadmium apatites.

The rather large difference in  $V_m$  as obtained from experimental crystal structures relative to the estimated  $V_m$  is moderated by the inverse cube root dependence of  $U_{\text{POT}}$  on  $V_m$ . For example, a 6% difference between experimental  $V_m$  (0.5288 nm<sup>3</sup>) and estimated  $V_m$  (0.4947 nm<sup>3</sup>, by ion volume sum) for Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub> leads to a corresponding difference of only 2.2% in the lattice energy derived from crystal structure volume (32993 kJ mol<sup>-1</sup>) (Table 2) compared to the value obtained from the ion volume sum (33735 kJ mol<sup>-1</sup>) (Table 4).

Moreover, the estimated ion volumes assign any free space or voids in the lattice to the anion volumes. Thus, the estimated anion volumes are slightly too large and the cation volumes too small (see discussion in ref 8a). The recombination of the volumes to obtain  $V_m$  for simple binary salts is

(9) Rich, R. *Periodic Correlations*; W. A. Benjamin, Inc.: New York, 1965.

**Table 5.** Comparison of Experimental and Predicted Standard Entropies,  $S^{\circ}_{298}/\text{J K}^{-1} \text{ mol}^{-1}$  Using Latimer's Rules and Jenkins–Glasser Rectilinear Entropy–Volume Relationship

phosphate/apatite	$S^{\circ}_{298}/(\text{J K}^{-1} \text{ mol}^{-1})$ exptl	$V/\text{nm}^3$	$S^{\circ}_{298}/(\text{J K}^{-1} \text{ mol}^{-1})$ predicted from Latimer's rules <sup>11</sup>	$S^{\circ}_{298}/(\text{J K}^{-1} \text{ mol}^{-1})$ predicted from $S = 1262V + 13$	$S^{\circ}_{298}/(\text{J K}^{-1} \text{ mol}^{-1})$ av <sup>b</sup>
Mg <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	189.2	0.0972 <sup>a</sup>	238	136	187
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> α phase	240.9	0.1820	259	243	251
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> β phase	236.0	0.1621	259	218	239
Sr <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	292.9	0.1650	293	221	257
Ba <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	356.1	0.2792	314	365	340
Ca <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub>	780.7	0.5288	853	680	768
Ca <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	775.7	0.5233	855	673	765

<sup>a</sup> Volume calculated from that of octahydrate by subtracting  $8V(\text{H}_2\text{O})$ , where  $V(\text{H}_2\text{O})/\text{nm}^3 = 0.0245$  from ref 5b. <sup>b</sup> Comparison with experimental values indicates that averaging estimates of the standard entropy predicted by Latimer's rules<sup>10,12</sup> and those from the Jenkins–Glasser entropy–volume equation<sup>11</sup> gives quite a good account of the standard entropies of these materials (both for parents and corresponding apatites).

such that these errors cancel out, giving a reasonable account of the true molecular (formula unit) volume by ion volume combination. However, in the apatites, we sum 10 cation volumes and 8 anion volumes, 6 of which are our phosphate ion volumes determined to be appropriate for apatites. This procedure, which provides a better estimate of the apatite lattice energy, results in a smaller  $V_m$ .

To calculate the free energy of dissolution, we need values of the absolute entropy of the apatites, which can then be used with ion entropies to calculate the entropy change during dissolution. Table 5 lists experimental absolute entropies for some of the parent phosphates and apatites for which standard entropies,  $S^{\circ}_{298}$ , are experimentally known. The table shows that the prediction of these entropies by using Latimer's rules<sup>10</sup> produces values that are generally slightly higher than the experimental values. Recently, Jenkins and Glasser<sup>11</sup> have reported a rectilinear correlation between entropy and volume which generalizes for minerals in the form

$$S^{\circ}_{298}/\text{J K}^{-1} \text{ mol}^{-1} = 1262 (V/\text{nm}^3) + 13 \quad (8)$$

For the apatites and related materials, this approach gives predictions which are equally as good as those of Latimer<sup>10,12</sup> but are slightly lower. Thus, the entropies of dissolution,  $\Delta S_{\text{diss}}$ , of our apatites are best estimated using a value for the absolute standard entropy of the solid apatite,  $S^{\circ}_{298}/\text{JK}^{-1} \text{ mol}^{-1}$ , which is obtained by taking an average of the Latimer and eq 8 estimates, combined with the entropies of the aqueous ions. The Gibbs energies of dissolution (at 298 K),  $\Delta G_{\text{diss}}$ , are then estimated and the results displayed in Tables 6 and 7.

$$\Delta G_{\text{diss}} = \Delta H_{\text{diss}} - T\Delta S_{\text{diss}} \quad (9)$$

## Discussion

The preparation of apatites in aqueous solution invariably involves the isolation of a precipitated solid, and even solid state preparations usually involve isolation by aqueous extraction of byproducts. Thus, the solubility of the apatite relative to starting materials and other possible products controls the feasibility of the synthetic procedure.

