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ESTIMATION OF ENTHALPIES OF FORMATION OF MINERALS BASED ON THEIR REFINED CRYSTAL STRUCTURES

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ABSTRACT. **This paper presents an improved method, in two steps, for calculating the enthalpies of formation of minerals. In the first step, the enthalpies of formation are estimated on the basis of a corresponding-state method.**

The enthalpies of formation of minerals from their constituent oxides are roughly linear functions of the empirical parameter $\Delta_H O^{2-} M^{z+}$, defined as the difference between the enthalpy of formation of oxides from the elements ($MO_x(c)$) and the enthalpy of their corresponding aqueous cation ($M^{z+}(aq)$):

$$\Delta_H O^{2-} M^{z+} = (1/x)[\Delta H_f^\circ MO_x(c) - \Delta H_f^\circ M^{z+}(aq)]$$

In the second step, this simple model is improved by correcting the initial linear relationships, introducing refractive indexes, molar volumes, electronic polarizabilities, cation-oxygen bond lengths, and refinements of the crystal structures. The latter refinement is introduced, through a calibration function, as a correction applied to the empirical parameter $\Delta_H O^{2-} M^{z+}$ characterizing each cation in its crystal site. The calibration function is analogous to the lattice energy function.

This approach has been used to estimate the enthalpies of formation of a large number of minerals. Results are presented for five families of compounds, made of two component oxides: silicates (SiO_2 and MO_x), aluminates ($AlO_{1.5}$ and MO_x), ferrites ($FeO_{1.5}$ and MO_x), chromites ($CrO_{1.5}$ and MO_x). and hydroxides ($HO_{0.5}$ and MO_x).

INTRODUCTION

In a series of publications (Tardy and Garrels, 1976, 1977; Tardy and Gartner, 1977; Tardy and Vieillard, 1977; Vieillard, 1978, 1982; Gartner, 1979; Tardy, 1979) we have proposed a method for estimating the Gibbs free energy of formation from the elements of a large number of minerals. The method is based on corresponding states and is similar to the one presented by Karapet' yants (1965).

In the earlier papers, the corresponding-state method was applied to the evaluation of the Gibbs free energy of formation of various oxygen components of two elements such as, for example, $MgSiO_3$, Ca_2SiO_4, $MgAl_2O_4$, et cetera, on the basis of the Gibbs free energies of formation of the corresponding oxides and aqueous cations.

In more recent works (Tardy and Vieillard, 1977; Vieillard, 1982), it was found that such thermodynamic estimations are more accurate if

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applied to enthalpies than to Gibbs free energies of formation of minerals. Furthermore, the accuracy of the estimating method was considerably improved by taking into consideration parameters characterizing the oxygen and cation environments, such as cation-oxygen bond length and effective electronic polarizabilities of ions in the crystals.

Definition of the parameter $\Delta_H O^{2-}M^{z+}(aq)$.—Both the previous and the revised methods proposed for the evaluation of the enthalpies are based on the use of parameter $\Delta_H O^{2-}M'^{z+}(aq)$ which characterizes one given cation M'^{z+} and which is defined as the difference between the enthalpy of formation of the corresponding oxides ($\Delta H_f^\circ MO_x(c)$) and the enthalpy of formation of the corresponding aqueous cation ($\Delta H_f^\circ M'^{z+}(aq)$):

$$\Delta_H O^{2-}M'^{z+} = (1/x)[\Delta H_f^\circ MO_x(c) - \Delta H_f^\circ M'^{z+}(aq)] \quad (1)$$

In this formulation, z is the charge on the cation M'^{z+}, and x is the number of oxygens combined with one atom of M in the oxide ($x = z/2$), so that the difference in definition (1) refers to one oxygen atom.

Let us calculate, for example, $\Delta_H O^{2-}Al^{3+}(aq)$ from the data of Robie, Hemingway, and Fisher (1978):

$$\begin{aligned}\Delta_H O^{2-}Al^{3+}(aq) &= (1/1.5)[1/2\ \Delta H_f^\circ Al_2O_3(c) - \Delta H_f^\circ Al^{3+}(aq)] \\ &= (1/3)(-1675.7\ \text{kJ/mol}) \\ &\quad - (1/1.5)(-531.00\ \text{kJ/mole}) \\ &= -204.57\ \text{kJ/mole} \end{aligned} \quad (2)$$

A set of internally consistent values of $\Delta_H O^{2-}M^{z+}(aq)$ given in table 1 was selected by Vieillard (1982). They are mostly from the collection of data recently published by Robie, Hemingway, and Fisher (1978). Some lacking (Cr^{3+}, Zr^{4+}) or inconsistent (Be^{2+}) values were collected from other sources (Naumov, Ryzhenko, and Khodakovsky, 1971; Vasil'ev and Lytkin, 1974). Recent and reliable data for Na^+ were published by Wagman and others (1982).

For double oxides, one introduces another parameter $\Delta_H M_p M'_q O_N$ which is simply the enthalpy of formation of a given compound $M_pM'_qO_N$ from its constituent oxides MO_x and $M'O_y$, where M'^{z+} and $M''^{z'+}$ are two cations for which $z = 2x$ and $z' = 2y$:

$$\Delta_H M_p M'_q O_N = \Delta H_f^\circ M_p M'_q O_N(c) - p\Delta H_f^\circ MO_x(c) - q\Delta H_f^\circ M'O_y(c) \quad (3)$$

The total number of oxygens N of the compound is equal to the sum of the number of oxygens n and n′ respectively related to the cations M and M′ in the individual oxides (MO_x and $M'O_y$):

$$N = n + n' = px + qy \quad (4)$$

TABLE 1

Enthalpy of formation from elements of oxides, enthalpy of formation of ion in aqueous state, $\Delta_H O^{2-} M^{z+}$ selected (kJ/mole)

Ion	$\Delta H°_f$oxide	$\Delta H°_f$ion (aq)	$\Delta_H O^{2-}M^{z+}$(aq)	Ion	$\Delta H°_f$oxide	$\Delta H°_f$ion (aq)	$\Delta_H O^{2-}M^{z+}$(aq)
H^+	- 279.82 (1)	0 (1)	- 279.82	Fe^{2+}	- 272.04 (2)	- 89.10 (2)	- 182.94
Li^+	- 598.73 (2)	- 278.46 (2)	- 41.82	Mn^{2+}	- 385.22 (2)	- 220.70 (2)	- 164.52
Na^+	- 414.22 (3)	- 240.12 (3)	66.02	Co^{2+}	- 237.94 (2)	- 58.20 (2)	- 179.74
K^+	- 363.17 (2)	- 252.17 (2)	141.17	Ni^{2+}	- 239.74 (2)	- 54.00 (2)	- 185.74
Rb^+	- 339. (3)	- 251.17 (3)	163.3	Zn^{2+}	- 350.46 (2)	- 153.39 (2)	- 197.07
Cs^+	- 345.98 (2)	- 258.04 (2)	170.11	Pb^{2+}	- 219.41 (2)	- 1.70 (2)	- 217.71
Be^{2+}	- 607.31 (4)	- 403.76 (4)	- 203.55	Al^{3+}	-1675.70 (2)	- 531.00 (2)	- 204.57
Mg^{2+}	- 601.49 (2)	- 466.85 (2)	- 134.65	Fe^{3+}	- 824.64 (2)	- 48.50 (2)	- 242.55
Ca^{2+}	- 635.09 (2)	- 542.83 (2)	- 92.26	Cr^{3+}	-1140.98 (4)	- 211.71 (4)	- 239.18
Sr^{2+}	- 590.49 (2)	- 545.8 (2)	- 44.69	Si^{4+}	- 910.70 (2)	-	-
Ba^{2+}	- 548.10 (2)	- 537.64 (2)	- 10.46	Zr^{4+}	-1100.56 (2)	- 607.39 (5)	- 246.59

(1) Robie and Waldbaum (1968); (2) Robie, Hemingway, and Fisher (1978); (3) Wagman and others (1982); (4) Naumov, Ryzhenko, and Khodakovsky (1971); (5) Vasil'ev and Lytkin (1974)

The same general relationship found by Tardy (1979) for Gibbs free energies was transposed to enthalpies (Vieillard, 1982) as follows:

$$\Delta_H M_p M'_q O_N = -\alpha(n \cdot n'/N)[\Delta_H O^{2-}M^{z+}(aq) - \Delta_H O^{2-}M'^{z'+}(aq)] \quad (5)$$

Again N is the total number of oxygens in the compound: n and n' are the numbers of oxygens respectively bonded with the cations M and M'; $\Delta_H O^{2-}M^{z+}(aq)$ and $\Delta_H O^{2-}M'^{z'+}(aq)$ are respectively the $\Delta_H O^{2-}$ parameter calculated for the cations M^{z+} and $M'^{z'+}$ in their aqueous states according to eq (1): α is a coefficient that characterizes a given family of compounds. In the case of $Ca_3Si_2O_7$, for example, one has: $\alpha = 1.299$ (table 2), $\Delta_H O^{2-}Ca^{2+}(aq) = -92.26$ kJ/mol (table 1), $\Delta_H O^{2-}Si^{4+}(aq) = -197.58$ kJ/mole (table 2), so that:

$$\begin{aligned}\Delta_H Ca_3Si_2O_7 &= -1.299\,(3 \times 4/7)[\Delta_H O^{2-}Ca^{2+}(aq) - \Delta_H O^{2-}Si^{4+}(aq)] \\ &= -1.29\,(3 \times 4/7)(-92.26 + 197.58) \\ &= -234.53 \text{ kJ/mole}\end{aligned}$$

This value calculated with eq (5) is close to the enthalpy of formation from the constituent oxides ($\Delta_H Ca_3Si_2O_7 = -229.158$ kJ/mole) (Parker and others, 1971). Thus, eq (5) suggests that the enthalpy of formation of a given compound from its oxides is proportional to a coefficient α, to a stoichiometric coefficient $n \cdot n'/N$, and to the difference $[\Delta_H O^{2-}M^{z+}(aq) - \Delta_H O^{2-}M'^{z'+}(aq)]$.

Eq (5), tested for a large number of compounds of two cations (silicates, phosphates, aluminates, carbonates, sulfates . . .) yields a

TABLE 2

Constant, parameter $\Delta_H O^{2-} M'^{z'+}(aq)$ of reference cation calculated, number of points, linear correlation coefficient and statistical deviation on Δ_H for a given $\Delta_H O^{2-} M^{z+}(aq)$ for several groups of compounds

Group of compounds	α	$\Delta_H O^{2-}M'(aq)$ (M' reference cation) (kJ/mole)	Number of minerals	Linear correlation coefficient	Statis. deviation of Δ_H for a given $\Delta_H O^{2-}$ (kJ/mole)
Hydroxides	1.076 (1)	- 229.6	36	- 0.994	± 7.8
Sulfates	1.679 (2)	- 349.9	28	- 0.988	± 50.0
Selenates	1.744 (2)	- 330.0	12	- 0.989	± 50.0
Chromates	1.541 (2)	- 247.7	13	- 0.991	± 39.0
Molybdates	1.349 (2)	- 240.9	15	- 0.988	± 46.0
Orthotitanates	1.006 (2)	- 197.9	7	- 0.961	± 42.0
Metatitanates	1.341 (2)	- 193.4	11	- 0.994	± 21.0
Phosphates	1.407 (3,4)	- 365.1	71	- 0.988	± 44.8
Silicates	1.299 (5)	- 197.6	37	- 0.992	± 28.4
Carbonates	1.419 (2)	- 238.7	18	- 0.993	± 31.1
Nitrates	1.74 (2)	- 265.4	23	- 0.992	± 44.9
Aluminates	0.797 (4)	- 224.5	12	- 0.937	± 22.3
Ferrites	0.803 (2)	- 195.7	12	- 0.956	± 32.3

(1) This study; (2) Gartner (1979); (3) Vieillard (1978); (4) Tardy and Vieillard (1977); (5) Vieillard (1982).

statistical deviation smaller than 35 kJ/mole (per one atom M'), depending on the family of compounds considered, for example, 10 kJ/mole for metasilicates, 26 kJ/mole, orthosilicates, et cetera. This statistical deviation is too large to allow the prediction of enthalpies of formation of minerals for which data are not available.

The observed deviations are attributed to the fact that the parameter $\Delta_H O^{2-} M^{z+}(aq)$ characterizes a cation in the aqueous state and not in a crystalline environment. The purpose of this paper is to justify the fundamental validity of eq (5) and to improve the method of estimation of the Δ_H of compounds by introducing corrections that take account of differences in the cation environments between the aqueous state, the crystal oxide, and the crystal compound considered. These corrections, based on recent structure refinements of minerals, allow a justification of the corresponding state method and can be used to predict the enthalpy of formation of minerals within (6 kJ/mole) a reasonable and considerably ameliorated statistical deviation. The validity of the method will be shown by using the enthalpy data available for the different families of silicates of the type $M_pSi_qO_N$.

JUSTIFICATION AND LIMITATIONS OF THE INITIAL MODEL

Enthalpies of formation of minerals from their oxides appear as the product of three parameters, and among them only the stoichiometric coefficient ($n \cdot n'/N$) and the difference ($\Delta_H O^{2-}M^{z+} - \Delta_H O^{2-}M'^{z'+}$) present fundamental significations. The coefficient α is empirical.

Significance of the parameter $\Delta_H O^{2-}M^{z+}(aq)$ (table 1).—The parameter $\Delta_H O^{2-}M^{z+}(aq)$ decreases as the cation electronegativity increases and appears related either to the oxygen affinity of the cation or to the enthalpy of dissolution of the corresponding oxide, according to the relation:

$$MO_x(c) + 2xH^+(aq) \rightarrow M^{z+}(aq) + xH_2O(l)$$

When two cations have the same oxygen affinity, the enthalpy of formation of a compound from the two oxides should be equal or close to zero. The lowest enthalpies of formation from oxides are obtained for the electropositive cations, which show a $\Delta_H O^{2-}M^{z+}(aq)$ value very different from $\Delta_H O^{2-}Si^{4+}(aq)$. Compared to their constituent oxides the corresponding compounds are the most stable.

The parameter $\Delta_H O^{2-}M^{z+}(aq)$ appears related to the cation electronegativity of Pauling (1932), and eq (5) is similar to the formula used to calculate the heat of formation (Q) of a gaseous compound AB:

$$Q = k(X_A - X_B) + \text{constant} \qquad (6)$$

in which X_A and X_B are, respectively, the Pauling's electronegativities of the gaseous elements A and B; the higher the difference between electronegativities, the lower the enthalpy of formation from elements ($k < 0$).

Variations of the coefficient α in different groups of compounds.—The general eq (5) was tested and applied to many groups of compounds such as silicates, phosphates, sulfates, et cetera (Gartner, 1979; Vieillard, 1982). In a given group, one first distinguishes the reference cation $M'^{z'+}$ in common with all the compounds considered, that is, Si^{4+} for silicates, P^{5+} for phosphates, S^{6+} for sulfates, et cetera, for which $\Delta_H O^{2-}M'^{z'+}(aq)$ are given in table 2.

For the different families of a group and for example for metasilicates, orthosilicates, et cetera, ($MSiO_3$, M_2SiO_4, $M_3Si_2O_7$, $M_2Si_3O_8$, M_3SiO_5, MSi_2O_5) one obtains a unique straight line by plotting $(1/n')\,\Delta_H$ compound versus the parameter mean $\Delta_H O^{2-}$:

$$\text{mean } \Delta_H O^{2-} \text{ compound} = [n \cdot \Delta_H O^{2-}M^{z+}(aq) + n' \cdot \Delta_H O^{2-}M'^{z'+}(aq)]/(n + n') \qquad (7)$$

It becomes either:

$$(1/n')\,\Delta_H \text{ compound} = -\alpha[\text{mean } \Delta_H O^{2-} \text{ compound} - \Delta_H O^{2-}Si^{4+}(aq)] \qquad (8)$$

$(1/n)\ \Delta_H$ compound

$$= +\alpha[\text{mean } \Delta_H O^{2-} \text{ compound} - \Delta_H O^{2-} M^{z+}(aq)] \quad (9)$$

Results for the group of silicates are presented in figure 1 and tables 3 and 4. For the 37 compounds listed, one finds $\alpha = -1.299$: $\Delta_H O^{2-} Si^{4+}(aq) = -197.58$ kJ/mole; the statistical deviation calculated for a given $\Delta_H O^{2-} M''^{z'+}(aq)$ is equal to ± 28.4 kJ/mole per silicon atom, and the correlation coefficient is -0.9923 (table 4). Thus, in a figure in which the parameter mean $\Delta_H O^{2-}$ compound is plotted in the abscissae axis and the parameter $[(1/n')\Delta_H$ compound] or $[(1/n)\ \Delta_H$ compound] in the ordinate axis, each compound $M_p M'_q O_N$ appears at the intersection of two straight lines crossing the abscissae axis respectively at mean $\Delta_H O^{2-}$ compound $= \Delta_H O^{2-} M^{z+}(aq)$ and $\Delta_H O^{2-} M''^{z'+}(aq)$. These lines have a slope of $+\alpha$ and $-\alpha$ (fig. 2).

