EMPIRICAL THERMOCHEMICAL VALUES FOR HIGHER ORDER OXIDES – AN UNCRITICAL CONSIDERATION

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Abstract

This paper presents empirical thermochemical data for a number of higher order oxides and introduces the method employed for their calculations. This method is based on experimentally measured data.

Key words: Thermochemistry, empirical values, oxides.

1. Method

The basis for the empirical calculation in the current study are the „uncritical“ values given in Table 1, which lists the average thermochemical data for the binary oxides from Woods and Garrels (1987). The values for $\Delta G^\circ_{\text{cal}}$ and $\Delta H^\circ_{\text{cal}}$ [kJ/mol] respectively presented in Table 2, are calculated according the following principle: The sum of the values for the binary oxides are multiplied by the ratio of the sum corresponding to the atoms of the higher-order oxide over the sum corresponding to the atoms of the individual binary oxides. This yields the coefficients $C_G = \Delta G^\circ_{\text{exp}}/\Delta G^\circ_{\text{cal}}$ and $C_H = \Delta H^\circ_{\text{exp}}/\Delta H^\circ_{\text{exp}}$ respectively for both the ternary and quaternary oxides in the same table. For most of these calculations, the coefficients are approximately 1.10, with minimum and maximum values of 0.85 and 1.36. The average for all coefficients is $C_{G,H} = 1.0658$.

In order to generate the empirical values for the oxides listed in Tables 3, 4 and 5, the quantities $\Delta G^\circ_{\text{cal}}$ and $\Delta H^\circ_{\text{cal}}$ are multiplied by these coefficients.

For the current investigation only stoichiometric oxide compounds in a crystalline state were considered, i.e. carbonates, phosphates, nitrates etc. were not included. Additionally, neither compounds of other elements, e.g. chlorides, sulfides or fluorides, nor hydrates or hydroxides were considered. In accordance with the work of Woods and Garrels (1987), compounds of certain elements such as Ga, Gd, In, Nd and Tb are also not included in the current study. All values given here are based on a temperature of 298.15 K.

To clarify the proposed method, the following numerical examples are provided:

1. $\text{Ba}_2\text{Fe}_2\text{O}_5 \Rightarrow \text{BaO} + \text{Fe}_2\text{O}_3$
1. \( \Delta G^o_{\text{calc}} = [-521-743] \times [9/7] = -1625 \text{ [kJ/mol]} \); \( \Delta G^o_{\text{emp}} = (-1625) \times 1.066 = -1732 \text{ [kJ/mol]} \)

2. \( \text{Na}_2\text{Mg}_2\text{Si}_2\text{O}_7 \rightarrow \text{Na}_2\text{O} + \text{MgO} + \text{SiO}_2 \);
   \( \Delta G^o_{\text{calc}} = [-377-569-853] \times [13/8] = -2923 \text{ [kJ/mol]} \); \( \Delta G^o_{\text{emp}} = (-2923) \times 1.066 = -3115 \text{ [kJ/mol]} \)

3. \( \text{PbCa}_3\text{Zn}_4\text{Si}_4\text{O}_{16} \rightarrow \text{PbO} + \text{CaO} + \text{ZnO} + \text{SiO}_2 \);
   \( \Delta G^o_{\text{calc}} = [-189-604-321-853] \times [28/9] = -6119 \text{ [kJ/mol]} \); \( \Delta G^o_{\text{emp}} = (-6119) \times 1.066 = -6522 \text{ [kJ/mol]} \)

4. \( \text{CaYFeBe}_2\text{Si}_2\text{O}_{10} \rightarrow \text{CaO} + \text{Y}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{BeO} + \text{SiO}_2 \);
   \( \Delta G^o_{\text{calc}} = [-604-1817-743-577-853] \times [17/17] = -4594 \text{ [kJ/mol]} \); \( \Delta G^o_{\text{emp}} = -4897 \text{ [kJ/mol]} \)

The values of \( \Delta H^o_{\text{emp}} \) were calculated in a similar fashion.

