

Estimating the thermodynamic properties of phosphate minerals at high and low temperature from the sum of constituent units

Estimación de las propiedades termodinámicas de fosfatos minerales a alta y baja temperatura por suma de sus unidades constituyentes

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RESUMEN

Usando el modelo de unidades poliédricas de Hazen, y empleando un método de ajuste por mínimos cuadrados, se ha calculado la contribución de diecinueve unidades constituyentes a la energía libre y de otras quince unidades a la entalpía de los fosfatos minerales en condiciones termodinámicas normales (298 °K de temperatura y 1 bar de presión) y a altas temperaturas (400-1.000 °K).

Con los valores de g_i y h_i calculados por este método se puede estimar las propiedades termodinámicas de cualquier fosfato mineral con mayor precisión que la conseguida hasta ahora por otros métodos.

Palabras clave: Energía libre de Gibbs, Entalpía, Fosfatos minerales, Propiedades termodinámicas.

ABSTRACT

Using the polyhedral units model of Hazen and employing a method of least-squares, the contribution of nineteen constituent units to the free energy and fifteen units to the enthalpy, at 298 K and 1 bar of pressure, have been calculated for mineral phosphates. The contribution of these constituent units to the free energy at higher temperatures has also been calculated.

From these data we can estimate the thermodynamic properties of phosphates by summing the contribution of the distinct units, with more accuracy than the methods published up until now.

Key words: Gibbs Free Energy, Enthalpy, Phosphate minerals, Thermodynamic properties.

Introduction

The estimation of the thermodynamic properties of silicate minerals has been considered by many investigators. Wilcox & Bromley (1963), Slaughter (1966), Karpov & Kashik (1968), Tardy & Garrels (1974), Nriagu (1975), Chen (1975), Robinson & Haas (1983), Sposito (1986) and La Iglesia & Aznar (1986, 1990) have published methods based on the hypothesis that the free energy or enthalpy of formation is related to the sum of free energies of formation of their constituent oxide or hydroxide components. This summation hypothesis has a firm

theoretical backing in that the macroscopic mineral thermodynamic properties are the cumulative result of the lattice vibrational energies of the various elements in the lattice, Grimwall (2001).

Following the polyhedral units model of Hazen (1985), Chermak & Rimstidt (1989, 1990), determined by multiple linear regression the Gibbs free energy of formation (g_i) and enthalpy of formation (h_i) of polyhedral units in silicate minerals:

$$\Delta G^\circ_f = \sum n_i g_i \quad (1)$$

and

$$\Delta H^\circ_f = \sum n_i h_i \quad (2)$$

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where n_i is the number of moles of i th component per formula unit. With this method ΔG°_f or ΔH°_f of many silicates can be calculated with an uncertainty of less than 1%. Using this approach, La Iglesia & Felix (1994) calculated values of g_i and h_i for carbonates to create a model that predicts their ΔG°_f and ΔH°_f with an uncertainty of less than 0.5%.

Tardy & Garrels (1976, 1977) published a method of estimation of the thermodynamic properties of minerals based on the fact that the free energy and enthalpy of formation within a family of compounds from their constituent oxides are linearly dependent on a parameter called ΔO_M^{2-} , which is a function of the electronegativity of the constituent cations (M^{2+}). This correlation provides a means of estimating values for unmeasured minerals. So, Tardy & Gartner (1977) and Tardy & Vieillard (1977) have obtained empirical equations that estimate the Gibbs free energy of formation and enthalpy of formation of carbonates, nitrates, sulfates and phosphates with a deviation less than 3% with respect to the experimental values. For the phosphates, these authors obtain the following equations:

$$\Delta G^\circ_f(\text{phosphate}) = \Delta G^\circ_f(\text{oxides}) - 1.40n_1n_2(\Delta_G O_M^{2-} + 76.9)/(n_1 + n_2) \text{ (kcal/mol)} \quad (3)$$

and

$$\Delta H^\circ_f(\text{phosphate}) = \Delta H^\circ_f(\text{oxides}) - 1.41n_1n_2(\Delta_H O_M^{2-} + 87.3)/(n_1 + n_2) \text{ (kcal/mol)} \quad (4)$$

in which n_1 and n_2 are in a given compound, the number of oxygens required to balance the cation and phosphorous, respectively.

Nriagu (1976), employing the hypothesis of sum of the free energy of constituents, proposed the following equation, which permit to estimate the ΔG°_f of complex phosphates and hydroxyphosphates:

$$\Delta G^\circ_f(\text{hydroxyphosphate}) = \sum \Delta G^\circ_{f(i)} + n \Delta G^\circ_{f(H_2O)} - Q \quad (5)$$

where $\Delta G^\circ_{f(i)}$ is the Gibbs free energy of formation of the i th reactant hydroxide or phosphate component within the hydroxyphosphate matrix and Q is a correction factor. According to Chen (1975), $Q = RT \sum(n_i \ln n_i)$ where n_i is the reaction coefficient for the i th hydroxide or phosphate. Using equation (5), values of $\Delta G^\circ_{f(\text{hydroxyphosphate})}$ with deviations less than 3% with regard to experimental values, can be obtained.

In this paper, employing a method of least-squares, the contribution of 19 constituent units to the Gibbs free energy and 15 units to the enthalpy of phosphates has been calculated. From these data we can estimate the thermodynamic properties of other phosphates with more accuracy than the methods published up until now.

Calculation of the Gibbs free energies, enthalpies and entropies of phosphate units at 298 °K

To evaluate the contribution of the units to the Gibbs free energy and enthalpy of phosphate minerals 41 crystalline phases (table 1) were selected. A system of 31 linear equations was established to calculate g_i and 23 linear equations were used to calculate h_i . To solve both systems we used the program MAPLE V release 2. The g_i and h_i coefficients were determined using a least-squares method.