(10) Latimer, W. M. *Oxidation Potentials*, 2nd ed.; Prentice Hall Inc: Englewood Cliffs, NJ, 1952.

(11) a) Jenkins, H. D. B.; Glasser, L. M. S. *Inorg. Chem.* **2003**, *42*, 8702.  
 (b) Glasser, L.; Jenkins, H. D. B. *Thermochim. Acta*, in press.

**Table 6.** Gibbs Energies of Dissolution Based on Experimental Lattice Energies

apatite	$U_{\text{POT}}$ , exptl (Table 1)	$\Delta H_{\text{diss}}^a$ , kJ mol <sup>-1</sup>	$\Delta S_{\text{diss}}^b$ pred., J K <sup>-1</sup> mol <sup>-1</sup>	$\Delta G_{\text{diss}}$ , kJ mol <sup>-1</sup>
Ca <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub>	34092	-242	-2656 <sup>c</sup>	+550
Ca <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	34118	-196	-2657 <sup>c</sup>	+596
Ca <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> Cl <sub>2</sub>	33784	-244	-2521	+507
Sr <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub>	32802	-212	-2494	+531
Sr <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	32814	-180	-2492	+563
Sr <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> Cl <sub>2</sub>	32487	-221	-2393	+492
Ba <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> Cl <sub>2</sub>	31202	-126	-2029	+479
Cd <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub>	36405	-239	-2888	+622
Cd <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	36334	-290	-2887	+570
Cd <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> Cl <sub>2</sub>	36046	-292	-2788	+539
Pb <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	33568	+188	-2126	+822
Pb <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> Cl <sub>2</sub>	33306	+212	-2028	+816
Pb <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> Br <sub>2</sub>	33291	+259	-1999	+855

<sup>a</sup> Enthalpies of hydration obtained from: Marcus, Y. J. *Chem. Soc., Faraday Trans. 1* **1987**, *83*, 339–349. <sup>b</sup> Unless otherwise indicated, entropies of aqueous ions obtained from: *Handbook of Chemistry and Physics*, 77th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1996–1997; pp 5-85 to 5-88. Contributions to entropies of solids as an average of estimates obtained from: Dasent, W. E. *Inorganic Energetics*, 2nd ed.; Cambridge University Press: Cambridge, U.K., 1982. These are also based on Latimer's rules<sup>10</sup> and estimates made using the Jenkins–Glasser correlation<sup>11</sup> of absolute entropy with volume in the following form:  $S^{\circ}_{298}(\text{apatite})/\text{J K}^{-1} \text{ mol}^{-1} \approx 1262[V(\text{apatite})/\text{nm}^3] + 13$ . <sup>c</sup> Experimental standard entropies.

The soluble apatites are less likely to emerge as products and are also less likely to be stable relative to other potentially more insoluble byproducts such as hydrogen phosphates or starting materials. For example, the existence of pure phase small cation apatites such as Mg<sub>3</sub>(PO<sub>4</sub>)<sub>3</sub>Cl and Zn<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>Cl is doubtful.<sup>13</sup> Likewise, the iodo apatites of Sr, Ba, and Pb are unknown even though the other haloapatites are known and relatively easy to prepare in aqueous solution.<sup>14</sup> Our calculation of the lattice energies and absolute entropies of the apatites allows us to calculate the Gibbs

(12) To illustrate the use of Latimer's rules,<sup>10</sup> we provide examples for the phosphates/apatites Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>, and Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>F<sub>2</sub>. From ref 10, Appendix III, Table 90, the entropic contributions to  $S^{\circ}_{298}$  from PO<sub>4</sub><sup>3-</sup>, OH<sup>-</sup>, and F<sup>-</sup> ions coupled with cations of +2 charge are seen to be 71.1, 18.8, and 19.7 J K<sup>-1</sup> mol<sup>-1</sup>, respectively, whilst the contributions from Mg and Ca (Table 87) are 31.8 and 38.9 J K<sup>-1</sup> mol<sup>-1</sup>, respectively. Hence,  $S^{\circ}_{298}(\text{Mg}_3(\text{PO}_4)_2) = 3(31.8) + 2(71.1) = 238 \text{ J K}^{-1} \text{ mol}^{-1}$ ;  $S^{\circ}_{298}(\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2) = 10(38.9) + 6(71.1) + 2(18.8) = 853 \text{ J K}^{-1} \text{ mol}^{-1}$ ;  $S^{\circ}_{298}(\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2) = 10(38.9) + 6(71.1) + 2(19.7) = 855 \text{ J K}^{-1} \text{ mol}^{-1}$ , as recorded in Table 5.