Table 1 - Experimental thermochemical (average) values of binary oxides [1]

| Compound | \( \Delta G^o_r \) [kJ/mol] | \( \Delta H^o_r \) [kJ/mol] | Compound | \( \Delta G^o_r \) [kJ/mol] | \( \Delta H^o_r \) [kJ/mol] | Compound | \( \Delta G^o_r \) [kJ/mol] | \( \Delta H^o_r \) [kJ/mol] |
|-----------|------------------|-----------------|-----------|------------------|-----------------|-----------|------------------|-----------------|
| AgO       | +11              | -25             | Fe$_2$O$_3$ | -743             | -824            | SeO$_2$   | -173             | -227            |
| Ag$_2$O   | -11              | -31             | GeO$_2$    | -498             | -559            | SiO$_2$   | -853             | -909            |
| Al$_2$O$_3$| -1578            | -1671           | HgO        | -58              | -90             | SnO       | -257             | -286            |
| As$_2$O$_3$| -580             | -659            | MnO        | -363             | -385            | SnO$_2$   | -519             | -581            |
| As$_2$O$_5$| -779             | -921            | K$_2$O     | -320             | -362            | SrO       | -564             | -594            |
| B$_2$O$_3$| -1191            | -1270           | La$_2$O$_3$| -1726            | -1824           | SrO$_2$   | -582             | -638            |
| BaO       | -521             | -549            | Li$_2$O    | -561             | -598            | Ta$_2$O$_5$ | -1926            | -2058           |
| BeO       | -577             | -606            | MgO        | -569             | -601            | TeO$_2$   | -270             | -322            |
| Bi$_2$O$_3$| -494             | -575            | Mn$_2$O$_3$ | -884             | -961            | ThO$_2$   | -1168            | -1226           |
| CaO       | -604             | -635            | MnO        | -569             | -601            | TiO$_2$   | -887             | -940            |
| CdO       | -228             | -257            | MoO$_2$    | -670             | -747            | TiO$_3$   | -1433            | -1521           |
| Ce$_2$O$_3$| -1025            | -1089           | Na$_2$O$_3$| -377             | -416            | UO$_2$    | -1032            | -1085           |
| CeO$_2$   | -1707            | -1796           | Nb$_2$O$_5$| -1765            | -1898           | UO$_3$    | -1146            | -1223           |
| CoO       | -213             | -236            | NiO        | -212             | -240            | V$_2$O$_3$ | -1138            | -1227           |
| CrO$_3$   | -1054            | -1136           | P$_2$O$_5$ | -1361            | -1506           | V$_2$O$_5$ | -1419            | -1551           |
| Cr$_2$O$_3$| -297             | -332            | PbO        | -189             | -218            | WO$_3$    | -764             | -842            |
| Cs$_2$O$_3$| -360             | -465            | PbO$_2$    | -217             | -276            | W$_2$O$_5$ | -1284            | -1413           |
| Cs$_2$O$_5$| -360             | -465            | Rb$_2$O$_3$| -291             | -333            | Y$_2$O$_3$ | -1817            | -1905           |
| CuO       | -127             | -156            | Rb$_2$O$_3$| -387             | -488            | Yb$_2$O$_3$| -1727            | -1815           |
| Cu$_2$O   | -147             | -169            | Sb$_2$O$_3$| -844             | -987            | ZnO       | -321             | -350            |
| FeO       | -250             | -271            | Sc$_2$O$_3$| -1819            | -1909           | ZrO$_2$   | -1040            | -1099           |

Table 2 - Experimental and calculated data for \( \Delta G^o_{\text{exp}}, \Delta G^o_{\text{calc}}, \Delta H^o_{\text{exp}}, \Delta H^o_{\text{calc}} \) with coefficients \( C_G=\Delta G^o_{\text{exp}}/\Delta G^o_{\text{calc}} \) and \( C_H=\Delta H^o_{\text{exp}}/\Delta H^o_{\text{calc}} \) respectively