The values of g_i and h_i obtained for each of the polyhedral units, together with their uncertainty ranges, are presented in table 2. Considering the easy substitution of O ligand by OH, F or Cl in these compounds, average values of $g_{H_2O(OH)}$, g_F , g_{Cl} , $h_{H_2O(OH)}$, h_F and h_{Cl} have been also calculated. These values represent the difference between the energy of polyhedral units $M-O_n$ and $M-O_{n-1}(OH)$ or $M-O_{n-1}F$. Therefore, the procedure to calculate $g_{Ca(OH)_2}$ for example, would be: $g_{Ca(OH)_2} = g_{CaO} + g_{H_2O(OH)}$. From the values of table 2, the ΔG°_f or ΔH°_f of any phosphate can be easily calculated using the equations (1) and (2). Thus, for example, to calculate the standard thermodynamic properties of ammonium taranakite, $(NH_4)_3Al_5(PO_4)_8H_618H_2O$:

$$\Delta G^\circ_f(NH_4)_3Al_5(PO_4)_8H_618H_2O = 3/2 g_{(NH_4)_2O} + 5/2 g_{Al_2O_3} + 4g_{P_2O_5} + 3 g_{H_2O(H)} + 18 g_{H_2O(cryst.)} = -16,106.33 \pm 41.60 \text{ kJ mol}^{-1}.$$

$$\Delta H^\circ_f(NH_4)_3Al_5(PO_4)_8H_618H_2O = 3/2 h_{(NH_4)_2O} + 5/2 h_{Al_2O_3} + 4h_{P_2O_5} + 3h_{H_2O(H)} + 18h_{H_2O(cryst.)} = -18,484.51 \pm 38.45 \text{ kJ mol}^{-1}.$$

These results are in perfect agreement with the values of $-16,129.15 \text{ kJ mol}^{-1}$ and $-18,532.60 \text{ kJ mol}^{-1}$ given by Vieillard & Tardy (1984). The deviations have been calculated using the equation:

$$\sigma = [\sum(n_i \sigma_i)^2]^{1/2} \quad (6)$$

Table 1.—Crystalline phases selected to calculate g_i and h_i values

Li ₃ PO ₄ (Lithiophosphatite)	h_i	Ca ₁₀ (PO ₄) ₆ F ₂ (Fluorapatite)	$g_i + h_i$
Li ₄ P ₂ O ₇	h_i	Ca ₁₀ (PO ₄) ₆ Cl ₂ (Chorapatite)	$g_i + h_i$
Na ₄ P ₂ O ₇ ·10H ₂ O	h_i	CaHPO ₄ ·2H ₂ O (Brushite)	$g_i + h_i$
Na ₅ P ₃ O ₁₀	$g_i + h_i$	Ca ₂ C1PO ₄	g_i
Na ₂ HPO ₄ ·12H ₂ O	$g_i + h_i$	Fe ₃ (PO ₄) ₂ ·8H ₂ O (Vivianite)	$g_i + h_i$
Na ₂ H ₂ P ₂ O ₇	g_i	Fe ₃ (PO ₄) ₂	g_i
Na ₃ HP ₂ O ₇	h_i	Co ₃ (PO ₄) ₂	g_i
KMgPO ₄ ·6H ₂ O	h_i	Co(UO ₂) ₂ (PO ₄) ₂ ·7H ₂ O	g_i
K ₂ HPO ₄	h_i	Ni ₂ P ₂ O ₇	g_i
KUO ₂ PO ₄ ·3H ₂ O	g_i	Ni(UO ₂) ₂ (PO ₄) ₂ ·7H ₂ O	g_i
KAl ₂ (PO ₄) ₂ OH·2H ₂ O (Minyulite)	g_i	Zn ₃ (PO ₄) ₂ ·4H ₂ O (Hopeite)	$g_i + h_i$
NH ₄ MgPO ₄ ·6H ₂ O (Struvite)	g_i	Zn ₃ (PO ₄) ₂	g_i
NH ₄ Al ₂ (PO ₄) ₂ OH·2H ₂ O (Am. Minyulite)	g_i	Zn ₂ P ₂ O ₇	h_i
NH ₄ UO ₂ PO ₄ ·3H ₂ O	g_i	Cu ₃ (PO ₄) ₂	$g_i + h_i$
NH ₄ H ₂ PO ₄	h_i	Cu ₂ P ₂ O ₇	g_i
(NH ₄) ₂ HPO ₄	h_i	Cu(H ₂ PO ₄) ₂	h_i
Mg ₃ (PO ₄) ₂ (Farringtonite)	$g_i + h_i$	Pb ₃ (PO) ₂	$g_i + h_i$
Mg ₄ (PO ₄) ₂	g_i	Pb ₄ (PO ₄) ₃	g_i
Mg ₅ (PO ₄) ₃ F	g_i	Al ₄ (PO ₄) ₃ (OH) ₃ (Trolleite)	$g_i + h_i$
Mg ₃ (PO ₄) ₂ ·8H ₂ O (Bobierrite)	g_i	AlPO ₄ (Berlinite)	$g_i + h_i$
Ca ₁₀ (PO ₄) ₆ (OH) ₂ (Hydroxyapatite)	$g_i + h_i$		

To evaluate the accuracy of method a new set of individual contributions for g_i and h_i using another 18 crystalline phases has been calculated and compared to results of table 2. The averages of differences are 0.62% for g_i and 0.43% for h_i (N = 10 values considered each).

The values of g_i and h_i of table 2 have also been checked for internal consistency versus values of Robie *et al.* (1979) of ΔG°_f and ΔH°_f free oxides obtaining the following relations:

$$g_i = 1.042 \Delta G^\circ_f(\text{oxides}) - 80.115 \text{ kJ mol}^{-1} \\ (r = 0.965)$$

$$h_i = 1.047 \Delta H^\circ_f(\text{oxides}) - 87.455 \text{ kJ mol}^{-1} \\ (r = 0.967)$$

equivalents to the equations (3) and (4).

In the same way in which the free energy or enthalpy of a compound has just been defined as the sum of the free energies or enthalpies of its constituent units, we can also define the entropy as: $S = \sum n_i s_i$, where s_i is the entropy of the constituent unit. Taking into account the thermodynamic equation: $\Delta G = \Delta H - T\Delta S$; it is easy to obtain the equation that relates the entropy of polyhedral units with free energy and enthalpy:

$s_i = (h_i - g_i)/T$, but it is recommendable to derivate these partial entropies following Holland (1989). This leads to lower propagated uncertainty on the resulting estimates.