Within a given group, it is also possible to distinguish several families of compounds. Within the silicates, for example, it is possible to separate metasilicates, orthosilicates, et cetera. In each of the families, the enthalpy of formation of any compound from its constituent oxides is proportional: (1) to the parameter $\Delta_H O^{2-} M^{z+}(aq)$ characteristic of the cation M^{z+}, which varies from one mineral to another, (2) to the stoichiometric coefficient $(n \cdot n'/N)$, and (3) to the specific coefficient α, which characterizes the family in question. Within metasilicates, for example, one obtains (table 4):

$\Delta_H MSiO_3 = -1.310\ (1x2/3)\ [\Delta_H O^{2-} M'^{z+}(aq) + 193.93]$

Correlation coefficient for 13 points: $r = -0.9987$

Statistical deviation on $\Delta_H MSiO_3$, for a given $\Delta_H O^{2-} M^{z+}(aq) = \pm 9.8$ kJ/mole.

The statistical deviation obtained for each family of silicates is generally smaller than 28.4 kJ/mole obtained for the whole silicate group (table 4). From one silicate family to another, α fluctuates slightly between 1.213 and 1.31, and the parameter $(\Delta_H O^{2-} M''^{z'+}(aq))$ fluctuates between -181.26 kJ/mole and -204.53 kJ/mole.

But from group to group α differs considerably from 0.803 for ferrites to 1.74 for nitrates (table 2).

Difficulty of evaluating a true value for the parameter $\Delta_H O^{2-} M''^{z'+}(aq)$ characterizing the reference cation.—An important concern here is the significance of the parameter $\Delta_H O^{2-} M''^{z'+}(aq)$, listed in table 2 and characterizing the reference cation $M''^{z'+}$. As previously proposed by Tardy and Garrels (1976, 1977) and Tardy (1979), the values at which the straight lines cross the abscissae axis are considered as equal to $\Delta_H O^{2-} M''^{z'+}(aq)$. Therefore, measured and calculated values differ considerably. The $\Delta_H O^{2-} Al^{3+}(aq)$ and $\Delta_H O^{2-} H^{+}(aq)$ values provide an

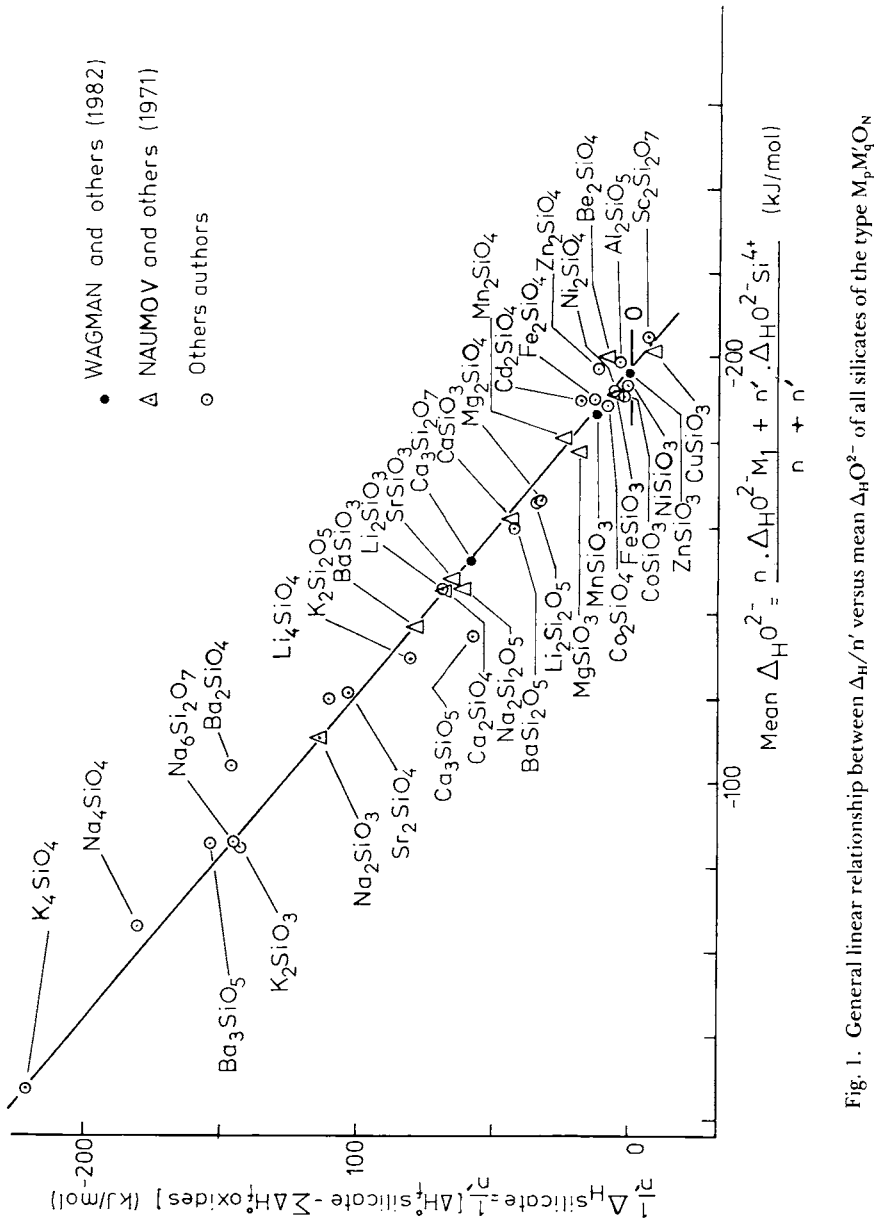

Fig. 1. General linear relationship between Δ_H/n' versus mean $\Delta_H O^{2-}$ of all silicates of the type $M_pM'_qO_N$

TABLE 3

Parameter $\Delta_H O^{2-}$ M^{z+}, n, n', $\Delta_H O^{2-}$ mean, Δ_H / n' observed, Δ_H / n' calculated and difference between observed and calculated Δ_H / n' for all families of silicates (kJ / mole)

Compounds	$\Delta_H O^{2-}$	n	n'	$\Delta_H O^{2-}$ mean	Δ_H/n' Observed (1)	Δ_H/n' calculated (2)	Difference (1) - (2)
Metasilicates							
Li_2SiO_3	- 40.96	1	2	- 145.08	- 69.88 (1)	- 68.20	- 1.68
Na_2SiO_3	- 62.92	1	2	- 110.45	- 114.35 (2)	- 113.18	- 1.17
K_2SiO_3	+ 140.92	1	2	- 84.45	- 142.99 (3)	- 146.95	+ 3.96
$MgSiO_3$	- 139.95	1	2	- 178.08	- 18.24 (4)	- 25.33	+ 7.09
$CaSiO_3$	- 92.42	1	2	- 162.23	- 44.46 (2)	- 45.92	+ 1.46
$SrSiO_3$	- 47.87	1	2	- 147.38	- 65.36 (2)	- 65.21	- 0.15
$BaSiO_3$	- 14.01	1	2	- 136.10	- 79.56 (2)	- 79.86	+ 0.30
$ZnSiO_3$	- 194.39	1	2	- 196.22	- 0.50 (4)	- 1.77	+ 1.27
$FeSiO_3$	- 179.37	1	2	- 191.22	- 6.68 (2)	- 8.27	+ 1.59
$MnSiO_3$	- 164.47	1	2	- 186.25	- 12.37 (4)	- 14.72	+ 2.35
$CuSiO_3$	- 221.46	1	2	- 205.25	+ 8.89 (2)	+ 9.96	- 1.07
$NiSiO_3$	- 185.77	1	2	- 193.35	- 1.68 (5)	- 5.50	+ 3.82
$CoSiO_3$	- 179.78	1	2	- 191.35	- 4.81 (5)	- 8.10	+ 3.29
Orthosilicates							
Li_4SiO_4	- 41.82	2	2	- 119.48	- 110.88 (6)	- 101.45	- 9.43
Na_4SiO_4	+ 65.78	2	2	- 65.68	- 180.96 (6)	- 171.33	- 9.63
K_4SiO_4	+ 143.12	2	2	- 27.01	- 221.55 (7)	- 221.56	+ 0.01
Be_2SiO_4	- 203.55	2	2	- 200.35	- 9.58 (2)	+ 3.59	- 13.17
Mg_2SiO_4	- 135.06	2	2	- 166.10	- 33.66 (7)	- 40.89	+ 7.23
Ca_2SiO_4	- 92.42	2	2	- 144.78	- 68.41 (2)	- 68.59	+ 0.18
Sr_2SiO_4	- 44.69	2	2	- 120.92	- 104.06 (8)	- 99.58	- 4.48
Ba_2SiO_4	- 10.46	2	2	- 103.80	- 134.27 (8)	- 121.81	- 12.46
Zn_2SiO_4	- 197.07	2	2	- 197.11	- 12.45 (9)	- 0.62	- 11.83
Fe_2SiO_4	- 182.92	2	2	- 190.03	- 13.45 (10)	- 9.81	- 3.64
Mn_2SiO_4	- 164.43	2	2	- 180.79	- 24.63 (2)	- 21.81	- 2.82
Co_2SiO_4	- 179.78	2	2	- 188.46	- 9.00 (2)	- 11.85	+ 2.85
Ni_2SiO_4	- 186.18	2	2	- 191.66	- 6.59 (5)	- 7.70	+ 1.11
Cd_2SiO_4	- 182.25	2	2	- 189.70	- 18.00 (11)	- 10.24	- 7.76
Pyrosilicates							
$Na_6Si_2O_7$	+ 62.92	3	4	- 85.69	- 137.56 (12)	- 145.34	+ 7.78
$Ca_3Si_2O_7$	- 92.26	3	4	- 152.19	- 57.29 (2)	- 58.96	+ 1.67
$Sc_2Si_2O_7$	- 214.94	3	4	- 204.77	+ 6.97 (13)	+ 9.33	- 2.36
$Li_2Si_2O_5$	- 40.96	1	4	- 165.90	- 35.15 (1)	- 41.15	+ 6.00
$Na_2Si_2O_5$	+ 62.92	1	4	- 145.13	- 62.56 (2)	- 68.13	+ 5.57
$K_2Si_2O_5$	+ 143.26	1	4	- 129.06	- 81.07 (2)	- 89.00	+ 7.93
$BaSi_2O_5$	- 10.46	1	4	- 159.80	- 42.55 (8)	- 49.08	+ 6.53
Ca_3SiO_5	- 92.59	3	2	- 134.41	- 57.57 (3)	- 82.06	+ 24.49
Ba_3SiO_5	- 10.46	3	2	- 85.13	- 154.77 (14)	- 146.06	- 8.71
Al_2SiO_5	- 200.09	3	2	- 198.91	- 4.40 (10)	+ 1.72	- 6.12

TABLE 4

Coefficient α, stoichiometric coefficient, parameter $\Delta_H O^{2-}Si^{4+}(aq)$, linear correlation coefficient, number of points and statistical deviation for different families of silicates

Families	α	Stoichiom. coefficient n.n'/N	$\Delta_H O^{2-}Si^{4+}(aq)$ (kJ/mole)	Linear correlation coefficient	Number of points	Statistical deviation (kJ/mole)
$MSiO_3$	1.310	1x2/3	- 193.93	- 0.9987	13	± 9.8
M_2SiO_4	1.305	2x2/4	- 204.53	- 0.9961	14	± 25.3
$M_3Si_2O_7$	1.213	3x4/7	- 201.92	- 0.9999	3	± 8.4
M_3SiO_5	1.297	3x2/5	- 193.91	- 0.9703	3	± 73.5
MSi_2O_5	1.258	1x4/5	- 181.26	- 0.9993	4	± 6.2
Silicates	1.299	-	- 197.58	- 0.9923	37	± 28.4

interesting example. In fact, the $\Delta_H O^{2-}Al^{3+}(aq)$ and $\Delta_H O^{2-}H^+(aq)$ calculated from Robie, Hemingway, and Fisher (1978) are:

$$\Delta H_f^\circ Al_2O_3(c) = -1675.7 \text{ kJ/mole},$$
$$\Delta H_f^\circ Al^{3+}(aq) = -531.0 \text{ kJ/mole},$$
$$\Delta_H O^{2-}Al^{3+}(aq) = -204.57 \text{ kJ/mole}$$

and from Robie and Waldbaum (1968):

$$\Delta H_f^\circ H_2O(c) = -279.83 \text{ kJ/mole},$$
$$\Delta H_f^\circ H^+(aq) = 0.0 \text{ kJ/mole},$$
$$\Delta_H O^{2-}H^+(aq) = -279.83 \text{ kJ/mole}$$

The first one, $\Delta_H O^{2-}Al^{3+}(aq)$, differs by about 20 kJ/mole from the one estimated from the aluminate straight line ($\Delta_H O^{2-}M'^{z'+}(aq) = -224.5$ kJ/mole, table 2). The second one $\Delta_H O^{2-}H^+(aq)$ comes out 50

Footnote to table 3:

(1) Stull and Prophet (1971); (2) Naumov, Ryzhenko, and Khodakovsky (1971); (3) Karpov, Kiselev, and Letnikov (1976); (4) Wagman and others (1968, 1969, 1971, 1981); Parker and others (1971); (5) Navrotsky (1978); (6) Spencer (1973); (7) Karpov, Kashik, and Pampura (1968); (8) Hemingway and Robie (1977); (9) Robie, Hemingway, and Fisher (1978); (10) Helgeson and others (1978); (11) Koether and Muller (1978); (12) corrected value from Newton and Mac Cready (1948) using enthalpy of formation of other silicates of sodium from Naumov, Ryzhenko, and Khodakovsky (1971); (13) Polyachenok, Nasarov, and Polyachenok (1978); (14) Alekseev, Stigunov, and Nekrich (1974).

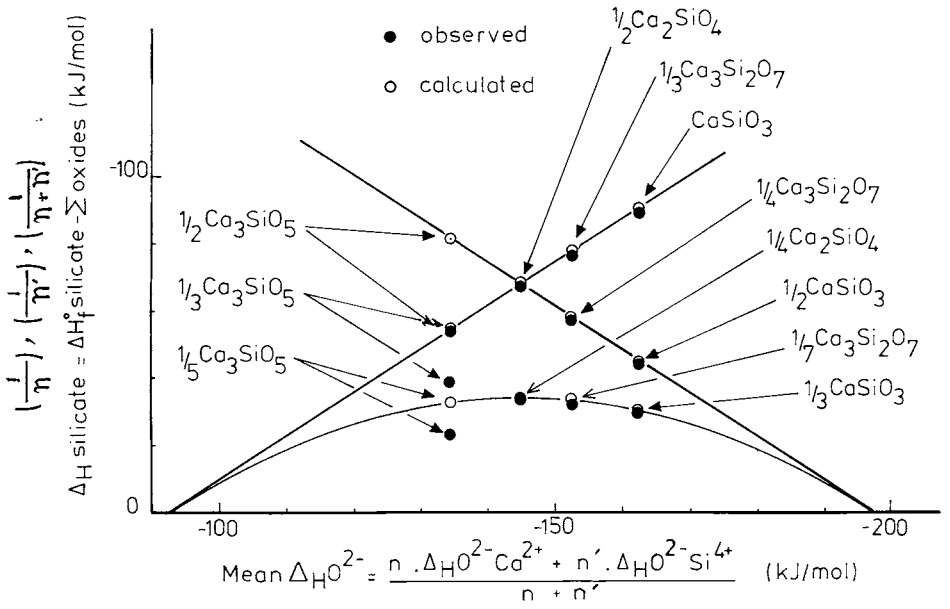

Fig. 2. Graphical representation of Δ_H/n, Δ_H/n', and $\Delta_H/(n + n')$ versus mean $\Delta_H O^{2-}$ silicate for all silicates.

kJ/mole lower than the intercept of the hydroxide straight line ($\Delta_H O^{2-} M''^{+}(aq) = -229.6$ kJ/mole, table 2). These discrepancies are interpreted as results of differences between aqueous and crystal environments.