| Compound  | \( \Delta G^o_{\text{exp}} \) [kJ/mol] | \( \Delta G^o_{\text{calc}} \) | \( C_G \) | \( \Delta H^o_{\text{exp}} \) [kJ/mol] | \( \Delta H^o_{\text{calc}} \) | \( C_H \) |
|-----------|------------------|-----------------|----------|------------------|-----------------|----------|
| AgMoO$_4$ | -822             | -659            | 1.25     | -731             | -620            | 1.18     |
| Ag$_2$CrO$_4$ | -749            | -681            | 1.10     | -839             | -778            | 1.08     |
| Ag$_2$MoO$_4$ | -852            | -775            | 1.10     | -925             | -873            | 1.06     |
| Ag$_2$WO$_4$ | -2441           | -2431           | 1.00     | -2589            | -2580           | 1.00     |
| Al$_2$SiO$_3$ | -3143           | -3343           | 0.94     | -3346            | -3547           | 0.94     |
| Compound          | ΔH (kJ/mol) | ΔS (J/mol·K) | T (K) | ΔG (kJ/mol) | ΔE (kJ/mol) |
|-------------------|------------|-------------|-------|------------|-------------|
| Al₂Si₂O₅         | -6381      | 1.01        | -6815 | -6772      | 1.01        |
| BaMoO₄            | -1546      | 1.20        | -1681 | -1391      | 1.21        |
| Ba₂Si₂O₅         | -2403      | 1.09        | -2543 | -2333      | 1.09        |
| Ba₂SiO₃           | -1969      | 1.19        | -2079 | -1750      | 1.19        |
| Ba₂SiO₄           | -2160      | 1.12        | -2279 | -2041      | 1.12        |
| Ba₃Si₄O₈          | -3948      | 1.10        | -4176 | -3791      | 1.10        |
| Ba₃SiO₅           | -2858      | 1.16        | -3002 | -2624      | 1.14        |
| BeAl₂O₄           | -2178      | 1.01        | -2300 | -2277      | 1.01        |
| Be₂SiO₃           | -1454      | 1.02        | -1540 | -1515      | 1.02        |
| Be₂SiO₄           | -2038      | 1.02        | -2153 | -2121      | 1.01        |
| CaFe₂O₄           | -1413      | 1.05        | -1520 | -1459      | 1.04        |
| CaFe₂O₅           | -2000      | 1.15        | -2134 | -1876      | 1.14        |
| CaMoO₄            | -1440      | 1.13        | -1547 | -1382      | 1.12        |
| Ca₂SiO₃           | -1547      | 1.06        | -1632 | -1544      | 1.06        |
| Ca₂SiO₄           | -2196      | 1.08        | -2312 | -2162      | 1.07        |
| Ca₂SiO₅           | -2785      | 1.06        | -2931 | -2779      | 1.05        |
| Ca₂Si₂O₇          | -3759      | 1.07        | -3960 | -3706      | 1.07        |
| CaWO₄              | -1538      | 1.12        | -1643 | -1477      | 1.11        |
| CdSiO₃            | -1104      | 1.02        | -1188 | -1166      | 1.02        |
| FeAl₂O₄           | -1864      | 1.02        | -1979 | -1942      | 1.02        |
| FeCr₂O₄           | -1358      | 1.04        | -1459 | -1407      | 1.04        |
| FeMoO₄            | -977       | 1.06        | -1076 | -1018      | 1.06        |
| Fe₂SiO₃           | -1119      | 1.01        | -1193 | -1180      | 1.01        |
| Fe₅SiO₄           | -1375      | 0.89        | -1475 | -1652      | 0.89        |
| Fe₃SiO₅           | -1159      | 1.02        | -1236 | -1211      | 1.02        |
| Fe₂WO₄            | -1061      | 1.05        | -1161 | -1113      | 1.04        |
| K₂SiO₃            | -1465      | 1.25        | -1553 | -1271      | 1.22        |
| K₂Si₂O₅           | -2335      | 1.33        | -2483 | -1906      | 1.30        |
| K₂Si₄O₉           | -4085      | 1.39        | -4330 | -3177      | 1.36        |
| LiAl₂O₃           | -1128      | 1.05        | -1190 | -1134      | 1.05        |
| Li₂SiO₃           | -1553      | 1.10        | -1640 | -1507      | 1.09        |
| Li₂Si₂O₃          | -2396      | 1.13        | -2540 | -2260      | 1.12        |
| MgAl₂O₄           | -2179      | 1.01        | -2304 | -2272      | 1.01        |