Table 2.— g_i and h_i values of each basic unit calculated by the method of least-squares (kJ mol⁻¹)

basic unit	g_i	error ±	h_i	error ±
P ₂ O ₅	-1,636.94	8.44	-1,726.84	7.22
Li ₂ O	—	—	-817.30	12.97
Na ₂ O	-665.22	4.54	-719.50	3.40
K ₂ O	-751.28	1.24	-774.50	3.26
(NH ₄) ₂ O	-359.62	6.12	-541.28	9.72
H ₂ O(H)	-227.54	2.52	-308.20	1.66
MgO	-628.52	3.87	-692.92	4.29
CaO	-742.46	3.64	-792.81	5.57
FeO	-269.53	3.17	-319.16	—
CoO	-251.88	3.00	—	—
NiO	-233.41	2.85	—	—
ZnO	-338.13	2.71	-392.62	4.06
CuO	-135.98	3.26	-171.82	3.42
PbO	-242.41	3.36	-289.49	—
UO ₃	-1,183.37	4.03	—	—
Al ₂ O ₃	-1,613.88	7.92	-1,780.92	6.72
H ₂ O (cryst.)	-239.10	0.42	-299.22	0.62
H ₂ O(OH ⁻)	-255.04	8.08	-267.20	6.06
F = O	-284.89	8.16	-285.35	5.52
Cl = O	-66.40	7.18	-52.39	16.87

Due to the scarce number of data found in the bibliography for ΔG°_f and ΔH°_f (phosphate), the contribution of the cation coordination number to the Gibbs free energy values of polyhedral units (which is important in calcium, aluminium and lead phosphates where different types of coordination

Table 3.—Temperature function $g_{i,T}$ of the basic units (kJ mol^{-1})

P_2O_5	$-1,726.84 + 0.30T$
Na_2O	$-719.80 + 0.18T$
K_2O	$-774.50 + 0.08T$
$(\text{NH}_4)_2\text{O}$	$-541.28 + 0.61T$
$\text{H}_2\text{O}_{(\text{H})}$	$-308.20 + 0.27T$
MgO	$-692.92 + 0.21T$
CaO	$-792.81 + 0.17T$
FeO	$-319.16 + 0.17T$
ZnO	$-392.62 + 0.18T$
CuO	$-171.82 + 0.12T$
PbO	$-289.49 + 0.16T$
Al_2O_3	$-1,780.92 + 0.55T$
$\text{H}_2\text{O}_{(\text{cryst.})}$	$-299.22 + 0.20T$
$\text{H}_2\text{O}_{(\text{OH})}$	$-267.20 + 0.04T$
$\text{F} \equiv \text{O}$	$-285.35 + 0.002T$
$\text{Cl} \equiv \text{O}$	$-52.39 - 0.05T$

take place) could not be considered, as was done for the case of silicates and carbonates (Chermak & Rimstidt, 1989 & 1990 and La Iglesia & Felix, 1994). For this reason, the precision of the values calculated for g_i and h_i phosphate, is lower than that of silicates and carbonates.

Calculation of the free energies of polyhedral phosphate units at high temperature

Chermak & Rimstidt (1990) published a method that permits the estimation of free energy of any silicate at high temperature, based on the approximation $\Delta C/\delta T = 0$, which gives for the free energy at the polyhedral units versus temperature:

$$g_{i,T} = h_{i,298} - [T(h_{i,298} - g_{i,298})]/298 \quad (7)$$

This equation allows the calculation of $\Delta G_{f,T}^\circ$ of any silicate, in the temperature range 298-650 K, with an uncertainty of 0.25% (in relation to experimental value of Robie *et al.* (1979)). For temperatures higher than 650K the estimated values of $\Delta G_{f,T}^\circ$ can carry an uncertainty of 0.5%. This method has been applied for the estimation $\Delta G_{f,T}^\circ$ in carbonates, in the temperature range 400 to 1.000K with difference less 0.60% (La Iglesia & Felix, 1994). This is therefore an excellent method for estimating the $\Delta G_{f,T}^\circ$ of silicates and carbonates.

Using Equation 7, we have calculated the temperature function $g_{i,T}$ of the phosphate units, which appears in table 3.

Results

Tables 4 and 5 compare the standard free energy and enthalpy values predicted in this paper with the bibliographic data; the differences are shown as percent of relative error (% residual), $R = 100(\Delta G_{\text{cal}} - \Delta G_{\text{bibl}})/\Delta G_{\text{bibl}}$. When several experimental values of ΔG_f° were found for one crystalline species we have calculated the residual error in relation to their average value (ΔG_{bibl} or ΔH_{bibl}). For ΔG_f° values, the calculated average residual error is: $R = 0.029$, and standard deviation, $\Delta_n = 0.619$ ($N = 82$ values considered). For ΔH_f° , $R = -0.003$, and $\Delta_n = 0.525$ ($N = 58$ values considered). From the 82 values of ΔG_f° estimated, 74 values have an error less than 1%, 7 values are between 1 and 2% and only 1 value is more than 2%. Similar distribution is found for ΔH_f° . All values are lower than 2%, and only 3 are over 1%. The preceding results confirm the goodness of the proposed method for the estimation of the thermodynamic properties of phosphates. Figures 1 and 2 present the frequency histogram of percent residual differences between bibliographic and calculated values for ΔG° and ΔH° . In both cases, a Gaussian distribution is obtained.