The stoichiometric coefficient $n \cdot n'/N$.—Because coefficient α is roughly constant in a given group of compounds involving different families, the *stoichiometric coefficient* n · n′/N which characterizes each family can be clearly identified (Tardy, 1979). Let us, for example, consider the following series of Ca-silicates: $CaSiO_3$, Ca_2SiO_4, $Ca_3Si_2O_7$, $CaSi_2O_5$, Ca_3SiO_5, et cetera, for which both the coefficient $\alpha = -1.299$ and the difference $[\Delta_H O^{2-}Ca^{2+}(aq) - \Delta_H O^{2-}Si^{4+}(aq)] = +105.3$ kJ/mole are the same for all compounds. In this case, the different values of $CaSiO_3$, Ca_2SiO_4, et cetera differ only by the stoichiometric coefficient n · n′/N (fig. 2). Furthermore, one may remark that the compounds of a group involving a given cation M^{z+}, all fit a regular solid solution analogy. In fact, eq (5) can be written as follows:

$$(1/N)\,\Delta_H \text{ compound} = -\alpha \cdot X \cdot X' \cdot [\Delta_H O^{2-} M'^{+}(aq) - \Delta_H O^{2-} M''^{z'}(aq)] \quad (10)$$

in which $N = n + n'$ is the total number of oxygens involved in the compound, and X and X′, the mole fraction of the oxygen formula calculated per one oxygen atom, so that:

$$X = n/(n + n') \tag{11}$$

$$X' = n'/(n + n') \tag{12}$$

and

$$X + X' = 1 \tag{13}$$

Despite the fact that compounds are not solid solutions of two different oxides and must depart from a solid solution model, eq (10) is formally analogous (but only formally) to the excess enthalpy of two component parabolic or regular solid solutions (fig. 2):

$$H^{ex} = -X \cdot (1 - X) \cdot A \tag{14}$$

for which

$$A = \alpha \cdot [\Delta_H O^{2-} M^{z+}(aq) - \Delta_H O^{2-} M'^{z'+}(aq)] \tag{15}$$

This expression is then similar to the classical regular solution formula given by Guggenheim (1965), Thompson (1969), and Saxena (1973).

The analogy with the regular solid solution model suggests a fundamental significance of the stoichiometric coefficient, which appears in eq (15) as the product of mole fractions $X \cdot X' = n \cdot n'/N^2$. The analogy with the regular solid solution model is in fact related to the formation of a compound from its constituent oxides and consequently is illustrated by the method followed to calculate the breaking bond energies.

The formulation of the relationship (eq 5) can be justified in a simple way, if one considers the compounds formed only by the combination of oxides in ordered sites, which is the case, for example, of the γ Ca_2SiO_4 (shannonite), Mg_2SiO_4 (forsterite), $MgSiO_3$ (enstatite), and Be_2SiO_4 (phenacite). The discussion was initiated by Ramberg (1953a and b) who calculated the stability of forsterite compared to the stabilities of the free oxides MgO and SiO_2.

Let us suppose that $\Delta_H O^{2-} M^{z+}$ and $\Delta_H O^{2-} M'^{z'+}$ are related to the enthalpies of breaking bonds: M–O and M′–O respectively, of each of the two cations M and M′ with the oxygen ions. The initial and the final states do not need to be known, because only a comparison between oxides and compounds is involved. Let us suppose also that each of the two cations occupies exactly the same site with the same coordination, respectively, in the free oxides and in the compound. Let us suppose finally that the enthalpies of breaking bonds are regularly distributed so that the enthalpy for breaking one individual bond is equal to the

enthalpy of formation of the oxide from the atoms, divided by the cation coordination number. The enthalpy of formation of one given compound from its oxides can be calculated by counting the total number of bonds M–O and M′–O broken in the individual oxides and the number of bonds M–O–M′ type created in the compound. The energy balance should be equal to the enthalpy of formation from the oxides.

Let us consider, for example, the enstatite ($MgSiO_3$), the shannonite (γ Ca_2SiO_4), the forsterite (Mg_2SiO_4), the phenacite (Be_2SiO_4), and the rankinite ($Ca_3Si_2O_7$) structural schematic formulas (fig. 3). In all five silicates as well as in quartz, Si^{4+} is tetracoordinated. In shanonnite (γ Ca_2SiO_4), in enstatite ($MgSiO_3$), in forsterite (Mg_2SiO_4) as well as in lime (CaO), and in periclase (MgO), calcium and magnesium are both six-fold coordinated. Furthermore, in phenacite (Be_2SiO_4) and in bromellite (BeO), beryllium is tetracoordinated. In rankinite ($Ca_3Si_2O_7$), each calcium is surrounded by seven oxygens.

For building $MgSiO_3$ from MgO and SiO_2, it should be remembered that in enstatite, there are two kinds of oxygens: O_1 is bonded with two silicons (each of them characterized by a Pauling's bond strength of $v = 2/3$) and with two magnesiums (each of them characterized by a Pauling's bond strength of $v = 1/3$). O_2 and O_3 are bonded with only one silicon ($v = 4/3$) and two magnesiums ($v = 1/3$). The Pauling's bond strength is calculated by dividing z, the charge of the ion, by its coordination number c, so that $v = z/c$. One of the three oxygens was initially bonded with Mg^{2+} in MgO. Each of the three oxygens has lost $(1/2) \cdot (1/3) \cdot 2\ \Delta_H O^{2-}\text{-}Mg^{2+}$ and gained $(1/2) \cdot (4/3) \cdot \Delta_H O_2\text{-}Si^{4+}$. On the other hand, (2/3) of the three oxygens was initially bonded with Si^{4+} in SiO_2. Each of the three oxygens has lost $(1/2) \cdot (4/3) \cdot \Delta_H O^{2-}\text{-}Si^{4+}$ and gained $(1/2) \cdot (1/3) \cdot 2\ \Delta_H O^{2-}\text{-}Mg^{2+}$. The total balance shows that each oxygen of MgSiO has lost $(2/3) \cdot (1/3)\ \Delta_H O^{2-}\text{-}Mg^{2+}$ and has gained $(2/3) \cdot (1/3)\ \Delta_H O^{2-}\text{-}Si^{4+}$ so that the analogy with the general formula (eq 5) is now demonstrated for $MgSiO_3$:

$$(1/3)\,\Delta_H\,MgSiO_3 = -(2/3) \cdot (1/3)\,(\Delta_H O^{2-}\text{-}Mg^{2+} - \Delta_H O^{2-}\text{-}Si^{4+}) \quad (16)$$

The structure of rankinite, $Ca_3Si_2O_7$, was presented by Saburi and others (1976). Each calcium is surrounded by seven oxygens, and each silicon by four oxygens. There are three kinds of oxygens: O_4 is bonded with two silicon and two calcium atoms, O_7 is linked to four calcium and one silicon atoms, while O_1, O_2, O_3, O_5, and O_6 are surrounded by three calcium and one silicon atoms (fig. 3). A balance between the number of bonds destroyed in the three CaO and the two SiO_2 free oxides and the number of bonds recreated in compound $Ca_3Si_2O_7$ is the following: $(12/49)\ \Delta_H O^{2-}\text{-}Ca^{2+}$ and $(12/49)\ \Delta_H O^{2-}\text{-}Si^{4+}$.

These coefficients correspond to those of general eq (5):

$$(1/7)\,\Delta_H Ca_3Si_2O_7 = -(3/7) \cdot (4/7)\,(\Delta_H O^{2-}\text{-}Ca^{2+} - \Delta_H O^{2-}\text{-}Si^{4+}) \quad (17)$$

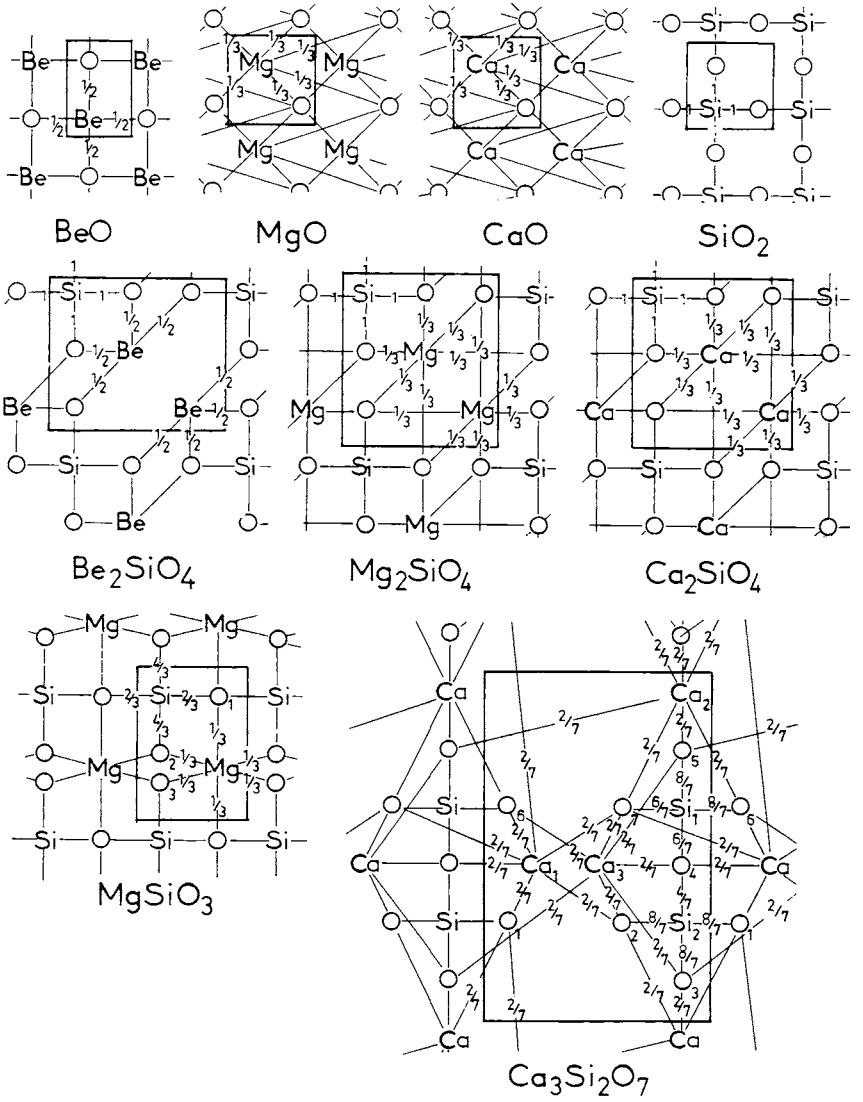

Fig. 3. Schematical structure of some oxides BeO, MgO, CaO, SiO_2, and some silicates Be_2SiO_4, Mg_2SiO_4, Ca_2SiO_4, $MgSiO_3$, and $Ca_3Si_2O_7$.

A similar demonstration can be conducted for Mg_2SiO_4 and Be_2SiO_4 which present an identical stoichiometry but a different coordination number for Mg^{vi} and Be^{iv}. They both give the same answer:

$$(1/4)\,\Delta_H\,Mg_2SiO_4 = -(1/2)\cdot(1/2)\,(\Delta_H O^{2-}Mg^{2+} - \Delta_H O^{2-}Si^{4+}) \quad (18)$$

$$(1/4)\,\Delta_H\,Be_2SiO_4 = -(1/2)\cdot(1/2)\,(\Delta_H O^{2-}Be^{2+} - \Delta_H O^{2-}Si^{4+}) \quad (19)$$

Furthermore the general equation:

$$(1/N)\,\Delta_H\,M_pM'_qO_N = -X\cdot X'\,(\Delta_H O^{2-}M - \Delta_H O^{2-}M') \quad (20)$$

presents an obvious analogy with eq (10) showing that the X and X′ are strictly derived from stoichiometric relationships and have nothing to do with the coordination numbers of cations in the oxides and in the compounds. Furthermore the stoichiometric coefficient $n\cdot n'/N$ has to be identified clearly and separated from the coefficient α which is related to the variations introduced in the parameter $\Delta_H O^{2-}M^{z+}$ when the cation M^{z+} is considered in an aqueous state instead of being considered in a crystal solid state. Finally, the expressions of eq (5) and its derivatives, which are eq (8) and eq (15), are very simple. They were determined empirically, but they are fundamental because of the formal analogy (formal only) with the regular solid solution and because of the stoichiometric justification of the energy calculations. Thus, it has seemed useful to keep this fundamental expression as a starting point for the enthalpy estimations by the corresponding state method. A correction of the parameter $\Delta_H O^{2-}M^{z+}(aq)$ will be introduced in such a way that the cation M^{z+} will be considered in its solid state in order to remove entirely the fluctuations of the coefficient α which has to be equal to unity in all cases. Therefore eq (20) instead of eq (5) will now be satisfied and used as the model of estimating enthalpies of formation of compounds from their constituent oxides.

PARAMETER $\Delta_H O^{2-}M^{z+}$(comp) AND ITS CALIBRATION FUNCTION

The parameter $\Delta_H O^{2-}M^{z+}(aq)$ characterizing the cation M^{z+} is closely related to the enthalpy of breaking the cation-oxygen bond but is not strictly equal to it. This is probably because the aqueous cation-oxygen environments differ from the cation-oxygen surroundings in oxides and in compounds. The method proposed here is based on a correction of the parameter $\Delta_H O^{2-}M^{z+}(aq)$ for the cations M and M′, in order that $\Delta_H O^{2-}M^{z+}$(comp) becomes in each crystal compound considered equal to the enthalpy of breaking the cation-oxygen bond. $\Delta_H O^{2-}M^{z+}$ is also corrected in such a way that all the α coefficients for all the compound families considered are equal to unity. Then eqs (5), (8), and (9) will become:

$$\Delta_H\,M_pM'_qO_N = -(n\cdot n')/N[\Delta_H O^{2-}M^{z+}(comp) - \Delta_H O^{2-}M'^{z'+}(comp)] \quad (21)$$

$$(1/n)\,\Delta_H\,M_pM'_qO_N = +\,[\text{mean}\,\Delta_HO^{2-}(\text{comp}) - \Delta_HO^{2-}M^{z+}(\text{comp})] \quad (22)$$

$$(1/n')\,\Delta_H\,M_pM'_qO_N = -[\text{mean}\,\Delta_HO^{2-}(\text{comp}) - \Delta_HO^{2-}M'^{z'+}(\text{comp})] \quad (23)$$

Furthermore, instead of making a correction based on the parameter $\Delta_HO^{2-}M^{z+}(aq)$ calculated from the enthalpy of the cation M^{z+} in the aqueous state, we prefer to base our correction on $\Delta_HO^{2-}M^{z+}(ox)$ calculated from the enthalpy of cation $M^{z+}(ox)$ in the oxide, so that:

$$\Delta_HO^{2-}M^{z+}(ox) = (1/x)\,[\Delta H_f^\circ MO_x(c) - \Delta H_f^\circ M^{z+}(ox)] \quad (24)$$

$\Delta_HO^{2-}M^{z+}(comp)$ is in fact the enthalpy of breaking cation-oxygen bond in a given compound. It will be written as follows:

$$\Delta_HO^{2-}M^{z+}(comp) = \Delta_HO^{2-}M^{z+}(ox) + \delta\,\Delta_HO^{2-}M^{z+} \quad (25)$$

Finally coefficient α is now chosen as constantly equal to unity.