| MgCr₂O₄           | -1669      | 1.03        | -1773 | -1737      | 1.02        |
| MgFe₅O₄           | -1326      | 1.01        | -1437 | -1425      | 1.01        |
| MgSiO₃            | -1461      | 1.03        | -1549 | -1510      | 1.02        |
| Mg₂SiO₄           | -2055      | 1.03        | -2175 | -2114      | 1.03        |
| Mg₂TiO₃           | -1484      | 1.02        | -1572 | -1541      | 1.02        |
| MnSiO₃            | -1241      | 1.02        | -1320 | -1294      | 1.02        |
| Mn₂SiO₅           | -1631      | 0.96        | -1729 | -1812      | 0.95        |
| Mn₂WO₄            | -1204      | 1.07        | -1305 | -1227      | 1.06        |
| Na₂SiO₃           | -1468      | 1.19        | -1560 | -1325      | 1.18        |
| Na₂UO₄            | -1773      | 1.16        | -1959 | -1639      | 1.19        |
| NiAl₂O₄           | -1819      | 1.02        | -1928 | -1911      | 1.01        |
| Ni₂FeO₄           | -972       | 1.02        | -1080 | -1064      | 1.01        |
| Ni₂SiO₃           | -1128      | 1.06        | -1065 | -1060      | 1.06        |
| Ni₂SiO₄           | -1294      | 0.87        | -1408 | -1609      | 0.87        |
| PbMoO₄            | -956       | 1.11        | -1071 | -965       | 1.11        |
| Pb₂SiO₃           | -1061      | 1.02        | -1134 | -1129      | 1.00        |
| Pb₂SiO₄           | -1253      | 0.86        | -1336 | -1578      | 0.85        |
| PbWO₄              | -1020      | 1.07        | -1122 | -1060      | 1.06        |
| Compound       | $\Delta G^\circ_{\text{exp}}$ [kJ/mol] | $\Delta G^\circ_{\text{cal}}$ | $C_G$ | $\Delta H^\circ_{\text{exp}}$ [kJ/mol] | $\Delta H^\circ_{\text{cal}}$ | $C_H$ |
|----------------|----------------------------------------|--------------------------------|-------|----------------------------------------|--------------------------------|-------|
| SrSiO$_3$      | -1560                                 | -1417                          | 1.10  | -1634                                  | -1503                          | 1.09  |
| Sr$_2$SiO$_4$  | -2212                                 | -1984                          | 1.11  | -2313                                  | -2104                          | 1.10  |
| Sr$_3$SiO$_5$  | -2887                                 | -2551                          | 1.13  | -3001                                  | -2705                          | 1.11  |
| SrWO$_4$       | -1538                                 | -1328                          | 1.16  | -1654                                  | -1436                          | 1.15  |
| USiO$_4$       | -1891                                 | -1885                          | 1.00  | -2000                                  | -1994                          | 1.00  |
| ZnAl$_2$O$_4$  | -2065                                 | -2021                          | 1.02  |                                        |                                |       |
| ZnSiO$_3$      | -1175                                 | -1174                          | 1.00  | -1265                                  | -1259                          | 1.00  |
| Zn$_2$SiO$_4$  | -1525                                 | -1644                          | 0.93  | -1638                                  | -1763                          | 0.93  |
| Zn$_2$TiO$_4$  | -1535                                 | -1691                          | 0.91  | -1649                                  | -1806                          | 0.91  |
| ZnWO$_4$       | -1124                                 | -1085                          | 1.04  | -1233                                  | -1192                          | 1.03  |
| ZrSiO$_4$      | -1915                                 | -1893                          | 1.01  | -2028                                  | -2008                          | 1.01  |