The accuracy of the proposed method was tested by predicting the thermodynamic properties of the phosphates not used to calculate g_i and h_i contribution (in tables 4 and 5 the values of ΔG_f° and ΔH_f° used to calculate g_i and h_i have been marked with *). The average residual error and standard deviation calculated from the above data for ΔG_f° and ΔH_f° are: $R = 0.002$ and $\Delta_n = 0.697$ ($N = 51$ values considered) and $R = 0.075$ and $\Delta_n = 0.583$ ($N = 35$ values considered), respectively. The uncertainty ranges of these estimates data are larger than those obtained by La Iglesia & Felix (1994) in the estimation of thermodynamic properties of carbonates. It was not possible to obtain better results for the following two reasons: 1) as indicated before, the contribution of the cation coordination to the Gibbs free energy values of the polyhedral units could not be considered as in the case of silicates and carbonates, and 2) the poorer agreement among the reported thermodynamic data for the phosphates. In this way, we have calculated the residual errors, in relation to the average values of ΔG_f° and ΔH_f° for some bibliographic data of fluorapatite and hydroxyapatite selected by Tacker & Stormer (1989) obtaining the following values of standard deviation: $\sigma_n = 0.666$ (for ΔG_f° , $N = 17$ values considered) and $\sigma_n = 0.645$ (for ΔH_f° , $N = 19$

Table 4.—Comparison of ΔG_f^0 (bibliography) versus ΔG_f^0 (calculated) for phosphates and residual error (kJ mol⁻¹)

Crystalline species	ΔG_f^0 (bibli.)	ΔG_f^0 (calc.)	R %
Na ₃ PO ₄	-1,788.80 (1)	-1,816.30 ± 7.11	1.54
Na ₄ P ₂ O ₇	-2,969.30 (1)	-2,967.38 ± 12.40	-0.07
Na ₅ P ₃ O ₁₀	-4,100.20 * (1)	-4,118.46 ± 17.00	0.45
Na ₅ P ₃ O ₁₀ ·6H ₂ O	-5,540.10 (1)	-5,553.06 ± 17.19	0.22
NaH ₂ PO ₄	-1,386.10 (1)	-1,378.62 ± 5.41	-0.54
Na ₂ HPO ₄	-1,608.20 (1)	-1,597.46 ± 6.21	-0.67
Na ₂ HPO ₄ ·2H ₂ O	-2,088.50 (1)	-2,075.66 ± 6.26	-0.62
Na ₂ HPO ₄ ·7H ₂ O	-3,279.80 (1)	-3,271.16 ± 6.98	-0.26
Na ₂ HPO ₄ ·12H ₂ O	-4,467.80 * (1)	-4,466.66 ± 8.09	-0.03
Na ₂ H ₂ P ₂ O ₇	-2,522.40 (1)	-2,529.70 ± 9.91	0.29
KH ₂ PO ₄	-1,415.85 (1)	-1,421.65 ± 4.95	0.41
	-1,418.30 (2)		0.17
KUO ₂ PO ₄	-2,386.60 (2)	-2,377.48 ± 5.87	-0.38
KUO ₂ PO ₄ ·3H ₂ O	-3,098.20 * (2)	-3,094.78 ± 6.00	-0.11
K ₃ Al ₅ (PO ₄) ₈ H ₆ ·18H ₂ O Pot. Taranakite	-16,760.80 (2)	-16,695.90 ± 41.26	-0.39
KA1 ₂ (PO ₄) ₂ OH·2H ₂ O Minyulite	-4,237.10 * (2)	-4,232.18 ± 11.79	-0.12
KMgPO ₄ ·6H ₂ O	-3,241.00 (2)	-3,257.23 ± 6.29	0.50
NH ₄ H ₂ PO ₄	-1,210.38 (1)	-1,225.26 ± 5.79	1.22
	-1,210.56 (3)		1.21
NH ₄ UO ₂ PO ₄	-2,201.60 (2)	-2,180.99 ± 6.59	-0.94
NH ₄ UO ₂ PO ₄ ·3H ₂ O	-2,907.60 * (2)	-2,898.29 ± 6.71	-0.32
NH ₄ MgPO ₄	-1,624.00 (2)	-1,626.14 ± 6.49	0.13
	-1,631.80 (4)		-0.35
NH ₄ MgPO ₄ ·6H ₂ O Struvite	-3,051.10 * (5)	-3,060.74 ± 6.96	0.32
(NH ₄) ₃ Al ₅ (PO ₄) ₈ H ₆ ·18H ₂ O Amm. Taranakite	-16,129.15 (2)	-16,106.33 ± 41.60	-0.14
	-16,164.80 (1)		0.36
NH ₄ Al ₂ (PO ₄) ₂ OH·2H ₂ O Amm. Minyulite	-4,044.70 * (2)	-4,035.69 ± 12.66	-0.30
Mg ₃ (PO ₄) ₂ Farringtonite	-3,538.70 * (1)	-3,522.51 ± 14.35	-0.46
	-3,538.80 * (5)		-0.46
	-3,548.40 * (6)		-0.73
Mg(H ₂ PO ₄) ₂	-2,730.10 (7)	-2,720.57 ± 10.56	-0.35
Mg(H ₂ PO ₄) ₂ ·2H ₂ O	-3,200.30 (7)	-3,198.76 ± 10.60	-0.05
Mg(H ₂ PO ₄) ₂ ·4H ₂ O	-3,674.40 (7)	-3,676.95 ± 10.63	0.07
MgHPO ₄	-1,577.30 (2)	-1,560.77 ± 5.80	-1.05
MgHPO ₄ ·3H ₂ O Newberyite	-2,288.90 (2)	-2,278.06 ± 6.01	-0.47
	-2,297.00 (7)		-0.82
Mg ₃ (PO ₄) ₂ ·8H ₂ O Bobjerrite	-5,443.40 * (2)	-5,435.28 ± 14.74	-0.15
	-5,450.50 * (2)		-0.28
Mg ₃ (PO ₄) ₂ ·22H ₂ O	-8,751.80 (2)	-8,782.61 ± 17.07	0.35
Mg ₅ (PO ₄) ₃ F	-5,854.25 * (7)	-5,882.91 ± 24.52	0.49
Mg ₅ (PO ₄) ₃ OH	-5,758.00 (7)	-5,725.55 ± 23.47	-0.56
Mg ₄ O(PO ₄) ₂	-4,172.70 * (7)	-4,151.03 ± 17.63	-0.52
Mg ₂ PO ₄ F Wagnerite	-2,305.40 (7)	-2,360.40 ± 12.01	2.39
Ca ₃ (PO ₄) ₂ low Whitlockite	-3,884.82 (5)	-3,864.33 ± 13.80	-0.53
	-3,884.70 (1)		-0.52
	-3,899.50 (8)		-0.90
	-3,889.40 (6)		-0.64
	-3,895.60 (9)		-0.80
CaHPO ₄ Monetite	-1,679.90 (8)	-1,674.71 ± 5.71	-0.31
	-1,680.00 (6)		-0.31
	-1,681.20 (1)		-0.39
CaHPO ₄ ·2H ₂ O Brushite	-2,154.75 * (2)	-2,152.90 ± 5.78	-0.09
	-2,153.10 * (8)		-0.01
	-2,153.80 * (6)		-0.04
Ca(H ₂ PO ₄) ₂	-2,824.80 (5)	-2,834.51 ± 10.48	0.34
	2,812.10 (4)		0.79