Definition of the two different parameters $\Delta_HO^{2-}M^{z+}$ involved in the calculation.—Initially the parameters $\Delta_HO^{2-}M^{z+}(aq)$ have been defined from the difference of enthalpies of formation of an oxide in crystalline state and the corresponding cation in aqueous state (eq 1). Now one defines a new parameter, $\Delta_HO^{2-}M^{z+}(ox)$ which refers to the cation M^{z+} in the oxide MO_x crystalline environment instead of in the aqueous state. $\Delta H_f^\circ M^{z+}(ox)$ is then defined as the enthalpy of formation from the elements of the cation in the corresponding pure crystal oxide. Eq (1) becomes:

$$\Delta_HO^{2-}M^{z+}(ox) = (1/x)\,[\Delta H_f^\circ MO_x(c) - \Delta H_f^\circ M^{z+}(ox)] \quad (26)$$

The values of $\Delta H_f^\circ M^{z+}(ox)$ are not known. However, one can choose a conventional value for $\Delta H_f^\circ H^+(ox)$:

$$\Delta H_f^\circ H^+(ox) = \Delta H_f^\circ H^+(aq) = 0 \quad (27)$$

$$\Delta_HO^{2-}H^+(ox) = \Delta H_f^\circ H_2O(c) \quad (28)$$

The parameter $\Delta_HO^{2-}H^+(ox)$ is then equal to $\Delta H_f^\circ H_2O(c)$, the enthalpy of formation from the elements of metastable ice ($\Delta H_f^\circ H_2O(c) = -278.83$ kJ/mole, Robie and Waldbaum (1968)) at 298.15°K.

Some other parameters are now defined:

1. $\Delta H_f^\circ M^{z+}(comp)$ is the enthalpy of formation of the cation M^{z+} in the crystalline compound;

2. $\Delta_HO^{2-}M^{z+}(comp)$ is given by the difference:

$$\Delta_HO^{2-}M^{z+}(comp) = (1/x)\,[\Delta H_f^\circ\,MO_x(comp) - \Delta H_f^\circ\,M^{z+}(comp)] \quad (29)$$

$\Delta H_f^\circ\,M^{z+}(comp)$ and $\Delta H_f^\circ\,MO_x(comp)$ are not known for the two cations M^{z+} and M'^{z+}. What is known from eq (21) is only the difference $[\Delta_HO^{2-}M^{z+}(comp) - \Delta_HO^{2-}M'^{z'+}(comp)]$. This difference can be calculated easily from measured values for a large number of compounds

$M_pM'_qO_N$ such as hydroxides, silicates, aluminates, et cetera, involving two cations M^{z+} and $M'^{z'+}$.

3. $\delta\ \Delta_H O^{2-}M'^{z+}$, a correction parameter, is defined by the difference expressed in eq (25):

$$\delta\ \Delta_H O^{2-}M'^{z+} = \Delta_H O^{2-}M'^{z+}(\text{comp}) - \Delta_H O^{2-}M'^{z+}(\text{ox}) \qquad (30)$$

Of course, again, $\delta\ \Delta_H O^{2-}M'^{z+}$ is not known, but it can be evaluated from crystallographical and optical data.

A calibration function:correction of the parameter $\Delta_H O^{2-}M'^{z+}(ox)$ as function of the crystalline environment.—According to eq (30), the correction $\delta\ \Delta_H O^{2-}M'^{z+}$, to be applied to the parameter $\Delta_H O^{2-}M'^{z+}(ox)$, takes account of the modification in the crystal environment due to the transfer of the cation M'^{z+} from an oxide MO_x to a compound $M_pM'_qO_N$. The correction $\delta\ \Delta_H O^{2-}M'^{z+}$ for one of the two M and M′ cations appears to be a function of several parameters distributed in four different terms (Vieillard, 1982):

$$\begin{aligned}\delta\Delta_H O^{2-}M'^{z+} = {} & \underbrace{A_v e^2 z^2 A_{comp}\left(\frac{1}{d} - \rho_{comp}\frac{e\left[\frac{(d_o - d)}{\rho_{comp}}\right]}{d_o^2}\right)}_{1} \\ & \underbrace{+ k_{comp}A_v e^2 \frac{\alpha^{comp}_{M'^{z+}} + \alpha^{comp}_{O^{2-}})}{d^4}}_{2} \\ & \underbrace{- A_v e^2 z^2 A_{ox}\left(\frac{1}{d_o} - \frac{\rho_{ox}}{d_o^2}\right)}_{3} \\ & \underbrace{- k_{ox}A_v e^2 \frac{(\alpha^{ox}_{M'^{z+}} + \alpha^{ox}_{O^{2-}})}{d_o^4}}_{4}\end{aligned} \qquad (31)$$

The terms (1) and (3) are the energies of attraction-repulsion of the M–O bond, in the compound and in the free oxide, respectively. The terms (2) and (4) are the energies of polarization of the M–O bond, in the compound and in the free oxide, respectively. The sum of the two first terms ((1) + (2)) is the total M–O bond energy in the compound, and the sum of the two last terms ((3) + (4)) is the total M–O bond energy in the free oxide, so that the sum of the four terms is the M–O bond energy difference from the compound and the oxide. In other words, the parameter $\delta\ \Delta_H O^{2-}M'^{z+}$ is the correction applied to the parameter $\Delta_H O^{2-}M'^{z+}(ox)$, when the cation M'^{z+} is transferred from the free oxide environment ($M'^{z+}(ox)$) into the compound crystal environ-

ment (M'^{z+}(comp)). The parameters used in eq (31) are derived from the Born lattice energies (Born, 1923; Born and Mayer, 1932; Ladd and Lee, 1958).

In eq (31):

A_v is the Avogadro's number;

e is the electron charge;

z is the cation valency;

the contribution of the Madelung constant, A_{comp} of MO_x into the compound is not known, but the Madelung's constant of the free oxides, A_{ox}, are almost all known (table 5). In further calculations, it was assumed that $A_{comp} = A_{ox}$;

d_o and d are observed values of shortest bond length M–O, respectively, in oxides (table 5) and in compounds;

ρ_{ox}, the repulsion constant, is calculated from the compressibility data given in literature (table 5; Vieillard, 1982);

k_{ox} is the polarization constant in the free oxide (table 5; Vieillard, 1982);

k_{comp} and ρ_{comp} are respectively the polarization and the repulsion constants of the bond M–O in the compound $M_pM'_qO_N$. They are not known but can be assumed to be equal respectively to k_{ox} and ρ_{ox};

$\alpha^{comp}_{M'^{z+}}$ is the effective polarizability of cation M'^{z+} in the compound $M_pM'_qO_N$;

$\alpha^{comp}_{O^{2-}}$ is the effective polarizability of oxygen in the compound $M_pM'_qO_N$;

$\alpha^{ox}_{M'^{z+}}$ is the effective polarizability of cation M'^{z+} in the reference oxide, MO_x;

$\alpha^{ox}_{O^{2-}}$ is the effective polarizability of oxygen in the reference oxide MO_x.

These four α values are not known but can be evaluated using optical and crystallographical data of minerals. The method of calculation of effective electronic polarizabilities in compounds is developed in app. 1.

The calibration function.—Suppose we wish to estimate the enthalpy of formation of a given compound $M_pM'_qO_N$ from its oxides MO_x(c) and $M'O_y$(c). According to eq (21) one has:

$$\Delta H^\circ_f M_pM'_qO_N(c) - p \cdot \Delta H^\circ_f MO_x(c) - q \cdot \Delta H^\circ_f M'O_y(c) = -(px \cdot qy)/N[\Delta_H O^{2-}M'^{z+}(ox) - \Delta_H O^{2-}M''^{z'+}(ox) + \delta\,\Delta_H O^{2-}M'^{z+} - \delta\,\Delta_H O^{2-}M''^{z'+})] \quad (32)$$

The aim of the calculation procedure is the determination for each compound $M_pM'_qO_N$ of the values and $\delta\,\Delta_H O^{2-}M'^{z+}$ for the ion M'^{z+} and $\Delta_H O^{2-}M''^{z'+}$(ox) and $\delta\,\Delta_H O^{2-}M''^{z'+}$ for the ion $M''^{z'+}$. This is obtained by a calibration curve that yields a relationship between the correction $\delta\,\Delta_H O^{2-}M'^{z+}$ and the difference $(d - d_o)$ for a given electronic polarizability of the bond M–O. Calibration curves are given in figure 4 for Si^{4+}

TABLE 5

Madelung constant, Shortest bond length, compressibility data, repulsion constant, lattice energy, polarization constant of crystalline oxides

	Madelung constant A_{ox}		Shortest bond Length (Å)		Compressibility data β $10^{-12}cm^2/dyne$		Repulsion constant ρ_{ox} (Å)	Lattice free oxides U_o (kJ/mole)	Polarization constant (k_{ox})
H_2O (ice)	4.14	(1)	1.0036	(1)	13.	(1)	0.449	- 4362.7	0.592
Li_2O	5.03878	(2)	1.997	(2)	0.85	(2)	0.309	- 2984.9	0.1207
Na_2O	5.03878	(2)	2.403	(3)	1.27	(2)	0.291	- 2648.0	0.7820
K_2O	5.03878	(2)	2.787	(3)	1.99	(2)	0.302	- 2407.7	1.8188
Rb_2O	5.03878	(2)	2.919	(3)	2.28	(2)	0.304	- 2336.1	1.6428
Cs_2O	4.489	(3)	2.86	(4)	-		-	- 2271.1	-
BeO	1.64132	(4)	1.645	(5)	0.41	(2)	0.311	- 4612.7	0.46807
MgO	1.747558	(2)	2.100	(6)	0.59	(3)	0.370	- 3963.2	1.2048
CaO	1.747558	(2)	2.405	(7)	0.88	(3)	0.385	- 3574.8	1.5013
SrO	1.747558	(2)	2.580	(8)	0.83	(3)	0.324	- 3395.4	0.8802
BaO	1.747558	(2)	2.762	(3)	1.30	(2)	0.395	- 3223.7	1.7751
MnO	1.747558	(2)	2.222	(7)	0.65	(4)	0.359	- 3917.8	1.5311
FeO	1.747558	(2)	2.152	(8)	0.65	(5)	0.378	- 4033.3	1.7113
CoO	1.747558	(2)	2.130	(7)	0.50	(5)	0.322	- 4092.2	1.2798
NiO	1.747558	(2)	2.084	(3)	0.48	(4)	0.326	- 4183.8	1.3641
CdO	1.747558	(2)	2.348	(7)	0.88	(5)	0.401	- 3896.2	1.772
CuO	1.6213	(5)	1.9509	(9)	-		-	-	-
ZnO	1.64132	(4)	1.973	(10)	0.75	(6)	0.345	- 4147.1	1.2604
Al_2O_3	2.693556	(3)	1.860	(11)	0.37	(7)	0.342	- 15681.8	5.408
Cr_2O_3	2.752111	(5)	1.970	(11)	0.43	(8)	0.359	- 15470.0	4.9305
Fe_2O_3	2.64012	(5)	1.96	(11)	0.56	(8)	0.401	- 15292.2	6.9436
V_2O_3	2.61967	(5)	1.970	(12)	0.48	(9)	0.366	- 15116.4	8.845
Ti_2O_3	2.711333	(5)	2.027	(13)	0.52	(2)	0.385	- 14776.7	-
SiO_2	1.10075	(6)	1.597	(14)	2.6	(7)	0.637	- 13365.9	13.567
TiO_2	1.19252	(3)	1.9485	(15)	0.43	(10)	0.401	- 12260.7	5.3014
ZrO_2	1.167877	(5)	2.051	(16)	-		-	- 11220.0	-

Column 1—Madelung constant: (1) estimated in this work; (2) Moelwyn-Hughes (1961); (3) Johnson and Templeton (1961); (4) Sakamoto (1958); (5) Van Gool and Piken (1969); (6) Shmin (1966).

Column 2—Shortest bond lengths: (1) Kuhs and Lehmann (1981); (2) A.S.T.M. 12-254; (3) Wyckoff (1965); (4) Helms and Klemm (1939); (5) Smith and others (1964); (6) value proposed in this work; (7) Robie, Bethke, and Beardsley (1967); (8) Robie, Hemingway, and Fisher (1978); (9) Asbrink and Norrby (1970); (10) Abrahams and Bernstein (1969); (11) Newnham and De Haan (1962); (12) Dernier (1970); (13) Rice and Robinson (1977); (14) Smith and Alexander (1963); (15) Abrahams and Bernstein (1971); (16) Smith and Newkirk (1965).

Column 3—Compressibility data B: (1) Kamb (1965); (2) estimated from Plendl and Gielisse (1970); (3) Weir (1956); (4) Landolt-Bornstein (1980); (5) Landolt-Bornstein (1975); (6) Plendl and Gielisse (1970); (7) Guareschi (1966); (8) Sato and Akimoto (1979); (9) Finger and Hazen (1980); (10) Hazen and Finger (1981)

and figure 5 for H^+. When the distance d(Si – O) in a hypothetical compound is equal to d_o(Si – O) in quartz and when the contributions of molecular volume and of mean refractive index in this hypothetical compound are equal to those of quartz then the correction parameter δ $\Delta_H O^{2-}Si^{4+}$ (fig. 4) must be equal to zero, and:

$$\Delta_H O^{2-}Si^{4+}(\text{comp}) = \Delta_H O^{2-}Si^{4+}(\text{ox}) \tag{33}$$

On the contrary, when the difference either between bond lengths or between contributions of molecular volumes and refractive index are important, the correction $\Delta_H O^{2-}Si^{4+}$ becomes important:

$$\Delta_H O^{2-}Si^{4+}(\text{comp}) = \Delta_H O^{2-}Si^{4+}(\text{ox}) + \delta\, \Delta_H O^{2-}Si^{4+} \tag{34}$$

and $\Delta_H O^{2-}Si^{4+}$(comp) differs greatly from $\Delta_H O^{2-}Si^{4+}$(ox).

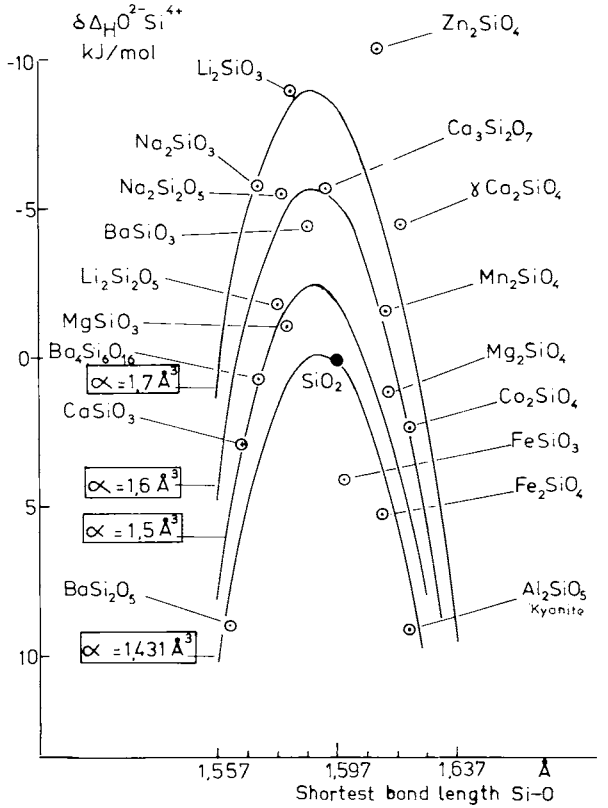

Fig. 4. Graphical representation of $\delta\Delta_H O^{2-}$ Si^{4+} (kJ/mole) versus shortest bond length, d(Å).