b. Quaternary oxides

| Compound       | $\Delta G^\circ_{\text{exp}}$ [kJ/mol] | $\Delta G^\circ_{\text{cal}}$ | $C_G$ | $\Delta H^\circ_{\text{exp}}$ [kJ/mol] | $\Delta H^\circ_{\text{cal}}$ | $C_H$ |
|----------------|----------------------------------------|--------------------------------|-------|----------------------------------------|--------------------------------|-------|
| CaAl$_2$SiO$_6$| -3122                                 | -3035                          | 1.03  | -3293                                  | -3215                          | 1.02  |
| CaAl$_2$Si$_2$O$_8$ | -3999                             | -3945                          | 1.04  | -4226                                  | -4179                          | 1.01  |
| Ca$_2$Al$_2$SiO$_7$ | -3791                           | -3642                          | 1.04  | -3989                                  | -3858                          | 1.03  |
| Ca$_3$Al$_2$Si$_3$O$_12$ | -6277                           | -6070                          | 1.03  | -6639                                  | -6430                          | 1.03  |
| CaFeSi$_2$O$_6$  | -2676                                 | -2438                          | 1.10  | -2840                                  | -2593                          | 1.09  |
| CaFe$_2$Si$_3$O$_12$ | -5416                           | -4400                          | 1.23  | -5760                                  | -4736                          | 1.22  |
| CaMg$_2$SiO$_4$  | -2143                                 | -2026                          | 1.06  | -2262                                  | -2145                          | 1.05  |
| CaMg$_2$Si$_2$O$_6$ | -3032                           | -2894                          | 1.05  | -3206                                  | -3064                          | 1.05  |
| Ca$_2$Mg$_2$Si$_3$O$_7$ | -3678                           | -3473                          | 1.05  | -3875                                  | -3677                          | 1.05  |
| CaTiSiO$_3$     | -2455                                 | -2344                          | 1.05  | -2590                                  | -2484                          | 1.04  |
| Fe$_2$Al$_3$Si$_5$O$_8$ | -7961                           | -7775                          | 1.02  | -8450                                  | -8268                          | 1.02  |
| Fe$_2$Al$_3$Si$_3$O$_12$ | -4970                           | -5362                          | 0.93  | -5302                                  | -5702                          | 0.93  |
| FeMg$_2$Si$_2$O$_6$ | -2593                           | -2388                          | 1.08  | -2756                                  | -2544                          | 1.08  |
| KAlSiO$_4$      | -2000                                 | -1751                          | 1.14  | -2115                                  | -1872                          | 1.13  |
| KAl$_2$SiO$_6$  | -2866                                 | -2501                          | 1.14  | -3028                                  | -2674                          | 1.13  |
| KAl$_3$Si$_2$O$_8$ | -3729                           | -3251                          | 1.15  | -3960                                  | -3477                          | 1.14  |
| LiAlSiO$_4$     | -2007                                 | -1904                          | 1.05  | -2121                                  | -2022                          | 1.05  |
| LiAl$_2$Si$_2$O$_6$ | -2868                           | -2720                          | 1.05  | -3038                                  | -2889                          | 1.05  |
| Mg$_2$Al$_4$Si$_4$O$_10$ | -4982                           | -5100                          | 0.98  | -5278                                  | -5408                          | 0.97  |
| Mg$_2$Al$_4$Si$_3$O$_18$ | -8666                           | -8700                          | 1.00  | -9161                                  | -9225                          | 0.99  |
| Mg$_3$Al$_2$Si$_3$O$_12$ | -5949                           | -6000                          | 0.99  | -6275                                  | -6362                          | 0.99  |
| NaAl$_2$SiO$_5$ | -1970                                 | -1787                          | 1.10  | -2085                                  | -1906                          | 1.09  |
| NaAl$_3$Si$_2$O$_6$ | -2833                           | -2553                          | 1.11  | -3023                                  | -2724                          | 1.11  |
| NaAl$_3$Si$_3$O$_8$ | -3704                           | -3318                          | 1.12  | -3924                                  | -3541                          | 1.11  |

2. Comments

The method outlined here provides an estimation and is intended only as a first approximation in those cases where, due to lack of thermochemical data, exact calculation of mineralogical processes is not possible. In these cases, an experimental determination of the unknown quantities should be undertaken. However, it should be not forgotten that the production of pure stoichiometric compounds and the experimental determination of there thermochemical data are not simple procedures.

Closer examination of Tables 2a and 2b reveals that the coefficients $C_G$ and $C_H$ for potassium compounds have a higher average value, while magnesium and zinc compounds exhibit an average...
value lower than 1.06 (the average for all compounds, as stated above). Thus, the empirical values for each group of elements can be determined individually.

The compounds in Tables 3, 4, 5 and 6 were taken either from the Mineralogical Tables compiled by Strunz (1977) or from the literature.

A similar study of the free-enthalpy changes for sulfides was published by Barton and Skinner (1967).