* Values selected to calculate g_i , (1) Wagman *et al.* (1982), (2) Vieillard & Tardy (1984), (3) Wagman (1968), (4) Latimer (1952), (5) Parker *et al.* (1971), (6) Naumov *et al.* (1971), (7) Duff (1971a), (8) Rossini *et al.* (1952), (9) Duff (1972), (10) Robie *et al.* (1979), (11) Duff (1971b), (12) Tacker & Stormer (1989), (13) Al-Borno & Tomson (1994), (14) Woods & Garrels (1987).

Table 4.—Comparison of ΔG_f^0 (bibliography) versus ΔG_f^0 (calculated) for phosphates and residual error (kJ mol⁻¹) (continuation)

Crystalline species	ΔG_f^0 (bibli.)	ΔG_f^0 (calc.)	R %
Ca(H ₂ PO ₄) ₂ ·2H ₂ O	-3,058.40 (5)	-3,073.60 ± 10.49	0.50
	-3,058.18 (2)		
Ca ₂ P ₂ O ₇	-3,132.00 (1)	-3,121.87 ± 11.15	-0.32
Ca ₄ O(PO ₄) ₂ Hilgenstockite	-4,588.00 (2)	-4,606.79 ± 16.83	0.41
Ca ₂ PO ₄ Cl	-2,371.70 * (2)	-2,369.80 ± 11.06	-0.08
Ca ₁₀ O(PO ₄) ₆ Oxiapatite	-12,272.10 (9)	-12,335.45 ± 44.34	0.52
	-12,307.80 (2)		
Ca ₈ H ₂ (PO ₄) ₅ ·5H ₂ O	-12,263.30 (1)	-12,273.56 ± 38.73	0.08
	-12,261.20 (11)		0.10
Ca(UO ₂) ₂ (PO ₄) ₂ ·10H ₂ O Autunite	-7,147.00 (2)	-7,137.14 ± 12.93	-0.14
CaAlH(PO ₄) ₂ ·6H ₂ O	-4,722.20 (2)	-4,734.71 ± 10.40	0.27
Ca ₁₀ (PO ₄) ₆ F ₂ Fluorapatite	-12,983.00 * (2)	-12,905.23 ± 47.25	-0.60
	-12,911.56 * (10)		
	-12,885.92 * (12)		
	-12,920.04 * (12)		
	-12,922.54 * (12)		
	-12,941.80 * (12)		
	-12,949.32 * (12)		
	-13,062.30 * (12)		
	-12,572.19 * (10)		
	-12,677.00 * (2)		
Ca ₁₀ (PO ₄) ₆ (OH) ₂ Hydroxyapatite	-12,590.50 ± 45.07	-12,590.50 ± 45.07	0.15
	-12,734.38 * (12)		
	-12,752.17 * (12)		
	-12,672.67 * (12)		
	-12,503.47 * (12)		
	-12,514.37 * (12)		
	-12,648.81 * (12)		
Ca ₁₀ (PO ₄) ₆ Cl ₂ Chlorapatite	-12,514.00 * (2)	-12,468.26 ± 43.05	-0.37
	-12,403.00 * (12)		
	-12,447.50 * (12)		
Fe ₃ (PO ₄) ₂ ·8H ₂ O Vivianite	-12,403.07 * (12)	-4,358.32 ± 13.15	-0.43
	-4,377.20 * (2)		
	-4,340.94 * (13)		0.40
Fe ₃ (PO ₄) ₂	-2,444.80 * (2)	-2,445.55 ± 12.72	0.03
CoHPO ₄	-1,182.00 (2)	-1,184.12 ± 5.33	0.18
Co ₃ (PO ₄) ₂	-2,399.10 * (2)	-2,392.58 ± 12.34	-0.27
	-2,398.60 * (1)		
Co(UO ₂) ₂ (PO ₄) ₂ ·7H ₂ O	-5,937.40 * (2)	-5,929.26 ± 12.40	0.05
Ni ₃ (PO ₄) ₂	-2,347.30 (2)	-2,337.17 ± 12.01	-0.43
	-2,353.00 (1)		
Ni ₂ P ₂ O ₇	-2,083.10 * (1)	-2,103.76 ± 10.18	0.99
Ni(UO ₂) ₂ (PO ₄) ₂ ·7H ₂ O	-5,926.30 * (2)	-5,910.79 ± 12.37	-0.26
Zn ₃ (PO ₄) ₂	-2,633.40 (2)	-2,651.33 ± 11.72	0.68
Zn ₃ (PO ₄) ₂ ·H ₂ O	-2,890.90 (2)	-2,890.43 ± 11.73	-0.01
Zn ₃ (PO ₄) ₂ ·2H ₂ O	-3,143.30 (2)	-3,129.52 ± 11.75	-0.44
Zn ₃ (PO ₄) ₂ ·4H ₂ O Hopeite	-3,616.40 * (2)	-3,607.71 ± 11.84	-0.24
	-3,606.30 * (2)		
Cu ₃ (PO ₄) ₂	-2,051.60 * (14)	-2,044.94 ± 12.92	-0.32
	-2,051.30 * (1)		
	-2,066.60 * (14)		
Cu ₂ P ₂ O ₇	-1,874.30 * (1)	-1,908.94 ± 10.67	1.84
Cu ₃ (PO ₄) ₂ ·2H ₂ O	-2,564.80 (2)	-2,523.14 ± 12.95	-1.62
Cu ₃ (PO ₄) ₂ ·3H ₂ O	-2,753.00 * (2)	-2,762.24 ± 12.98	0.33
Cu ₅ (PO ₄) ₃ OH	-3,261.80 (2)	-3,262.93 ± 21.03	0.04
Cu(UO ₂) ₂ (PO ₄) ₂ ·8H ₂ O	-6,071.20 (2)	-6,052.48 ± 12.28	-0.31
Pb ₃ (PO ₄) ₂	-2,364.00 * (2)	-2,364.17 ± 13.15	0.01

* Values selected to calculate g_i , (1) Wagman *et al.* (1982), (2) Vieillard & Tardy (1984), (3) Wagman (1968), (4) Latimer (1952), (5) Parker *et al.* (1971), (6) Naumov *et al.* (1971), (7) Duff (1971a), (8) Rossini *et al.* (1952), (9) Duff (1972), (10) Robie *et al.* (1979), (11) Duff (1971b), (12) Tacker & Stormer (1989), (13) Al-Borno & Tomson (1994), (14) Woods & Garrels (1987).