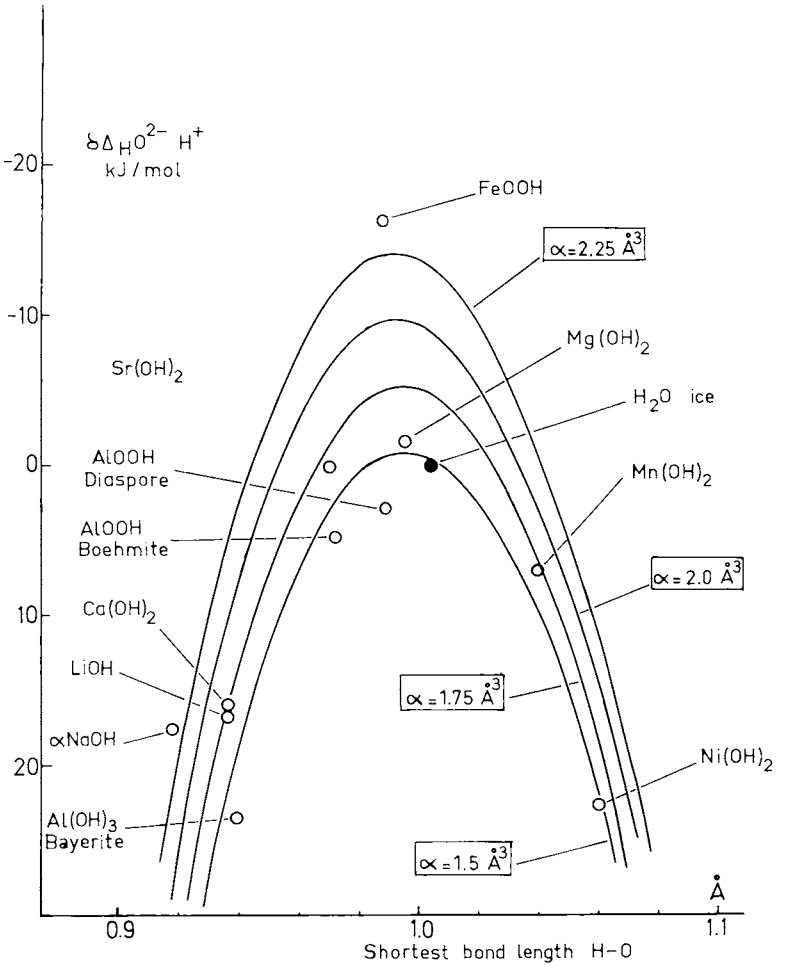

Fig. 5. Graphical representation of $\delta\Delta_H O^{2-}H^+$ (kJ/mole) versus shortest bond length, d(Å).

Finally, the shape of the calibration curve depends on the physical parameters: electronic polarizability, ionic radius, Madelung constant, repulsion constant, and polarization constant of each cation in its free state, in free oxides, and involved in the compound.

Method of calculation.—A set of 54 compounds for which crystal structures are well known and refined was selected in order to calculate the corresponding unknown parameters: polarization constant, k_{comp}, the repulsion constant, ρ_{comp}, the electronic polarizability of ions, $\alpha_{M^{z+}}$, the ionic radius of the ions, $r_{M^{z+}}$ in a free state, and the value of

$\Delta_H O^{2-} M^{z+}(ox)$. These unknown parameters were determined by minimization of the difference between the calculated and the observed enthalpy of formation from oxides, according to eq (21), (30), (31); see also app. 1. They are reported in table 6.

RESULTS AND DISCUSSION

Presentation of results.—For each family of minerals (metasilicates, orthosilicates, other silicates, aluminates, ferrites, chromites, and hydroxides) the results of the computation of enthalpy of formation from their constituent oxides are given in a series of tables (tables 7 and 8 for metasilicates, tables 9 and 10 for orthosilicates, tables 11 and 12 for other silicates, tables 13 and 14 for aluminates and ferrites, tables 15 and 16 for chromites, and tables 17 and 18 for hydroxides).

TABLE 6

Ionic radius in free state, electronic polarizabilities in free state, repulsion constant, polarization constant and parameter $\Delta_H O^{2-} M^{z+}(ox)$ of cations, used for calibration equation (eq 31)

Ions	Ionic radius (free state) r_{Mz+} (Å)	Electronic polarizability (free state) α_{Mz+} (Å^3)	Repulsion constant ρ_{comp} (Å)	Polarization constant k_{comp}	$\Delta_H O^{2-}{}_{Mz+(ox)}$ (kJ/mole)
H^+	0.1	0.0001	0.244	0.01230	- 279.82
Li^+	0.67	0.031	0.320	0.22439	- 78.00
Na^+	0.97	0.154	0.285	0.71693	+ 30.52
K^+	1.30	0.9	0.310	1.89704	+ 135.00
Be^{2+}	0.35	0.008	0.330	0.72657	- 218.00
Mg^{2+}	0.725	0.069	0.367	1.15572	- 204.00
Ca^{2+}	0.99	0.535	0.360	1.15691	- 143.00
Sr^{2+}	1.15	0.978	0.290	0.46402	- 102.00
Ba^{2+}	1.36	1.562	0.444	2.30201	- 36.50
Fe^{2+}	0.74	0.510	0.346	1.34413	- 225.00
Mn^{2+}	0.833	0.580	0.382	1.80473	- 214.00
Co^{2+}	0.735	0.550	0.320	1.25510	- 221.00
Ni^{2+}	0.710	0.555	0.325	1.35185	- 223.00
Zn^{2+}	0.735	0.430	0.213	0.08718	- 263.50
Pb^{2+}	1.23	3.85	0.575	0.32838	- 275.50
Al^{3+}	0.510	0.042	0.334	4.93011	- 214.57
Cr^{3+}	0.600	0.423	0.226	0.02268	- 266.23
Fe^{3+}	0.620	0.275	0.214	1.05601	- 280.00
Si^{4+}	0.42	0.026	0.211	0.22332	- 256.00
Zr^{4+}	0.72	0.638	0.390	4.20805	- 264.00

The nine columns in the first of each pair of tables are:

Column 1. Name of compound
2. Enthalpy of formation from the oxides calculated in this work from eq 21 (in kJ/mole)
3. Observed enthalpy of formation from constituent oxides (kJ/mole)
4. Difference between calculated and observed enthalpy of formation from constituent oxides (kJ/mole)
5. Mean refractive index
6. Reference of the crystal structure used in the computation of its enthalpy of formation from constituent oxides
7. Molecular volume ($Å^3$)
8. Electronic polarizability of the compound (see app. 1) (A^3)
9. Effective electronic polarizability of oxygen in the compound, ($Å^3$), (see app. 1)

The second table of each pair has the following columns:

Column 1. Name of the compound
2. Cations of the considered compound with their respective coordination numbers
3. Observed average bond length M^{z+}–O used for the calculation of electronic effective polarizability of ions in the compound assuming the additivity of the polarizabilities of ions (see app.) (Å)
4. Observed shortest bond length M^{z+}–O used in eq (31) of the calibration function (Å)
5. Electronic effective polarizabilities of ions in the compound ($Å^3$) (see app. 1)
6. Polarization energy of the bond M^{z+}–O ($U_p = k_{comp} \cdot A_v \cdot e^2 \cdot ((\alpha_{M^{z+}}^{comp} + \alpha_{O^{2-}}^{comp}/d^4)$ (kJ/mole)
7. Attraction-repulsion energy of the bond M^{z+}–O, U_a(term 1 of expression (31)) (kJ/mole)
8. Total energy of cation-oxygen bond in the compound given by the following expression: $U = U_a + k_{comp} \cdot U_p$ (k_{comp} is the polarization constant given in table 6) (kJ/mole)
9. Total number of oxygens respectively bound to cations M and M′
10. $\Delta_H O^{2-}M^{z+}$(ox) (given in table 6) (kJ/mole)
11. $\Delta_H O^{2-}M^{z+}$(comp) given by expression (25) (kJ/mole).

Using the values of $\Delta_H O^{2-}M^{z+}$(comp) and $\Delta_H O^{2-}M'^{z'+}$(comp), the enthalpy of formation from eq (21) is given in the second column of the first table of each set of tables.

Discussion.—The direct application of eq (5) to the 54 compounds selected by using $\alpha = 1.299$ for silicates, 0.797 for aluminates, 0.803 for ferrites, 1.541 for chromates, and 1.076 for hydroxides yields between

the predicted and observed Δ_H comp. a statistical deviation of about ±15 kJ/mole. After correction and use of the structure refinements in eqs (21), (31), and app. 1, the statistical deviation between predicted and observed Δ_H comp. is only ±5 kJ/mole for a given $\Delta_H O^{2-}M^{z+}$, which is considerably lower and of the same order of magnitude as errors listed in the thermodynamic data atlas of Robie, Hemingway, and Fisher (1978). However some important discrepancies persist. They certainly correspond to errors either in the crystal-structure data or in the calorimetric measurements.

Among the metasilicates (tables 7 and 8), the mineral $SrSiO_3$ shows a calculated enthalpy of formation from the oxides far different from the experimental one. The probable cause of this discrepancy is the bond length Si–O = 1.48 Å, value never found in other silicate minerals; consequently, its crystal structure probably needs to be refined.

Our model allows the calculation of the enthalpy of formation from the oxides of several polymorphs of $MgSiO_3$ (clinoenstatite, orthoenstatite, protoenstatite, perovskite type, and ilmenite type). Among these five polymorphs, only two compounds (protoenstatite and ilmenite type) show a discrepancy between calculated and predicted values. Consequently, either the crystal structure of protoenstatite from Smith (1959) and of $MgSiO_3$ ilmenite type from Horiuchi and others (1982) need refinements, or the enthalpies of formation from oxides need to be revised.

The minerals wollastonite $Ca^{VII}Ca_2^{VI}Si_3O_9$ and rhodonite $Mn^{VII}Mn_4^{VI}Si_5O_{15}$ are not treated here, because they are really three-site compounds.

Among the orthosilicates, (tables 9 and 10), the only compound that presents a large difference in the enthalpy of formation, compared to the others, is Na_4SiO_4 (+17 kJ/mole or −31 kJ/mole). This is probably due to the lack of precision in determining the crystal environment, because the bond Na–O represents the average of the 4 and 5 coordinated sites and not the shortest bond lengths.

The predicted enthalpy of formation of the three polymorphs, α Mg_2SiO_4, β Mg_2SiO_4, and γ Mg_2SiO_4 (or spinel type), are very close to the experimental ones.

Among the other silicates, Ca_3SiO_5 and Sr_3SiO_5 need more examination (tables 11 and 12). For the first mineral, alite, the predicted enthalpy of formation from oxides differs greatly from the one tabulated; it is not surprising because the alite crystal structure (Golovastikov, Mateeva, and Belov, 1975) is characterized by high factor (R = 0.11), which indicates that this structure is not accurate. The crystal structure of Sr_3SiO_5 is not entirely resolved, and this is probably why its calculated enthalpy of formation is so different from the value tabulated by Karpov, Kiselev, and Letnikor (1976).

Among the aluminates and the ferrites (tables 13 and 14), only α $LiAlO_2$ shows a very large discrepancy between observed and predicted enthalpy of formation from oxides. The crystal structure of α

TABLE 7

Enthalpy of formation predicted and observed for metasilicates.

[1]	[2]	[3]	[4]	[5]	[6]	[7]	[8]	[9]
Li_2SiO_3	- 130.53	- 139.20 (1)	- 8.67	1.657 (1)	(1)	59.079	5.187	1.69
		- 139.75 (2)	- 9.22					
		- 102.93 (3)	27.60					
Na_2SiO_3	- 221.33	- 229.74 (1)	- 8.41	1.520 (1)	(2)	76.654	5.565	1.71
		- 228.70 (4)	- 7.37					
		- 243.30 (5	- 21.97					
		- 232.63(2)	- 11.30					
$MgSiO_3$, clinoenstatite	- 41.68	- 36.36 (6)	5.32	1.655 (1)	(3)	52.270	4.578	1.47
		- 36.36 (1)	5.32					
		- 36.48 (4)	5.20					
		- 35.56 (7)	6.12					
		- 36.99 (5)	4.69					
		- 32.94 (8)	8.74					
$MgSiO_3$, orthoenstatite	- 40.88	- 34.98 (9)	5.90	1.666 (2)	(4)	52.031	4.617	1.48
		- 32.79 (8)	8.09					
$MgSiO_3$, protoenstatite	- 35.23	- 19.98 (8)	15.25	1.666 (2)	(5)	53.750	4.774	1.53
$MgSiO_3$, perovskite type	86.55	77.53 (10)	- 9.02	1.866 (3)	(6)	40.586	4.386	1.37
$MgSiO_3$, ilmenite type	81.58	18.95 (10)	- 62.63	1.803 (3)	(7)	43.760	4.479	1.42
$CaSiO_3$, pseudowollastonite	- 77.72	- 82.13 (6)	- 4.41	1.624 (4)	(8)	66.820	5.632	1.42
		- 82.38 (1)	- 4.66					
		- 85.56 (4)	- 7.84					
		- 79.22 (5)	- 1.50					
		- 81.09 (11)	- 3.37					
		- 82.01 (12)	- 4.29					
		- 82.75 (8)	- 5.03					
$SrSiO_3$, alpha	- 50.09	- 130.88 (1)	- 80.79	1.606 (3)	(9)	74.124	6.102	1.37
		- 130.71 (4)	- 80.62					
		- 125.11 (13)	- 75.02					
		- 115.14 (5)	- 65.05					
		- 130.54 (12)	- 80.45					
$BaSiO_3$	- 160.41	- 159.12 (1)	1.29	1.675 (1)	(10)	79.864	7.163	1.52
		- 159.12 (4)	1.29					
		- 157.87 (13)	2.54					
		- 158.99 (12)	1.42					
$FeSiO_3$, clinoferrosilite	- 20.98	- 22.09 (1)	- 1.11	1.775 (4)	(11)	54.700	5.452	1.40
		- 13.35 (4)	7.63					
		- 12.36 (14)	8.62					
		- 13.80 (5)	7.18					
$FeSiO_3$, orthoferrosilite	- 19.45	- 9.11 (5)	10.34	1.782 (4)	(12)	54.722	5.489	1.41
$CoSiO_3$, orthorhombique	- 15.12	- 9.62 (15)	5.50	1.820 (3)	(4)	53.099	5.519	1.44
$ZnSiO_3$, orthorhombique	- 4.15	- 1.00 (1)	3.15	1.620 (1)	(13)	54.568	4.573	0.95
		- 25.09 (5)	- 20.94					
		- 1.25 (12)	2.90					

Column 3—Thermodynamic values: (1) Wagman and others (1982); (2) Stull and Prophet (1971); (3) Karpov, Kashik, and Pampura (1968); (4) Naumov, Ryzhenko, and Khodakovsky, and others (1971); (5) Karpov, Kiselev, and Letnikov (1976); (6) Robie and Waldbaum (1968); (7) Robie, Hemingway, and Fisher (1978); (8) Haas, Robinson, and Hemingway and others (1980); (9) Zen and Chernosky (1976); (10) Barsukov and Urusov (1982); (11) Charlu, Newton, and Kleppa (1978); (12) Spencer (1973); (13) Hemingway and Robie (1977); (14) Helgeson and others (1978); (15) Navrotsky (1978).

Column 5—Refractive index: (1) Winchell and Winchell (1964); (2) Winchell (1931); (3) Estimated by density; (4) Winchell and Winchell (1956).

Column 6—Structural data: (1) Vollenkle (1981); (2) MacDonald and Cruikshank (1967); (3) Panhorst (1984); (4) Sasaki and others (1982); (5) Smith (1959); (6) Horiuchi (1983); (7) Horiuchi and others (1982); (8) Yamanaka and Mori (1981); (9) Machida and others (1982); (10) Grosse and Tillmans (1974); (11) Burnham (1967); (12) Sueno, Cameron, and Prewitt (1976); (13) Morimoto and others (1975).