(13) Kreider, E. R.; Hummel, F. A. *Am. Mineral.* **1970**, *55*, 170.

(14) Flora, N. J.; Hamilton, K. W.; Schaeffer, R. W.; Yoder, C. H. *Synth. React. Inorg. Met.-Org. Chem.*, accepted for publication.

**Table 7.** Gibbs Energies of Dissolution Based on Estimated Lattice Energies

apatite	$U_{\text{POT}}$ , <sup>c</sup> estimated kJ mol <sup>-1</sup>	$\Delta H_{\text{diss}}$ , kJ mol <sup>-1a</sup>	$\Delta S_{\text{diss}}$ , <sup>b</sup> pred. J K <sup>-1</sup> mol <sup>-1</sup>	$\Delta G_{\text{diss}}$ kJ mol <sup>-1</sup>
Mg <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub>	34446	-3358	-3417	-2339
Mg <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	34799	-2985	-3415	-1967
Mg <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> Cl <sub>2</sub>	33735	-3763	-3317	-2774
Sr <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> I <sub>2</sub>	31449	-1107	-2338	-410
Ba <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub>	32230	596	-2130	+1231
Ba <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	32499	885	-2128	+1520
Ba <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> I <sub>2</sub>	30843	-333	-1974	+256
Zn <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub>	34519	-4495	-3225	-3534
Zn <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	34875	-4119	-3224	-3158
Zn <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> Cl <sub>2</sub>	33802	-4906	-3125	-3975
Pb <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub>	33277	-123	-2128	+512
Pb <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> I <sub>2</sub>	31715	-1227	-1973	-640

<sup>a</sup> Enthalpies of hydration obtained from: Marcus, Y. J. *Chem Soc., Faraday Trans. 1* **1987**, 83, 339–349. <sup>b</sup> Entropies of hydration obtained from: *Handbook of Chemistry and Physics*, 77th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1996–1997; pp 5-85 to 5-88. Contributions to entropies of solids as an average of estimates obtained from: Dasent, W. E. *Inorganic Energetics*, 2nd ed.; Cambridge University Press: Cambridge, U.K., 1982. These are also based on Latimer's rules<sup>10</sup> and estimates made using the Jenkins-Glasser correlation<sup>11</sup> of absolute entropy with volume in the following form:  $S_{298}^{\circ}(\text{apatite})/\text{J K}^{-1} \text{ mol}^{-1} \approx 1262[V(\text{apatite})/\text{nm}^3] + 13$ . <sup>c</sup> Estimated using ion volume summations (Table 4) to obtain  $V_m$  for use in eq 5.

energy of dissolution; a negative Gibbs energy of dissolution indicates a significant solubility for the apatite, with a potentially lower probability of being synthetically viable. Tables 6 and 7 show the results of our calculations. Table 6 contains the Gibbs energies of dissolution obtained from Born–Haber lattice energies and either experimental absolute entropies or entropies calculated as indicated above. Table 7 contains the Gibbs energies of dissolution estimated for selected apatites whose existences are uncertain. The lattice energies for these apatites were estimated with the Glasser–Jenkins equation using ion volumes.

For the apatites in Table 6, all of the free energies of dissolution are positive, as expected for these insoluble,

relatively easily prepared compounds. For the apatites in Table 7, on the other hand, all but four of the Gibbs energies of dissolution are negative, indicating a significant solubility (for those that have negative free energies of dissolution) that probably prevents isolation of the apatite under the conditions normally employed in their synthesis. The exceptions include the barium hydroxy and fluoro apatites and lead hydroxy apatite, all of which are known stable apatites. Barium iodo apatite, which has not been prepared, has a small positive Gibbs energy of dissolution, which may indicate an error in the lattice energy (or absolute entropy) or that this compound may indeed be insoluble and potentially isolable. The Gibbs energies of dissolution of the magnesium and zinc derivatives are all negative, which correlates to the uncertain existence of those apatites. Although it is probably true that the ion summation procedure underestimates the lattice energy of the zinc apatites because of their covalency, a value for the lattice energy more than 10% larger would be required to make the compounds stable. The solubility of the magnesium and zinc apatites is primarily a result of the high enthalpies of hydration of their cations, due to their small sizes and, in the case of zinc, larger polarizability.<sup>9</sup> The iodo apatites, on the other hand, are more soluble because their relatively low lattice energy, a result of the large size of the iodide ion, is more significant than the lower (more positive) enthalpy of hydration of the iodide ion.

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