Table 4.—Comparison of ΔG_f^0 (bibliography) versus ΔG_f^0 (calculated) for phosphates and residual error (kJ mol⁻¹) (continuation)

Crystalline species	ΔG_f^0 (bibli.)	ΔG_f^0 (calc.)	R %
Pb ₄ O(PO ₄) ₂	-2,582.80 * (2)	-2,606.58 ± 15.87	0.91
Pb ₅ (PO ₄) ₃ Cl Pyromorphite	-3,791.50 (2)	-3,733.86 ± 22.23	-1.52
Pb ₅ (PO ₄) ₃ OH	-3,774.10 (2)	-3,794.98 ± 21.42	0.53
PbHPO ₄	-1,178.90 (2)	-1,174.65 ± 5.54	-0.36
(UO ₂) ₃ (P ₀) ₄ ₂	-5,160.00 (2)	-5,187.05 ± 14.74	0.52
H ₂ (UO ₂) ₂ (PO ₄) ₂	-4,217.50 (2)	-4,231.22 ± 11.94	0.33
H ₂ (UO ₂) ₂ (PO ₄) ₂ ·10H ₂ O	-6,605.60 (2)	-6,622.22 ± 12.66	0.25
UO ₂ HPO ₄	-2,102.90 (2)	-2,115.61 ± 5.97	0.60
UO ₂ HPO ₄ ·4H ₂ O	-3,051.30 (2)	-3,072.01 ± 6.20	0.68
AlPO ₄ Berlinite	-1,617.90 * (1)	-1,625.44 ± 5.79	0.46
	-1,601.20 * (2)		1.51
	-1,618.00 * (14)		0.46
	-1,623.30 * (14)		0.13
AlPO ₄ ·2H ₂ O Variscite	-2,111.40 (14)	-2,103.61 ± 5.85	-0.37
	-2,104.20 (2)		-0.03
Al ₄ (PO ₄) ₃ (OH) ₃ Trolleite	-6,077.47 * (2)	-6,065.73 ± 23.62	-0.19
Al ₂ PO ₄ (OH) ₃ Augelite	-2809.56 (2)	-2814.91 ± 15.08	0.19

* Values selected to calculate g_f , (1) Wagman *et al.* (1982), (2) Vieillard & Tardy (1984), (3) Wagman (1968), (4) Latimer (1952), (5) Parker *et al.* (1971), (6) Naumov *et al.* (1971), (7) Duff (1971a), (8) Rossini *et al.* (1952), (9) Duff (1972), (10) Robie *et al.* (1979), (11) Duff (1971b), (12) Tacker & Stormer (1989), (13) Al-Borno & Tomson (1994), (14) Woods & Garrels (1987).

values considered), an uncertainty level similar to the method here proposed!

Table 6 compares the calculated values of free energy at high temperature, using equation 8, to the published experimental data of Robie *et al.* (1979)

for berlinite, whitlockite, fluorapatite and hydroxapatite in the temperature range of 400 to 700 K. In all of the studied cases, the relative error is less than 0.9%, with R = -0.044 and $\sigma_n = 0.428$ (N = 16 values considered).

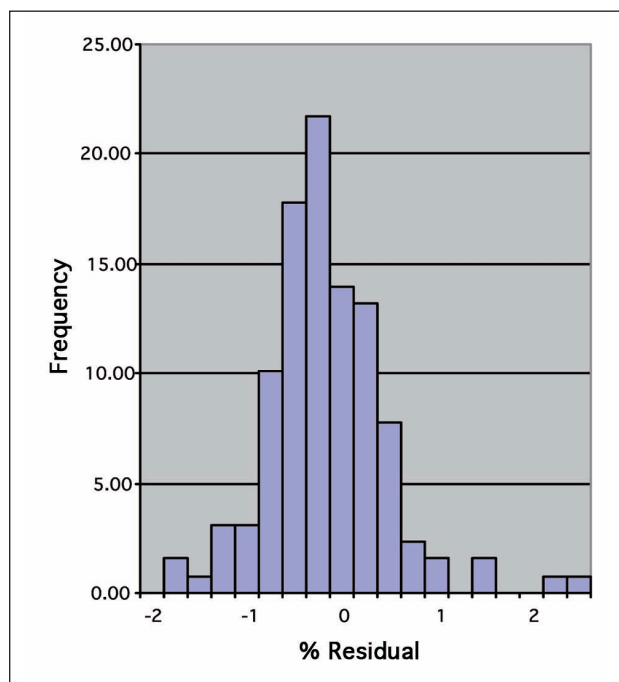


Fig. 1.—Frequency histogram of residual differences between bibliographic and calculated values of ΔG_f^0 (phosphates).

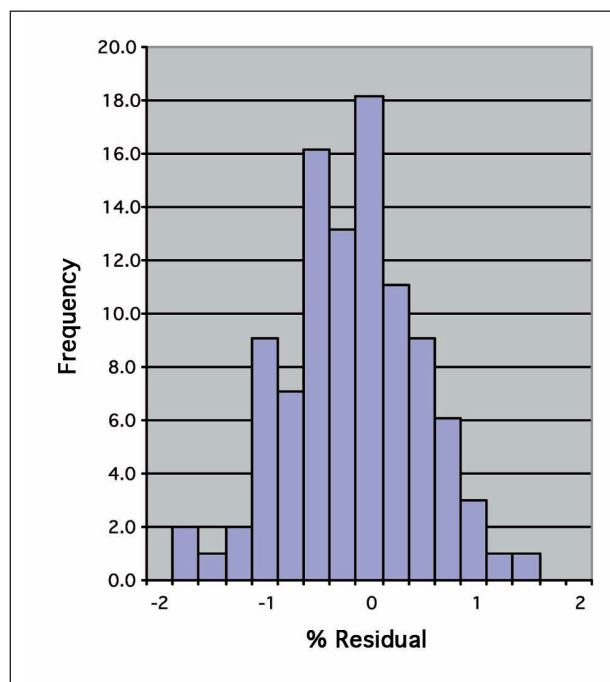


Fig. 2.—Frequency histogram of residual differences between bibliographic and calculated values of ΔH_f^0 (phosphates).