Table 3 - Empirical data of $\Delta G^\circ_{\text{emp}}$ and $\Delta H^\circ_{\text{emp}}$ for ternary oxides

| Compound         | $\Delta G^\circ_{\text{emp}}$ [kJ/mol] | $\Delta H^\circ_{\text{emp}}$ [kJ/mol] | Compound         | $\Delta G^\circ_{\text{emp}}$ [kJ/mol] | $\Delta H^\circ_{\text{emp}}$ [kJ/mol] |
|------------------|----------------------------------------|----------------------------------------|------------------|----------------------------------------|----------------------------------------|
| Al$_2$ZnO$_4$    | -2024                                  | -2154                                  | LaVO$_4$         | -1676                                  | -1798                                  |
| Ba$_2$Fe$_2$O$_5$| -1732                                  | -1881                                  | Li$_2$Ge$_7$O$_{15}$ | -4515                                  | -4932                                  |
| BaTiO$_3$        | -1501                                  | -1587                                  | Li$_2$SiO$_3$     | -1507                                  | -1606                                  |
| BaSi$_2$O$_5$    | -2343                                  | -2486                                  | Li$_2$Si$_3$O$_5$ | -2260                                  | -2409                                  |
| BaZrO$_3$        | -1664                                  | -1756                                  | Li$_2$SiO$_4$     | -2260                                  | -2409                                  |
| Bi$_2$Si$_3$O$_12$ | -3409                                | -3756                                  | Li$_2$WO$_4$      | -1412                                  | -1535                                  |
| Bi$_2$Sn$_2$O$_7$ | -1485                                  | -1693                                  | Mg$_2$B$_2$O$_3$  | -2412                                  | -2564                                  |
| Bi$_2$O$_4$      | -1019                                  | -1133                                  | Mg$_2$B$_2$O$_6$  | -2948                                  | -3133                                  |
| CaB$_2$O$_4$     | -1913                                  | -2030                                  | MgGeO$_3$        | -1137                                  | -1236                                  |
| CaGeO$_3$        | -1174                                  | -1273                                  | Mg$_2$GeO$_4$    | -1592                                  | -1731                                  |
| Ca$_3$GeO$_3$    | -1644                                  | -1782                                  | Mg$_2$Nb$_2$O$_6$ | -2487                                  | -2663                                  |
| CaMn$_2$O$_4$    | -1586                                  | -1701                                  | Mg$_2$Sb$_2$O$_6$ | -1506                                  | -1692                                  |
| Ca$_3$Ta$_2$O$_7$| -3295                                  | -3507                                  | MgTi$_2$O$_3$    | -2483                                  | -2628                                  |
| CeAs$_4$         | -1325                                  | -1447                                  | Mg$_2$TiO$_4$    | -2172                                  | -2299                                  |
| CeWO$_4$         | -1666                                  | -1783                                  | MnGeO$_3$        | -918                                   | -1006                                  |
| Co$_2$B$_2$O$_5$ | -1924                                  | -2063                                  | Mn$_2$GeO$_4$    | -1284                                  | -1409                                  |
| Co$_2$B$_2$O$_6$ | -2351                                  | -2523                                  | Mn$_2$GeO$_4$    | -1284                                  | -1409                                  |
| Co$_2$GeO$_3$    | -758                                   | -847                                   | Mn$_2$GeO$_4$    | -1284                                  | -1409                                  |
| Co$_2$SiO$_4$    | -1590                                  | -1708                                  | Mn$_2$GeO$_4$    | -1284                                  | -1409                                  |
| CoWO$_4$         | -1041                                  | -1149                                  | Mn$_2$GeO$_4$    | -1284                                  | -1409                                  |
| Cr$_2$CuO$_4$    | -1259                                  | -1377                                  | Mn$_2$GeO$_4$    | -1284                                  | -1409                                  |
| Cr$_2$MnO$_4$    | -1510                                  | -1621                                  | Mn$_2$GeO$_4$    | -1284                                  | -1409                                  |
| Cr$_2$NiO$_4$    | -1349                                  | -1466                                  | Mn$_2$GeO$_4$    | -1284                                  | -1409                                  |
| CuAs$_2$O$_4$    | -753                                   | -869                                   | Mn$_2$GeO$_4$    | -1284                                  | -1409                                  |
| CuFe$_2$O$_4$    | -402                                   | -455                                   | NaGeO$_3$        | -932                                   | -1039                                  |
| CuFe$_2$O$_4$    | -474                                   | -529                                   | NaGeO$_3$        | -932                                   | -1039                                  |
| Fe$_2$BO$_5$     | -1746                                  | -1891                                  | Na$_2$Si$_2$O$_3$ | -1966                                  | -2118                                  |
| FeGeO$_3$        | -797                                   | -885                                   | Na$_2$U$_2$O$_7$  | -2550                                  | -2745                                  |
| Fe$_2$MnO$_4$    | -1179                                  | -1288                                  | Na$_2$U$_2$O$_7$  | -2550                                  | -2745                                  |
| FeNb$_2$O$_6$    | -1336                                  | -1450                                  | NiAs$_2$O$_4$    | -844                                   | -958                                   |
| Fe$_2$Nb$_2$O$_6$ | -2147                                  | -2312                                  | Ni$_2$WO$_4$     | -1040                                  | -1153                                  |
| Fe$_2$Si$_2$O$_4$ | -3935                                  | -4272                                  | PbCu$_4$O$_8$    | -1100                                  | -1381                                  |
| Fe$_2$ZnO$_4$    | -1134                                  | -1251                                  | PbSeO$_3$        | -386                                   | -474                                   |
| Hg$_2$TeO$_4$    | -489                                   | -615                                   | PbSeO$_3$        | -386                                   | -474                                   |
| K$_2$Cr$_2$O$_7$ | -1014                                  | -1114                                  | Zn$_2$BO$_7$     | -1242                                  | -1425                                  |
| Pb$_2$V$_2$O$_7$ | -2094                                  | -2304                                  | Zn$_2$BO$_7$     | -1242                                  | -1425                                  |
| Pb$_2$V$_2$O$_7$ | -1985                                  | -2203                                  | Zn$_2$BO$_7$     | -1242                                  | -1425                                  |