TABLE 8

Cation-oxygen bond length and their energetic cost, parameter $\Delta_H O^{2-} M^{z+}(ox)$ and $\Delta_H O^{2-} M^{z+}(comp)$ for metasilicates

(1)	(2)		(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
Li_2SiO_3	Li^+	4	2.002	1.932	0.041	173.22	2935.28	2974.13	1.000	- 78.00	- 67.28
	Si^{4+}	4	1.634	1.591	0.017	371.48	13297.10	13380.05	2.000	- 256.00	- 263.07
Na_2SiO_3	Na^+	4	2.340	2.282	0.205	98.28	2539.50	2609.96	1.000	30.52	68.56
	Si^{4+}	4	1.632	1.592	0.016	373.96	13297.28	13380.79	2.000	- 256.00	- 263.44
$MgSiO_3$	Mg^{2+}	6	2.117	1.991	0.135	142.12	3790.19	3954.45	1.000	- 204.00	- 195.30
Clinoenstatite	Si^{4+}	4	1.635	1.589	0.026	326.62	13296.62	13369.56	2.000	- 256.00	- 257.82
$MgSiO_3$	Mg^{2+}	6	2.115	1.993	0.132	142.67	3791.01	3955.90	1.000	- 204.00	- 196.75
Orthoenstatite	Si^{4+}	4	1.634	1.588	0.026	330.61	13296.23	13370.06	2.000	- 256.00	- 258.08
$MgSiO_3$	Mg^{2+}	6	2.173	2.020	0.154	140.77	3802.81	3965.50	1.000	- 204.00	- 206.35
Protoenstatite	Si^{4+}	4	1.615	1.590	0.020	337.72	13296.87	13372.29	2.000	- 256.00	- 259.19
$MgSiO_3$	Mg^{2+}	6	2.207	1.997	0.195	136.84	3793.18	3951.33	1.000	- 204.00	- 192.18
Perovskite type	Si^{4+}	6	1.789	1.770	0.077	205.02	12932.82	12978.61	2.000	- 256.00	- 62.35
$MgSiO_3$	Mg^{2+}	6	2.077	1.990	0.123	137.34	3789.68	3948.40	1.000	- 204.00	- 189.25
Ilmenite type	Si^{4+}	6	1.799	1.768	0.075	213.56	12939.97	12987.66	2.000	- 256.00	- 66.88
$CaSiO_3$	Ca^{2+}	8	2.536	2.271	1.322	143.63	3399.44	3565.61	1.000	- 143.00	- 133.82
Pseudowollastonite	Si^{4+}	4	1.626	1.565	0.027	336.91	13279.48	13354.72	2.000	- 256.00	- 250.40
$SrSiO_3$	Sr^{2+}	8	2.630	2.420	1.952	134.70	3278.56	3341.06	1.000	- 102.00	- 47.66
alpha	Si^{4+}	6	1.627	1.480	0.030	406.45	13008.75	13099.52	2.000	- 256.00	- 122.80
$BaSiO_3$	Ba^{2+}	7	2.828	2.624	2.558	119.75	2929.89	3205.56	1.000	- 36.50	- 18.32
	Si^{4+}	4	1.623	1.587	0.022	339.38	13296.00	13371.79	2.000	- 256.00	- 258.94
$FeSiO_3$	Fe^{2+}	6	2.181	1.985	1.224	234.82	3716.92	4032.55	1.000	- 225.00	- 224.30
Clinoferrosilite	Si^{4+}	4	1.629	1.599	0.029	303.66	13297.64	13365.45	2.000	- 256.00	- 255.77
$FeSiO_3$	Fe^{2+}	6	2.182	1.994	1.210	230.87	3725.03	4035.35	1.000	- 225.00	- 227.10
Orthoferrosilite	Si^{4+}	4	1.632	1.598	0.029	308.00	13297.69	13366.47	2.000	- 256.00	- 256.28
$CoSiO_3$	Co^{2+}	6	2.143	1.982	1.148	233.72	3812.25	4105.60	1.000	- 221.00	- 234.40
Orthorhombic	Si^{4+}	4	1.632	1.597	0.027	315.04	13297.70	13368.06	2.000	- 256.00	- 257.07
$ZnSiO_3$	Zn^{2+}	6	2.197	1.920	1.646	265.76	4110.68	4133.85	1.000	- 263.50	- 250.29
Orthorhombic	Si^{4+}	4	1.625	1.610	0.067	210.92	13294.95	13342.05	2.000	- 256.00	- 244.07

TABLE 9

Enthalpy of formation predicted and observed for orthosilicates

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Na_4SiO_4	- 330.58	- 361.92 (1) - 379.91 (2) - 313.38 (3) - 391.62 (4)	- 31.34 - 49.33 17.20 - 61.04	1.536 (1)	(1)	114.387	8.515	1.935
Be_2SiO_4, phenacite	- 13.33	- 19.16 (5) - 19.16 (6) - 18.40 (2) - 17.99 (1) - 24.77 (7)	- 5.83 - 5.83 - 5.07 - 4.66 - 11.44	1.659 (2)	(2)	61.757	5.433	1.340
Mg_2SiO_4, forsterite	- 55.48	- 63.26 (8) - 59.66 (5) - 57.99 (6) - 61.71 (9) - 56.69 (10) - 63.60 (11) - 60.90 (12) - 56.70 (13) - 59.58 (14)	- 7.78 - 4.18 - 2.51 - 6.23 - 1.21 - 8.12 - 5.42 - 1.22 - 4.10	1.652 (1)	(3)	72.488	6.327	1.510
Mg_2SiO_4, beta	- 47.67	- 46.48 (15)	1.19	1.702 (3)	(4)	67.268	6.220	1.489
Mg_2SiO_4, spinel	- 33.04	- 41.80 (15)	- 8.76	1.720 (3)	(5)	65.463	6.172	1.478
Ca_2SiO_4, shannonite	- 140.68	- 136.98 (8) - 136.78 (5) - 136.82 (6) - 135.74 (9) - 147.30 (11) - 136.67 (14)	3.70 3.90 3.86 4.94 - 6.62 4.01	1.647 (1)	(6)	98.152	8.515	1.743
Fe_2SiO_4, fayalite	- 22.85	- 24.49 (8) - 24.96 (5) - 25.31 (6) - 26.90 (9) - 24.58 (10) - 34.30 (11) - 17.20 (12) - 22.82 (2) - 23.38 (16)	- 1.64 - 2.11 - 2.46 - 4.05 - 1.73 - 11.45 5.65 0.03 - 0.53	1.866 (2)	(7)	76.856	8.306	1.551
Mn_2SiO_4, tephroite	- 48.93	- 49.25 (8) - 49.12 (5) - 49.25 (6) - 47.10 (10) - 48.83 (2) - 49.40 (11) - 50.80 (13)	- 0.32 - 0.19 - 0.32 1.83 0.10 - 0.47 - 1.87	1.801 (4)	(7)	81.254	8.295	1.611
Co_2SiO_4, olivine	- 16.94	- 90.12 (5) - 12.10 (11) - 17.99 (17) - 23.00 (13)	- 73.18 4.84 - 1.05 - 6.06	1.901 (3)	(8)	74.317	8.262	1.548
Co_2SiO_4, beta	- 16.82			1.945 (3)	(9)	69.12	7.940	1.460
Ni_2SiO_4, olivine	- 12.47	- 39.25 (6) - 6.30 (11) - 8.37 (18) - 13.18 (17) - 6.30 (19)	- 26.78 6.17 4.10 - 0.71 6.17	1.994 (1)	(10)	70.686	8.402	1.648
Zn_2SiO_4, willemite	- 31.29	- 29.25 (8) - 29.25 (5) - 29.25 (6) - 24.89 (10) - 29.25 (2) - 31.00 (11)	2.04 2.04 2.04 6.40 2.04 0.29	1.702 (1)	(11)	86.918	8.033	1.841
$ZrSiO_4$, zircon	- 29.08	- 21.92 (5) - 21.17 (6) - 22.14 (10) - 16.95 (2)	7.16 7.91 6.94 12.13	1.933 (1)	(12)	65.512	7.461	1.432

TABLE 10

Cation oxygen bond length and their energetic cost, parameter $\Delta_H O^{2-} M^{z+}(ox)$ and $\Delta_H O^{2-} M^{z+}(comp.)$ for ortho-silicates

(1)	(2)		(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
Na_4SiO_4	Na^+	4	2.367	2.252	0.190	114.84	2521.73	2604.06	2.000	30.52	74.46
	Si^{4+}	4	1.644	1.630	0.011	383.12	13280.60	13366.15	2.000	- 256.00	- 256.12
Be_2SiO_4	Be^{2+}	4	1.646	1.631	0.020	267.04	4432.02	4626.04	2.000	- 218.00	- 231.31
Phenacite	Si^{4+}	4	1.631	1.628	0.033	271.60	13282.55	13343.20	2.000	- 256.00	- 244.65
Mg_2SiO_4	Mg^{2+}	6	2.120	2.060	0.132	126.65	3813.24	3959.61	2.000	- 204.00	- 200.46
Forsterite	Si^{4+}	4	1.635	1.610	0.025	317.24	13294.95	13365.79	2.000	- 256.00	- 255.94
Mg_2SiO_4	Mg^{2+}	6	2.081	2.017	0.118	134.87	3801.71	3957.59	2.000	- 204.00	- 198.44
beta	Si^{4+}	4	1.651	1.631	0.029	297.94	13279.58	13346.11	2.000	- 256.00	- 246.10
Mg_2SiO_4	Mg^{2+}	6	2.070	2.070	0.115	120.52	3814.69	3953.98	2.000	- 204.00	- 194.83
Spinelle	Si^{4+}	4	1.655	1.655	0.030	279.30	13247.28	13309.65	2.000	- 256.00	- 227.87
Ca_2SiO_4	Ca^{2+}	6	2.394	2.289	0.762	126.81	3408.58	3555.29	2.000	- 143.00	- 123.50
Shannonite	Si^{4+}	4	1.644	1.589	0.017	383.56	13296.62	13382.27	2.000	- 256.00	- 264.18
Fe_2SiO_4	Fe^{2+}	6	2.169	2.065	1.039	197.91	3770.08	4036.10	2.000	- 225.00	- 227.85
Fayalite	Si^{4+}	4	1.636	1.625	0.023	313.63	13285.27	13355.31	2.000	- 256.00	- 250.70
Mn_2SiO_4	Mn^{2-}	6	2.217	2.137	0.916	168.30	3605.98	3909.72	2.000	- 214.00	- 205.92
Tephroite	Si^{4+}	4	1.639	1.619	0.021	329.94	13289.94	13363.62	2.000	- 256.00	- 254.86
Co_2SiO_4	Co^{2+}	6	2.146	2.073	1.065	196.57	3866.40	4113.11	1.000	- 221.00	- 241.91
Olivine	Co^{2+}	6	2.122	2.095	0.982	182.49	3871.59	4100.63	1.000	- 221.00	- 229.43
	Si^{4+}	4	1.641	1.621	0.024	316.26	13288.50	13359.13	2.000	- 256.00	- 252.61
Co_2SiO_4	Co^{2+}	6	2.114	2.053	1.035	195.15	3859.25	4104.18	2.000	- 221.00	- 232.98
Beta	Si^{4+}	4	1.642	1.623	0.028	298.10	13286.94	13353.52	2.000	- 256.00	- 249.80
Ni_2SiO_4	Ni^{2+}	6	2.089	2.043	0.896	202.86	3929.28	4203.52	2.000	- 223.00	- 242.75
Olivine	Si^{4+}	4	1.639	1.620	0.019	336.30	13289.24	13364.34	2.000	- 256.00	- 255.21
Zn_2SiO_4	Zn^{2+}	4	1.975	1.900	0.328	231.23	4097.68	4117.83	2.000	- 263.50	- 234.27
Willemite	Si^{4+}	4	1.645	1.580	0.014	413.46	13292.71	13385.04	2.000	- 256.00	- 265.57
$ZrSiO_4$	Zr^{4+}	8	2.198	2.129	1.706	212.18	10231.85	11124.72	2.000	- 264.00	- 216.34
Zircon	Si^{4+}	4	1.630	1.630	0.028	287.27	13280.60	13344.75	2.000	- 256.00	- 245.42

Footnote to table 9:

Column 3—Thermodynamic values: (1) Spencer (1973); (2) Karpov, Kiselev, and Letnikov (1976); (3) Karpov, Kashik, Pampura (1968); (4) Matveev and Agarkov (1972); (5) Wagman and others (1982); (6) Naumov, Ryzhenko, and Khodakovsky (1971); (7) Kiseleva and Shuriga (1983); (8) Robie and Waldbaum (1968); (9) Helgeson and others (1978); (10) Robie, Hemingway and Fisher (1978); (11) Koether and Muller (1978); (12) Thierry and others (1981); (13) Robie, Hemingway and Takei (1982b); (14) Haas, Robinson and Hemingway (1980); (15) Barsukov and Urusov (1982); (16) Robie, Finch, and Hemingway (1982a); (17) Navrotsky (1974); (18) Levitskii and others (1975); (19) Robie and others (1984).

Column 5—Refractive index: (1) Winchell and Winchell (1964); (2) Winchell (1931); (3) Estimated by density; (4) Winchell (1932).

Column 6—Structural data: (1) Barker and Gadd (1981); (2) Zachariassen (1972); (3) Baur (1972); (4) Horiuchi and Sawamoto (1981); (6) Horiuchi (1983); (6) Smith, Majumder, and Ordway (1963); (7) Fujino and others (1981); (8) Kratochvil, Podlahorai and Hasek (1979); (9) Morimoto and others (1974); (10) Lager and Meagher (1978); (11) Hang and others (1970); (12) Finger (1973).

TABLE 11

Enthalpy of formation predicted and observed for other silicates

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
$Li_2Si_2O_5$	- 148.11	- 139.95 (1)	8.16	1.533 (1)	(1)	102.172	7.565	1.487
		- 140.58 (2)	7.53					
$Na_2Si_2SO_5$, alpha	- 261.64	- 229.20 (1)	32.44	1.503 (2)	(2)	120.980	8.542	1.598
		- 250.25 (3)	11.39					
		- 230.33 (4)	31.31					
		- 230.54 (5)	31.10					
		- 234.35 (6)	27.29					
		- 263.59 (7)	- 1.95					
		- 275.73 (8)	- 14.09					
$BaSi_2O_5$, sanbornite	- 182.09	- 172.63 (1)	9.46	1.610 (2)	(3)	120.313	9.958	1.358
		- 170.21 (9)	11.88					
		- 172.76 (4)	9.33					
		- 172.80 (5)	9.29					
		- 170.21 (10)	11.88					
$Ca_3Si_2O_7$, rankinite	- 230.66	- 233.84 (1)	- 3.18	1.645 (2)	(4)	160.242	13.873	1.519
		- 229.16 (3)	1.50					
		- 215.48 (5)	15.18					
		- 229.14 (11)	1.52					
		- 225.94 (8)	4.72					
		- 258.75 (12)	- 28.09					
		- 248.73 (13)	- 18.07					
Ca_3SiO_5, alite	- 182.06	- 113.01 (1)	69.05	1.715 (3)	(5)	121.825	11.425	1.822
		- 115.10 (3)	66.96					
		- 115.14 (4)	66.92					
		- 112.97 (5)	69.09					
		- 117.75 (13)	64.31					
		- 117.16 (12)	64.90					
Sr_3SiO_5	- 179.34	- 307.37 (4)	- 128.03	1.724 (4)	(6)	128.855	12.198	1.320
Al_2SiO_5, kyanite	- 10.83	- 7.87 (14)	2.96	1.723 (3)	(7)	73.397	6.940	1.330
		- 7.87 (3)	2.96					
		- 7.95 (15)	2.88					
		- 5.33 (16)	5.50					
		- 7.65 (1)	3.18					
		- 9.94 (13)	0.89					
		- 9.37 (17)	1.46					
$Ba_2Si_3O_8$	- 348.85	- 344.93 (1)	3.92	1.630 (2)	(3)	203.384	17.280	1.481
		- 344.85 (3)	4.00					
		- 344.85 (11)	4.00					
		- 340.98 (8)	7.87					
		- 344.76 (4)	4.09					

Column 3—Thermodynamic values: (1) Wagman and others (1982); (2) Stull and Prophet (1971); (3) Naumov, Ryzhenko, and Khodakovsky (1971); (4) Karpov, Kashik, and Pampura (1976); (5) Spencer (1973); (6) Matveev, Frenkel, and Matveev (1965); (7) Matveev and Agarkov (1972); (8) Urusov (1965); (9) Hemingway and Robie (1977); (10) Glushkova (1957); (11) Karpov, Kashik, and Pampura (1968); (12) Hemingway, Haas, and Robinson (1982); (13) Haas, Robinson, and Hemingway (1980); (14) Robie and Waldbaum (1968); (15) Helgeson and others (1978); (16) Robie, Hemingway, and Fisher (1978); (17) Robie and Hemingway (1984).

Column 5—Refractive index: (1) Winchell and Winchell (1956); (2) Winchell and Winchell (1964); (3) Winchell (1931); (4) estimated by density.