Table 5.—Comparison of ΔH_f^0 (bibliography) versus ΔH_f^0 (calculated) for phosphates and residual error (kJ mol^{-1})

Crystalline species	$\Delta H_f^0(\text{bibli.})$	$\Delta H_f^0(\text{Calc.})$	R %
Li ₃ PO ₄ Lithiophosphatite	-2,095.80 * (1)	-2,088.32 ± 19.79	-0.36
	-2,092.20 * (2)		-0.19
LiP ₂ O ₇	-3,356.00 * (1)	-3,360.20 ± 26.93	0.13
LiH ₂ PO ₄	-1,586.60 (2)	-1,579.99 ± 7.61	-0.42
	-1,573.60 (1)		0.41
Na ₃ PO ₄	-1,917.40 (1)	-1,942.32 ± 6.25	1.30
	-1,913.60 (2)		1.50
Na ₄ P ₂ O ₇	-3,188.00 (1)	-3,165.53 ± 9.92	-0.71
Na ₄ P ₂ O ₇ ·10H ₂ O	-6,138.00 * (1)	-6,158.12 ± 11.70	0.33
Na ₄ P ₄ O ₁₂	-4,862.00 (1)	-4,892.81 ± 15.96	0.63
Na ₅ P ₃ O ₁₀	-4,409.90 * (1)	-4,388.74 ± 13.78	-0.48
Na ₅ P ₃ O ₁₀ ·6H ₂ O	-6,194.80 (1)	-6,184.29 ± 14.26	-0.17
NaH ₂ PO ₄	-1,536.80 (1)	-1,531.33 ± 4.32	-0.36
	-1,543.90 (2)		-0.81
NaH ₂ PO ₄ ·H ₂ O	-1,833.00 (1)	-1,830.59 ± 4.37	-0.13
NaH ₂ PO ₄ ·2H ₂ O	-2,128.40 (1)	-2,129.85 ± 4.41	0.07
Na ₂ HPO ₄	-1,748.10 (1)	-1,736.83 ± 5.03	-0.64
	-754.80 (2)		0.20
Na ₂ HPO ₄ ·2H ₂ O	-2,346.00 (1)	-2,335.32 ± 5.18	-0.46
Na ₂ HPO ₄ ·7H ₂ O	-3,821.70 (1)	-3,831.57 ± 6.64	0.26
Na ₂ HPO ₄ ·12H ₂ O	-5,297.80 * (1)	-5,327.82 ± 8.98	0.57
Na ₂ H ₂ P ₂ O ₇	-2,764.80 (1)	-2,754.52 ± 8.15	0.37
Na ₂ H ₂ P ₂ O ₇ ·6H ₂ O	-4,531.00 (1)	-4,550.02 ± 8.96	0.42
Na ₃ HP ₂ O ₇	-2,965.60 * (1)	-2,960.03 ± 16.94	-0.19
Na ₃ HP ₂ O ₇ ·H ₂ O	-3,276.50 (1)	-3,259.29 ± 8.90	-0.53
Na ₃ HP ₂ O ₇ ·6H ₂ O	-4,740.90 (1)	-4,755.52 ± 9.63	0.31
NaNH ₄ HPO ₄ ·4H ₂ O	-2,852.27 (1)	-2,848.27 ± 6.81	-0.14
NaCaPO ₄	-2,004.14 (2)	-2,014.36 ± 6.85	0.51
KH ₂ PO ₄	-1,568.33 (1)	-1,550.36 ± 4.29	-1.15
	-1,570.70 (2)		1.30
K ₂ HPO ₄	-1,779.90 * (2)	-1,774.89 ± 4.93	0.28
K ₂ H ₂ P ₂ O ₇	-2,816.00 (1)	-2,792.60 ± 8.09	-0.83
K ₃ A ₁₅ (PO ₄) ₈ H ₆ ·18H ₂ O Pot. Taranakite	-18,908.20 (2)	-18,757.23 ± 35.91	-0.80
	-18,919.20 (1)		-0.86
KMgPO ₄ ·6H ₂ O	-3,724.30 * (2)	-3,729.29 ± 6.92	0.13
NH ₄ H ₂ PO ₄	-1,445.07 * (1)	-1,445.77 ± 6.28	0.05
	-1,445.10 * (3)		0.05
(NH ₄) ₂ HPO ₄	-1,566.90 * (1)	-1,565.72 ± 10.40	-0.08
(NH ₄) ₃ PO ₄	-1,671.90 (1)	-1,685.67 ± 15.02	0.82
(NH ₄) ₃ PO ₄ ·3H ₂ O	-2,555.60 (1)	-2,583.42 ± 15.13	1.09
(NH ₄)MgPO ₄ ·6H ₂ O Struvite	-3,681.90 (1)	-3,624.70 ± 8.30	-1.55
	-3,681.92 (5)		-1.55
(NH ₄) ₃ Mg(PO ₄) ₆ ·18H ₂ O Amm. Taranakite	-18,532.60 (2)	-18,484.51 ± 38.45	-0.26
	-18,547.70 (1)		-0.34
Mg ₃ (PO ₄) ₂ Farringtonite	-3,780.70 * (1)	-3,801.93 ± 14.76	0.56
	-3,780.66 * (5)		0.56
	-3,790.30 * (6)		0.31
Ca ₃ (PO ₄) ₂ low Whitlockite	-4,120.82 (2)	-4,100.76 ± 18.20	-0.49
	-4,120.80 (1)		-0.49
	-4,137.60 (8)		-0.89
	-4,125.40 (6)		-0.60
	-4,120.80 (9)		-0.49
CaHPO ₄ Monetite	-1,820.90 (8)	-1,808.86 ± 6.69	-0.66
	-1,813.20 (6)		-0.24
	-1,814.40 (1)		-0.31
CaHPO ₄ ·2H ₂ O Brushite	-2,403.60 * (2)	-2,407.36 ± 6.80	0.16
	-2,410.00 * (8)		-0.11
	-2,402.70 * (6)		0.19

* Values selected to calculate h_f , References (1) to (14) see Table 4.