Table 3 - Empirical data of $\Delta G^\circ_{\text{emp}}$ and $\Delta H^\circ_{\text{emp}}$ for ternary oxides
Table 4 - Empirical data of $\Delta G^o_{\text{emp}}$ and $\Delta H^o_{\text{emp}}$ for quaternary oxides

| Compound | $\Delta G^o_{\text{emp}}$ [kJ/mol] | $\Delta H^o_{\text{emp}}$ [kJ/mol] |
|----------|----------------------------------|----------------------------------|
| Al$_2$B$_6$Si$_2$O$_{17}$ | -18113 | -19254 |
| Al$_4$MgBeO$_8$ | -4516 | -4772 |
| Al$_2$Be$_2$Si$_2$O$_8$ | -9297 | -9847 |
| Ba$_2$Ge$_2$O$_8$ | -3598 | -3851 |
| Ba$_2$Si$_2$O$_8$ | -4090 | -4336 |
| BaBe$_2$Si$_2$O$_7$ | -3565 | -3771 |
| BaCa$_2$Si$_2$O$_9$ | -4518 | -4780 |
| BaCuSi$_2$O$_9$ | -3657 | -3932 |
| BaFe$_2$Si$_2$O$_9$ | -3596 | -4212 |
| BaSn$_2$O$_8$ | -3531 | -3803 |
| BaTi$_2$O$_4$ | -3554 | -3820 |
| BaTi$_2$O$_4$ | -4217 | -4472 |
| Ba$_4$Ti$_2$O$_6$ | -3916 | -4153 |
| Be$_2$Al$_2$O$_4$ | -6774 | -7157 |
| Be$_2$Si$_2$O$_5$ | -9033 | -9543 |
| Ca$_2$Al$_2$O$_4$ | -6406 | -6983 |
| Ca$_2$Al$_2$O$_4$ | -18114 | -19189 |
| Ca$_2$Be$_2$O$_4$ | -3668 | -3899 |
| Ca$_2$Be$_2$O$_4$ | -3716 | -3928 |
| Ca$_2$Bi$_2$O$_9$ | -3051 | -3312 |
| Ca$_2$Cr$_2$O$_8$ | -4596 | -4967 |
| Ca$_2$Cr$_2$O$_8$ | -5352 | -5713 |
| Ca$_2$Cu$_2$O$_6$ | -3859 | -4142 |
| CaFe$_2$O$_4$ | -1819 | -1934 |
| CaFe$_2$O$_4$ | -2599 | -2764 |
| CaFe$_2$O$_4$ | -4352 | -4684 |
| CaK$_2$Si$_2$O$_7$ | -1815 | -2044 |
| CaLa$_2$Si$_3$O$_12$ | -7124 | -7538 |
| CaMg$_2$Al$_2$O$_4$ | -12705 | -13426 |
| CaMg$_2$Al$_2$O$_4$ | -14986 | -15836 |
| CaMg$_2$Ge$_2$O$_6$ | -1781 | -1913 |
| CaMg$_2$Si$_2$O$_4$ | -4319 | -4572 |
| CaMn$_2$O$_4$ | -1940 | -2056 |
| CaMn$_2$O$_4$ | -2771 | -2973 |
| CaMn$_2$Si$_2$O$_4$ | -6928 | -7342 |
| CaNa$_2$Si$_2$O$_4$ | -3115 | -3336 |
| CaNa$_2$Si$_2$O$_4$ | -2048 | -2248 |
| CaNa$_2$Si$_2$O$_4$ | -8122 | -8759 |
| CaNa$_2$Si$_2$O$_4$ | -2643 | -2832 |
| CaNa$_2$Si$_2$O$_4$ | -2076 | -2319 |
| CaNa$_2$Si$_2$O$_4$ | -2954 | -3133 |
| CaNa$_2$Si$_2$O$_4$ | -3009 | -3219 |
| CaNa$_2$Si$_2$O$_4$ | -4512 | -4828 |
| CaNa$_2$Si$_2$O$_4$ | -3760 | -4023 |
| CaNa$_2$Si$_2$O$_4$ | -4839 | -5167 |