Column 6—Structural data: (1) Liebau (1960); (2) Pant and Cruickshank (1968); (3) Hesse and Liebau (1980); (4) Saburi and others (1976); (5) Golovastikov, Mateeva, and Belov (1975); (6) Dent Glasser and Glasser (1965); (7) Winter and Ghose (1979).

TABLE 12

Cation oxygen bond length and their energetic cost, parameter $\Delta_H O^{2-}\ M^{z+}(ox)$ and $\Delta_H O^{2-}\ M^{z+}(comp.)$ for other silicates

(1)	(2)		(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
$Li_2Si_2O_5$	Li^+	4	1.940	1.940	0.039	149.76	2937.33	2970.92	1.000	- 78.00	- 64.07
	Si^{4+}	4	1.630	1.560	0.025	254.75	13273.10	13352.32	4.000	- 256.00	- 249.20
$Na_2Si_2O_5$	Na^+	5	2.397	2.290	0.259	93.80	2543.41	2610.66	1.000	30.52	67.86
alpha	Si^{4+}	4	1.617	1.578	0.018	361.99	13291.44	13372.28	4.000	- 256.00	- 259.18
$BaSi_2O_5$	Ba^{2+}	9	2.889	2.734	3.112	111.16	2950.24	3206.12	1.000	- 36.50	- 18.88
Sanbornite	Si^{4+}	4	1.614	1.561	0.029	324.38	13274.46	13346.89	4.000	- 256.00	- 246.49
$Ca_3Si_2O_7$	Ca^{2+}	7	2.468	2.273	1.064	134.49	3400.54	3556.13	3.000	- 143.00	- 124.34
Rankinite	Si^{4+}	4	1.620	1.593	0.022	332.49	13297.43	13371.68	4.000	- 256.00	- 258.89
Ca_3SiO_5	Ca^{2+}	6	2.416	2.242	0.768	142.40	3381.18	3545.92	3.000	- 143.00	- 114.13
Alite	Si^{4+}	4	1.634	1.586	0.013	402.85	13295.64	13385.60	2.000	- 256.00	- 265.85
Sr_3SiO_5	Sr^{2+}	6	2.590	2.540	1.854	105.96	3337.90	3387.07	3.000	- 102.00	- 93.67
	Si^{4+}	4	1.630	1.630	0.034	266.61	13280.60	13340.14	2.000	- 256.00	- 243.11
Al_2SiO_5	Al^{3+}	6	1.908	1.816	0.127	186.14	14837.22	15754.92	3.000	- 214.57	- 238.94
Kyanite	Si^{4+}	4	1.636	1.621	0.035	274.68	13288.50	13349.84	2.000	- 256.00	- 247.97
$Ba_2Si_3O_8$	Ba^{2+}	8	2.840	2.640	2.678	118.95	2934.76	3208.60	2.000	- 36.50	- 21.36
	Si^{4+}	4	1.627	1.570	0.025	344.36	13284.86	13361.76	6.000	- 256.00	- 253.92

$LiAlO_2$ has been studied by Marezio and Remeika (1965) who have given only an average bond length without any mention of the regularity or the irregularity of polyhedra in which lithium and aluminum are located.

Predicted enthalpies of formation from oxides of normal spinel ($MgAl_2O_4$, spinel, and $ZnAl_2O_4$, gahnite) are also included. Other minerals such as hercynite ($FeAl_2O_4$), galaxite ($MnAl_2O_4$), and almost all the ferrites ($MgFe_2O_4$, magnesioferrite, $FeFe_2O_4$, magnetite, $NiFe_2O_4$, trevorite, $MnFe_2O_4$, jacobsite) are not treated here, because they are inverse spinel in reason of a disorder in tetrahedral and octahedral sites and because they cannot be considered as ordered two site compounds.

Among the chromites, all the compounds considered (tables 15 and 16) are normal spinel. Only $ZnCr_2O_4$ shows a predicted enthalpy of formation very different from the one tabulated. This probably requires a revision of the enthalpy of formation of the zinc chromite.

TABLE 13

Enthalpy of formation predicted and observed for aluminates and ferrites

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
$LiAlO_2$, alpha	- 68.09	- 56.50 (1)	11.59	1.781(1)	(1)	32.167	3.224	1.526
		- 52.93 (2)	15.16					
		- 51.46 (3)	16.63					
		- 52.63 (4)	15.46					
		- 53.20 (5)	14.89					
		- 49.58 (6)	18.51					
		- 54.27 (7)	13.82					
		- 51.90 (8)	16.19					
$BeAl_2O_4$, chrysoberyl	- 18.82	- 15.48 (1)	3.34	1.751 (2)	(2)	56.994	5.548	1.316
		- 16.61 (2)	2.21					
		- 15.68 (3)	3.14					
$MgAl_2O_4$, spinelle	- 21.60	- 35.98 (9)	- 14.38	1.719 (2)	(3)	65.954	6.211	1.479
		- 22.50 (1)	- 0.90					
		- 37.70 (10)	- 16.10					
		- 23.43 (11)	- 1.83					
		- 22.13 (3)	- 0.53					
		- 29.71 (12)	- 8.11					
		- 44.77 (6)	- 23.17					
		- 30.17 (7)	- 8.57					
		- 36.40 (13)	- 14.80					
$SrAl_2O_4$	- 82.25	- 56.90 (1)	25.35	1.656 (2)	(4)	95.949	8.416	1.275
		- 102.51 (6)	- 20.26					
		- 79.08 (7)	3.17					
$BaAl_2O_4$	- 166.49	- 97.07 (1)	69.43	1.683 (2)	(5)	104.650	9.474	1.600
		- 100.46 (14)	66.04					
$ZnAl_2O_4$, gahnite	- 30.80	- 41.22 (1)	- 10.42	1.805 (2)	(6)	66.143	6.781	1.539
		- 41.00 (13)	- 10.20					
$LiFeO_2$	- 58.77	- 54.72 (10)	4.05	2.400 (2)	(7)	52.940	7.752	3.825
		- 39.10 (1)	19.67					
$NaFeO_2$, beta	- 85.66	- 78.95 (1)	6.71	1.916 (3)	(8)	55.781	6.270	3.065
		- 77.19 (10)	8.47					
$CaFe_2O_4$	- 78.88	- 60.61 (3)	18.27	2.529 (2)	(9)	73.596	11.291	2.595
		- 61.05 (1)	17.83					
		- 61.42 (10)	17.46					
$ZnFe_2O_4$, franklinite	- 7.16	3.01 (10)	10.17	2.360 (2)	(10)	75.237	10.842	2.565
		3.02 (1)	10.18					
		- 5.02 (15)	2.14					
		- 29.30 (13)	- 22.14					

Column 3—Thermodynamic values: (1) Wagman and others (1982); (2) Naumov, Ryzhenko, and Khodakovsky (1971); (3) Robie, Hemingway, and Fisher (1978); (4) Stull and Prophet (1971); (5) Ikeda and others (1980); (6) Wen and others (1979); (7) Schwitzgebel (1971); (8) Byker and others (1979); (9) Robie and Waldbaum (1968); (10) Naumov, Ryzhenko, and Khodakovsky (1971); (11) Helgeson and others (1978); (12) Spencer (1973); (13) Reznitskii (1977); (14) Alekseev, Striozunor, and Nekrich (1974); (15) Kubaschewki (1972).

Column 5—Refractive index: (1) Estimated from Mandarino (1976); (2) Winchell and Winchell (1964); (3) estimated by density.

Column 6—Structural data: (1) Marezio and Remeika (1966); (2) Farrell and others (1963); (3) Yamanaka and Takeuchi (1983); (4) Schulze and others (1981); (5) Hoerkner and Muller-Buschbaum (1979); (6) Wyckoff (1965); (7) Anderson and Schieber (1964); (8) Bertaut and Blum (1954); (9) Hill, Peiser, and Rait (1956); (10) Hill, Craig, and Gibbs (1979).

TABLE 14

Cation oxygen bond length and their energetic cost, parameter $\Delta_H O^{2-}\ M^{z+}(ox)$ and $\Delta_H O^{2-}\ M^{z+}(comp.)$ for aluminate and ferrites

(1)	(2)		(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
$LiAlO_2$	Li^+	6	2.120	2.120	0.074	110.07	2919.07	2919.73	0.500	- 78.00	- 37.57
alpha	Al^{3+}	6	1.900	1.900	0.097	173.10	14842.12	15695.54	1.500	- 214.57	- 219.15
$BeAl_2O_4$	Al^{3-}	6	1.914	1.861	0.132	167.78	14856.33	15863.49	3.000	- 214.57	- 215.13
Chrysoberyl	Be^{2-}	4	1.632	1.579	0.019	298.44	4418.12	4634.96	1.000	- 218.00	- 240.23
$MgAl_2O_4$	Mg^{2+}	4	1.922	1.922	0.065	157.17	3740.41	3922.06	1.000	- 204.00	- 162.91
Spinelle	Al^{3-}	6	1.926	1.926	0.115	161.06	14819.18	15613.20	3.000	- 214.57	- 191.70
$SrAl_2O_4$	Sr^{2-}	9	2.857	2.510	3.180	155.96	3330.67	3403.03	1.000	- 102.00	- 109.63
	Al^{3+}	4	1.752	1.729	0.068	208.78	14666.69	15695.97	3.000	- 214.57	- 219.29
$BaAl_2O_4$	Ba^{2-}	9	2.932	2.617	2.987	135.87	2927.54	3240.32	1.000	- 36.50	- 53.08
	Al^{3+}	4	1.757	1.665	0.043	297.04	14398.87	15863.31	3.000	- 214.57	- 275.07
$ZnAl_2O_4$	Zn^{2+}	4	1.961	1.961	0.427	184.68	4123.44	4139.54	1.000	- 263.50	- 255.98
Gahnite	Al^{3-}	6	1.908	1.908	0.099	171.76	14836.07	15682.84	3.000	- 214.57	- 214.92
$LiFeO_2$	Li^+	6	2.095	2.050	0.008	301.58	2938.97	3006.61	0.500	- 78.00	- 99.76
	Fe^{3-}	6	2.095	2.050	0.093	308.23	14896.12	15221.62	1.500	- 280.00	- 256.49
$NaFeO_2$	Na^+	4	2.253	2.160	0.060	199.46	2430.52	2573.52	0.500	30.52	105.00
beta	Fe^{3-}	4	1.955	1.790	0.080	425.60	14372.96	14822.40	1.500	- 280.00	- 123.42
$CaFe_2O_4$	Ca^{2-}	8	2.419	2.290	0.484	155.57	3409.05	3589.02	1.000	- 143.00	- 157.23
	Fe^{3-}	6	2.031	1.890	0.213	305.78	14916.44	15239.36	3.000	- 280.00	- 262.40
$ZnFe_2O_4$	Fe^{3-}	6	2.018	2.018	0.205	231.93	14956.08	15201.00	3.000	- 280.00	- 249.62
Franklinite	Zn^{2-}	4	1.996	1.996	0.171	239.39	4121.85	4142.72	1.000	- 263.50	- 259.16

The predicted enthalpies of formation of hydroxides (tables 17 and 18) are very close to the observed values. The crystal structure of the polymorph β NaOH is known. Using the β NaOH crystal structure described by Stehr (1967) and the refractive index estimated by the Gladstone-Dale relationships (Mandarino, 1976), the enthalpy of formation from oxides of β NaOH is found to be -58.0 kJ/mole, which gives an enthalpy of formation from the elements equal to -405 ± 5 kJ/mole. This is a good example which shows the ability of the method proposed to evaluate the unknown enthalpies of formation of minerals.

TABLE 15

Enthalpy of formation predicted and observed for chromites

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
$NaCrO_2$	- 113.56	- 101.25 (1)	12.31	2.072 (1)	(1)	40.487	5.058	2.292
$MgCr_2O_4$ Picrochromite	- 38.67	- 47.45 (2) - 42.70 (1) - 46.44 (3)	- 8.78 - 3.53 - 7.77	2.000 (2)	(2)	72.329	8.634	1.794
$CaCr_2O_4$ beta	- 103.80			2.081 (1)	(3)	71.60	8.992	1.585
$SrCr_2O_4$	- 224.39			2.051 (1)	(4)	87.56	10.800	2.225
$FeCr_2O_4$ Chromite	- 46.11	- 40.67 (4) - 33.05 (1) - 47.28 (5) - 54.40 (3)	5.44 13.06 - 1.17 - 8.29	2.120 (2)	(5)	73.877	9.489	2.008
$MnCr_2O_4$	- 40.39			2.208 (1)	(5)	75.07	10.101	2.242
$CoCr_2O_4$	- 39.97	- 51.63 (4) - 76.53 (5)	- 11.66 - 36.56	2.250 (1)	(5)	72.303	9.928	2.185
$NiCr_2O_4$	- 11.02	- 50.38 (4) - 1.26 (5)	- 39.36 9.76	2.271 (1)	(6)	71.876	9.967	2.195
$ZnCr_2O_4$	- 11.53	- 58.91 (5) - 59.00 (3)	- 47.38 - 47.47	2.235 (1)	(5)	72.017	9.820	2.193

Column 3—Thermodynamic values: (1) Wagman and others (1982); (2) Robie, Hemingway, and Fisher (1978); (3) Reznitskii (1977); (4) Naumov, Ryzhenko, and Khodakovsky (1971); (5) Karapet'Yants (1965).

Column 5—Refractive index: (1) Estimated by density; (2) Winchell and Winchell (1964).

Column 6—Structural data: (1) Rudorff and Becker (1954); (2) Wyckoff (1965); (3) Hoerkner and Muller-Buschbaum (1976); (4) Pausch and Muller-Buschbaum (1974); (5) Hill, Craig, and Gibbs (1979); (6) Armbruster and others (1983).

TABLE 16

Cation oxygen bond length and their energetic cost, parameter $\Delta_H O^{2-} M^{z+}$ (ox) and $\Delta_H O^{2-} M^{z+}$ (comp.) for chromites

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
$NaCrO_2$	Na^{+} 6	2.490	2.490	0.217	90.69	2556.89	2621.91	0.500	30.52	56.61
	Cr^{3+} 6	1.910	1.910	0.256	266.06	15403.94	15409.98	1.500	- 266.23	- 246.22
$MgCr_2O_4$	Mg^{2+} 4	1.948	1.948	0.051	178.06	3762.66	3968.45	1.000	- 204.00	- 209.30
Picrochromite	Cr^{3+} 6	2.003	2.003	0.703	215.55	15449.00	15453.89	3.000	- 266.23	- 260.86
$CaCr_2O_4$	Ca^{2+} 8	2.420	2.357	0.906	112.13	3429.78	3559.50	1.000	- 143.00	- 127.71
beta	Cr^{3+} 6	2.004	1.968	0.874	227.69	15464.48	15469.65	3.000	- 266.23	- 266.11
$SrCr_2O_4$	Sr^{2+} 6	2.458	2.350	0.787	137.20	3197.54	3261.21	1.000	- 102.00	32.19
	Cr^{3+} 6	2.046	1.980	0.557	251.46	15463.06	15468.76	3.000	- 266.23	- 265.82
$FeCr_2O_4$	Fe^{2+} 4	2.009	2.009	0.374	203.19	3737.11	4010.22	1.000	- 225.00	- 201.97
Chromite	Cr^{3+} 6	1.993	1.993	0.542	224.36	15456.60	15461.69	3.000	- 266.23	- 263.46
$MnCr_2O_4$	Mn^{2+} 4	2.033	2.033	0.264	203.93	3544.48	3912.52	1.000	- 214.00	- 208.72
	Cr^{3+} 6	1.997	1.997	0.435	233.63	15453.73	15459.03	3.000	- 266.23	- 262.57
$CoCr_2O_4$	Co^{2+} 4	1.961	1.961	0.272	230.72	3791.16	4080.74	1.000	- 221.00	- 209.54
	Cr^{3+} 6	1.996	1.996	0.458	231.23	15454.56	15459.80	3.000	- 266.23	- 262.83
$NiCr_2O_4$	Ni^{2+} 4	1.969	1.969	0.313	231.88	3897.12	4210.59	1.000	- 223.00	- 249.82
	Cr^{3+} 6	1.989	1.989	0.436	233.86	15459.53	15464.84	3.000	- 266.23	- 264.51
$ZnCr_2O_4$	Zn^{2+} 4	2.018	2.018	0.279	207.16	4116.19	4134.19	1.000	- 263.50	- 250.63
	Cr^{3+} 6	1.963	1.963	0.386	241.04	15463.88	15469.34	3.000	- 266.23	- 266.01

CONCLUSIONS

The improved method presented here for estimating the enthalpy of formation of minerals from their oxides consists of two steps.