Table 5.—Comparison of ΔH_f^0 (bibliography) versus ΔH_f^0 (calculated) for phosphates and residual error (kJ mol⁻¹) (continuation)

Crystalline species	ΔH_f^0 (bibli.)	ΔH_f^0 (Ca1c.)	R %
Ca(H ₂ PO ₄) ₂	-3,104.10 (5)	-3,134.68 ± 9.70	0.99
	-3,104.60 (4)		0.97
	-3,104.70 (1)		0.97
	-3,113.60 (6)		0.68
Ca(H ₂ PO ₄) ₂ ·2H ₂ O	-3,409.70 (5)	-3,433.93 ± 9.72	0.71
	-3,409.67 (1)		0.71
Ca ₂ P ₂ O ₇	-3,338.80 (1)	-3,309.6 ± 13.28	-0.88
Ca ₁₀ (PO ₄) ₆ F ₂ Fluorapatite	-13,744.00 * (2)	-13,679.34 ± 60.77	-0.47
	-13,614.08 * (12)		0.48
	-13,639.72 * (10)		0.29
	-13,648.20 * (12)		0.23
	-13,650.70 * (12)		0.21
	-13,669.96 * (12)		0.07
	-13,677.48 * (12)		0.01
	-13,790.46 * (12)		-0.81
Ca ₁₀ (PO ₄) ₆ (OH) ₂ Hydroxyapatite	-13,338.52 * (10)	-13,385.62 ± 0.07	0.35
	-13,510.12 * (12)		-0.92
	-13,518.50 * (12)		-0.98
	-13,439.00 * (12)		-0.40
	-13,269.80 * (12)		0.87
	-13,280.68 * (12)		0.79
Ca ₁₀ (PO ₄) ₆ C ₁₂ Chlorapatite	-13,415.14 * (12)	-13,184.10 ± 67.56	-0.22
	-13,271.64 * (12)		-0.66
	-13,272.00 * (2)		-0.66
	-13,096.54 * (12)		0.67
Fe ₃ (PO ₄) ₂ ·8H ₂ O Vivianite	-5,078.09 * (13)	-5,078.09 ± 10.21	0.00
Zn ₃ (PO ₄) ₂	-2,896.60 (2)	-2,902.65 ± 14.16	0.21
	-2,892.40 (1)		0.35
Zn ₂ P ₂ O ₇	2,510.40 * (1)	-2,510.86 ± 10.87	0.02
Zn ₃ (PO ₄) ₂ ·2H ₂ O	-3,211.70 (2)	-3,201.91 ± 14.17	-0.31
Zn ₃ (PO ₄) ₂ ·2H ₂ O	-3,516.30 (2)	-3,501.17 ± 14.21	-0.43
Zn ₃ (PO ₄) ₂ ·4H ₂ O Hopeite	-4,091.50 * (2)	-4,099.68 ± 14.27	0.20
Cu ₃ (PO ₄) ₂	-2,231.40 * (14)	-2,242.08 ± 12.55	0.48
Cu(H ₂ PO ₄) ₂	-2,526.70 * (2)	-2,515.12 ± 8.65	-0.46
Cu ₃ (PO ₄) ₂ ·2H ₂ O	-2,842.20 (2)	-2,840.58 ± 12.61	-0.06
Cu ₃ (PO ₄) ₂ ·3H ₂ O	-3,139.70 (2)	-3,139.83 ± 12.68	0.00
Pb ₃ (PO ₄) ₂	-2,595.30 * (14)	-2,595.30 ± 3.22	0.00
AlPO ₄ Berlinite	-1,733.80 * (1)	-1,752.14 ± 4.93	1.06
	-1,733.85 * (2)		1.06
AlPO ₄ ·2H ₂ O Variscite	-2,353.30 (14)	-2,350.64 ± 5.09	-0.11
Al ₄ (PO ₄) ₃ (OH) ₃ Trolleite	-6,567.67 * (2)	-6,583.19 ± 19.51	0.24

* Values selected to calculate h_f References (1) to (14) see Table 4.

Table 6.—Experimental and calculated data of $\Delta G_{f,T}$ (kJ mol⁻¹)

	400 K		500 K		600 K		700 K	
	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
AlPO ₄ Berlinite	-1,568.01	-1,583.88	-1,530.86	-1,541.38	-1,493.88	-1,498.88	-1,457.13	-1,456.38
Ca ₃ (PO ₄) ₂ Whitlockite	-3,783.85	-3,781.27	-3,708.57	-3,700.27	-3,633.63	-3,619.27	-3,559.16	-3,538.27
Ca ₅ (PO ₄) ₃ F Fluorapatite	-6,331.51	-6,318.86	-6,210.19	-6,188.66	-6,089.65	-6,058.46	-5,969.91	-5,928.26
Ca ₅ (PO ₄) ₃ OH Hydroxyapatite	-6,155.33	-6,159.91	-6,027.76	-6,027.91	-5,901.11	-5,895.91	-5,775.32	-5,763.91

(1) Robie *et al.* (1979); (2) Calculated using values of Table 3.

Conclusions

The method proposed by Chermak & Rimstidt (1989) for calculation of free energy and enthalpy of silicates, by summing the contributions of polyhedral units, is applicable to the estimation of ΔG°_f and ΔH°_f of phosphate minerals. This method allowed us to calculate the thermodynamic properties of phosphates with more accuracy than the methods published until now, with the following additional advantages: *a*) use of a simple easy computed mathematical procedure, and *b*) the ability to obtain a wider field of application among the phosphates.

The calculation of free energy at high temperature proposed by Chermak & Rimstidt (1990) for silicates is also applicable to phosphates, giving values very close to the experimental data.

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