The enthalpies of formation of minerals from their oxides are roughly linear functions of the empirical parameter $\Delta_H O^{2-} M^{z+}(aq)$, defined as the difference between the enthalpies of formation from the elements of oxides $MO_x(c)$ and their corresponding aqueous cations $M^{z+}(aq)$.

The linear relationship is then corrected on the basis of refractive indexes, molecular volumes, electronic polarizabilities of ions, and cation-oxygen bond lengths from refinements of the crystal structures. This correction is introduced through a calibration function and is applied to the empirical parameter $\Delta_H O^{2-} M^{z+}(ox)$ that characterizes each cation in its crystal oxide environment. The calibration function is analogous to the lattice energy function.

TABLE 17

Enthalpy of formation predicted and observed for hydroxides

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
LiOH	- 47.77	- 45.74 (1)	2.03	1.460 (1)	(1)	27.294	1.785	1.757
NaOH, alpha	- 75.25	- 76.71 (1)	- 1.46	1.567 (2)	(2)	32.860	2.562	2.439
		- 76.70 (2)	- 1.45					
NaOH, beta	- 57.97			1.556 (3)	(2)	33.67	2.583	2.442
$Mg(OH)_2$, brucite	- 43.67	- 44.02 (3)	- 0.34	1.573 (1)	(3)	40.747	3.202	1.542
		- 43.01 (1)	0.66					
		- 43.01 (2)	0.66					
		- 44.81 (4)	- 1.14					
		- 43.22 (5)	0.45					
$Ca(OH)_2$, portlandite	- 68.79	- 70.88 (3)	- 2.09	1.564 (1)	(4)	54.816	4.258	1.785
		- 71.17 (1)	- 2.38					
		- 69.71 (2)	- 0.92					
$Sr(OH)_2$	- 96.98	- 87.11 (1)	9.87	1.599 (3)	(5)	59.288	4.836	1.640
$Mn(OH)_2$	- 43.37	- 30.33 (1)	13.04	1.709 (1)	(6)	45.244	4.216	1.731
		- 37.32 (2)	6.05					
$Ni(OH)_2$	- 20.84	- 10.13 (1)	10.71	1.820 (3)	(7)	39.283	4.082	1.434
$Al(OH)_3$, bayerite	- 26.71	- 18.74 (1)	7.97	1.583 (1)	(8)	51.724	4.126	1.335
		- 31.97 (2)	- 5.26					
AlOOH, boehmite	- 17.38	- 15.31 (5)	2.07	1.660 (4)	(9)	32.411	2.856	1.367
		- 9.67 (1)	7.71					
		- 10.08 (2)	7.30					
AlOOH, diaspore	- 22.05	- 22.84 (5)	- 0.79	1.706(4)	(10)	29.503	2.738	1.302
		- 22.22 (1)	- 0.17					
		- 22.26 (2)	- 0.21					
FeOOH, goethite	- 8.87	- 6.95 (1)	1.92	2.365 (1)	(11)	34.592	4.995	2.337
		- 6.95 (2)	1.92					
		- 7.10 (5)	1.77					

Column 3—Thermodynamic values: (1) Wagman and others (1982); (2) Naumov, Ryzhenko, and Khodakovsky (1971); (3) Robie and Waldbaum (1968); (4) Helgeson and others (1978); (5) Robie, Hemingway, and Fisher (1978).

Column 5—Refractive index: (1) Winchell and Winchell (1964); (2) Stehr (1967); (3) estimated by density; (4) Deer, Howie, and Zussman (1965).

Column 6—Structural data: (1) Mair (1978); (2) Stehr (1967); (3) Zigan and Rothbauer (1967); (4) Busing and Levy (1957); (5) Giese (1977); (6) Christensen and Ollivier (1972); (7) Szytula, Murazik, and Blanda (1970); (8) Zigan, Joswig, and Burger (1978); (9) Farkas, Gado, and Werner (1977); (10) Hill (1979); (11) Forsyth, Hedley, and Johnson (1968).

Several concluding remarks may be emphasized.

The proposed method makes it possible to calculate the enthalpy of formation, from oxides, of silicates, aluminates, hydroxides, chromites, and ferrites of two cations in well ordered sites with an

TABLE 18

Cation oxygen bond length and their energetic cost, parameter $\Delta_H O^{2-}\ M^{z+}$ *(ox) and* $\Delta_H O^{2-}\ M^{z+}$ *(comp.) for hydroxides*

(1)	(2)		(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
LiOH	Li^+	4	1.960	1.960	0.032	168.44	2941.18	2978.96	0.500	- 78.00	- 72.11
	H^+	1	0.936	0.936	- 0.004	3173.28	4306.99	4346.03	0.500	- 279.82	- 263.17
NaOH	Na^+	4	2.365	2.301	0.137	127.66	2548.24	2639.76	0.500	30.52	38.76
alpha	H^+	1	0.918	0.918	- 0.014	4744.32	4286.75	4345.12	0.500	- 279.82	- 262.26
NaOH	Na^+	4	2.410	2.350	0.158	118.45	2562.87	2647.79	0.500	30.52	30.73
beta	H^+	1	0.875	0.875	- 0.017	5748.11	4213.30	4284.01	0.500	- 279.82	- 201.15
$Mg(OH)_2$	Mg^{2+}	6	2.102	2.102	0.121	118.33	3816.50	3953.25	1.000	- 204.00	- 194.10
Brucite	H^+	1	0.995	0.995	- 0.001	2184.08	4337.44	4364.31	1.000	- 279.82	- 281.45
$Ca(OH)_2$	Ca^{2+}	6	2.371	2.371	0.696	109.09	3431.79	3558.00	1.000	- 143.00	- 126.21
Portlandite	H^+	1	0.936	0.936	- 0.004	3223.29	4306.99	4346.65	1.000	- 279.82	- 263.79
$Sr(OH)_2$	Sr^{2+}	7	2.598	2.496	1.561	114.57	3325.73	3378.89	1.000	- 102.00	- 85.49
	H^+	1	0.970	0.970	- 0.002	2569.90	4330.70	4362.31	1.000	- 279.82	- 279.45
$Mn(OH)_2$	Mn^{2+}	6	2.187	2.187	0.756	151.06	3617.24	3889.87	1.000	- 214.00	- 186.07
	H^+	1	1.040	1.040	- 0.001	2054.44	4330.40	4355.68	1.000	- 279.82	- 272.82
$Ni(OH)_2$	Ni^{2+}	6	2.121	2.121	1.214	181.80	3930.38	4176.16	1.000	- 223.00	- 215.39
	H^+	1	1.060	1.060	0.000	1578.15	4320.51	4339.93	1.000	- 279.82	- 257.07
$Al(OH)_3$	Al^{3+}	6	1.904	1.855	0.124	171.20	14856.10	15700.12	1.500	- 214.57	- 220.68
Bayerite	H^+	1	0.973	0.939	- 0.001	2383.73	4309.87	4339.15	1.500	- 279.82	- 256.29
AlOOH	Al^{3+}	6	1.912	1.852	0.124	176.03	14855.73	15723.59	1.500	- 214.57	- 228.50
Boehmite	H^+	1	0.972	0.972	- 0.001	2125.98	4331.55	4357.70	0.500	- 279.82	- 274.84
AlOOH	Al^{3+}	6	1.915	1.852	0.136	169.72	14855.73	15692.47	1.00	- 214.57	- 218.13
Diaspore	H^+	1	0.989	0.989	- 0.001	1892.45	4336.50	4359.78	0.500	- 279.82	- 276.92
FeOOH	Fe^{3+}	6	2.020	1.950	0.250	252.41	15002.61	15269.16	1.500	- 280.00	- 272.34
Goethite	H^+	1	0.987	0.987	- 0.008	3467.63	4336.19	4378.84	0.500	- 279.82	- 295.98

accuracy of about 5 kJ/mole by using the following fundamental expression:

$$\Delta H_f^\circ M_p M'_q O_N(c) - \Sigma\, \Delta H_f^\circ(\text{constituent oxides}) = -X\ X'\ N(\Delta_H O^{2-} M^{z+}(\text{comp}) - \Delta_H O^{2-} M'^{z'+}(\text{comp})) \quad (35)$$

in which N is the total number of oxygens in the compound, X and X′ are the mole fractions of oxygen bound to cations M^{z+} and $M'^{z'+}$, respectively.

The parameters $\Delta_H O^{2-}M^{z+}$ and $\Delta_H O^{2-}M'^{z'+}$ are corrected as functions of the difference between the energy of the M^{z+}–O bond in oxides and in compounds. These corrections allow the suppression of the α coefficient used in previous articles.

The corrections represent in fact the energetic cost involved in changing both the cation-oxygen bond length and the cation environment from the free oxides to the considered compound.

The model allows us to calculate the enthalpy of formation from oxides of polymorphs by using their crystal structure refinements. This method was applied here to clinoenstatite, orthoenstatite, protoenstatite, et cetera.

This model can be applied widely. In a following paper, the same calibration will be used to calculate the enthalpy of formation of several kinds of more complex compounds:

1. $M_pM'_qO_N$, compound composed of two cations but in different sites:

two disordered sites (or 4 individual sites) such as inverse spinels $MgFe_2O_4$, $FeFe_2O_4$, and nearly all ferrites:

three ordered sites such as wollastonite ($Ca^{VII}Ca_2^{VI}Si_3O_9$), rhodonite ($Mn^{VII}Mn_4^{VI}Si_5O_{15}$), et cetera;

four ordered sites such as $Li_{3.0}^{IV}\ Li_{0.57}^{V}\ Li_{0.43}^{VI}\ SiO_4$;

two ordered and one disordered sites such as mullite, $Al_{2.67}^{VI}\ Al_{1.33}^{IV}\ (Al_2, Si_2)^{IV}O_{13}$.

and

2. $M_pM'_qM''_rO_N$, compounds composed of three cations in several different sites:

three ordered sites, such as pyroxene ($NaAlSi_2O_6$);

four ordered sites, such as merwinite ($Ca^{VII}Ca_2^{VI}Mg^{VI}Si_2O_8$);

one disordered site such as in plagioclase feldspars.

The procedure of the calculation of the enthalpy of formation of these compounds will be shown in a following paper.

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APPENDIX I

Polarizability of ions in oxides and in minerals.—In minerals or compounds, the ions forming crystals are deformed or polarized. The radius of a given crystal ion (cation or oxygen) (1) is not equal to its radius in the free gazeous state and (2) is not constant from a crystal to another. The radius changes are a function of the coordination number, of the bond length M–O, and of the nature of the surrounding ions.

The electronic polarizability α_i of an ion measures the susceptibility of the ion's electron density to deformation under an electrical field. In a crystal, α_m, the molecular polarizability is the sum of the effective electronic polarizabilities of the constituent ions of the compound:

$$\alpha_m = \Sigma\, \alpha_{M^{z+}}^{comp} + \Sigma\, \alpha_{O^{2-}}^{comp} \tag{36}$$

in which $\alpha_{M^{z+}}^{comp}$ and $\alpha_{O^{2-}}^{comp}$ are respectively the effective electronic polarizability of a cation M^{z+} and of an oxygen ion O^{2-}. These two values are not directly known but can be evaluated. The molecular polarizability of a crystal can be determined from the optical refractive index η by the Lorentz-Lorenz equation:

$$\alpha_m = (3\ V_m/4\pi)[(\eta^2 - 1)/(\eta^2 + 2)] \tag{37}$$

where V_m is the molecular volume of the crystalline compound and π is the average optical refractive index (at D line):

$$\eta = \sqrt[3]{\eta_\alpha \eta_\beta \eta_\gamma} \tag{38}$$

$$\eta = \sqrt[3]{\eta_\epsilon \eta_\omega^2} \tag{39}$$

$$\eta = \eta_\beta \tag{40}$$

Using the known mineral refractive index and molecular volume, the Lorentz-Lorenz relation makes it possible to calculate the molecular electronic polarizabilities for any compound: free oxides, hydroxides, silicates, et cetera.

Effective electronic polarizability of ions determined by the additivity rule.—The molecular polarizability of a compound such as $MgSiO_3$ can be expressed as a contribution from each of the ions in the crystal as follows:

$$\alpha_m = (\alpha_{Mg^{2+}}^{comp}) + (\alpha_{Si^{4+}}^{comp}) + (3\ \alpha_{O^{2-}}^{comp}) \tag{41}$$

Fajans and Joos (1924), Pauling (1927), Tessman, Kahn, and Shockley (1953), Pirenne and Kartheuser (1964), Lasaga and Cygan (1982) have proposed a set of universal values of electronic polarizabilities of ions. However, several authors (Jai Shanker, Kumar, and Verma, 1973; Jain, Jai Shanker, and Khandelwal, 1975; Jai Shanker, Lashkari, and Sharma, 1978; Chakrabarti, Sarkar, and Sengupta, 1976) have shown that in minerals the reciprocal influences of ions are very sensitive. In view of these deformations, one should expect that the sizes of positive and negative ions in crystal environments would be different from those in free gases; that is, when an ion is transferred from a gas to a crystal, the radius of the ion will increase if the ion is positive and decrease if the ion is negative.

Jai Shanker, Kumar, and Verma (1973) have shown that the electronic polarizability of an ion is proportional to the cube of its ionic radius so that if:

$\alpha_{M^{z+}}^{comp}$ is the effective electronic polarizability of a cation M^{z+} in a crystal;
$\alpha_{O^{2-}}^{comp}$ is the effective electronic polarizability of an oxygen in a crystal;
$\alpha_{M^{z+}}$ is the electronic polarizability of a cation M^{z+} in free state;
$\alpha_{O^{2-}}$ is the electronic polarizability of an oxygen in free state;
$r_{M^{z+}}^{comp}$ is the effective ionic radius of a cation M^{z+} in a crystal;
$r_{O^{2-}}^{comp}$ is the effective ionic radius of an oxygen in a crystal;
$r_{M^{z+}}$ is the ionic radius of a cation M^{z+} in free gazeous state;
$r_{O^{2-}}$ is the ionic radius of an oxygen in free gazeous state;
one has:

$$[(\alpha_{M^{z+}}^{comp})/(\alpha_{M^{z+}})] = [(r_{M^{z+}}^{comp})/(r_{M^{z+}})]^3 \tag{42}$$

$$[(\alpha_{O^{2-}}^{comp})/(\alpha_{O^{2-}})] = [(r_{O^{2-}}^{comp})/(r_{O^{2-}})]^3 \tag{43}$$

For any compound, the values of $\alpha_{M^{z+}}^{comp}$ and $\alpha_{O^{2-}}^{comp}$ can be calculated if we know the average bond length M–O. This is expressed by the following expression:

$$d_{M-O} = r_{M^{z+}}^{comp} + d_{O^{2-}}^{comp} \quad (44)$$

The values of electronic polarizability of a cation $\alpha_{M^{z+}}$ in free state are known from numerous references (Fajans and Joos, 1924; Pauling, 1960; Shevelko and Vinogradov, 1979; Feiock and Johnson, 1969). According to Tosi (1964), the values of ionic radius of cations in free state, $r_{M^{z+}}$ can be assumed to be equal to those of Pauling (1960). These two parameters are listed in table 6.

The polarizability of oxygen ion, $\alpha_{O^{2-}}$, in free state is equal to 2.75 A^3 (Fajans and Joos, 1924). The value of the ionic radii of O^{2-} in free state has been chosen to be equal to 1.49 Å because of the compatibility between predicted effective radii of cations and oxygen with observed effective distribution radius (Takeuchi, 1984).

Thus, all parameters of the calibration equation (eq 31) being defined, it is possible to understand the application of the calibration equation and the procedure of the calculation of the enthalpy of formation from constituent oxides by using the crystallographical, physical, and optical parameters.

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