$\Delta G^o_{\text{emp}}$ and $\Delta H^o_{\text{emp}}$ values in [kJ/mol] for various compounds. The table includes empirical data for the formation of quaternary oxides.

1. $\text{Ca}_2\text{Fe}^{2+}\text{Fe}^{3+}\text{Si}_2\text{O}_{12}$
2. $\text{NaFe}^{2+}\text{Fe}^{3+}\text{Si}_2\text{O}_{20}$
3. $\text{Na}_3\text{Mn}^{2+}\text{Mn}^{2+}\text{Si}_3\text{O}_{24}$
4. $\text{Sr}^{2+}\text{Sr}^{4+}\text{V}^{2+}\text{Si}_4\text{O}_{14}$

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Table 5 - Empirical data of $\Delta G_{emp}^o$ and $\Delta H_{emp}^o$ for quinary oxides

| Compound                  | $\Delta G_{emp}^o$ [kJ/mol] | $\Delta H_{emp}^o$ [kJ/mol] |
|---------------------------|----------------------------|-----------------------------|
| $\text{BaFe}_2\text{TiSi}_3\text{O}_9$ | -4014                      | -4266                       |
| $\text{BaMg}_2\text{Al}_6\text{Si}_9\text{O}_{30}$ | -15011                     | -15902                      |
| $\text{BaNa}_2\text{Al}_4\text{Si}_4\text{O}_{16}$ | -7369                      | -7847                       |
| $\text{BaSr}_2\text{Mn}_2\text{Si}_4\text{O}_{14}$ | -5765                      | -6155                       |
| $\text{CaAlFeSiO}_6$      | -2685                      | -2870                       |
| $\text{CaCrAlSiO}_6$      | -2905                      | -3092                       |
| $\text{Ca}_2\text{Fe}_2\text{Si}_3\text{O}_{10}$ | -4375                      | -4657                       |
| $\text{Ca}_6\text{Mg}_3\text{Mn}_2\text{B}_2\text{Si}_12\text{O}_{30}$ | -14268                     | -15126                      |
| $\text{CaMn}_2\text{Be}_3\text{Si}_12\text{O}_{12}$ | -5961                      | -6304                       |
| $\text{CaNa}_2\text{Al}_4\text{Si}_4\text{O}_{16}$ | -7552                      | -8037                       |
| $\text{Ca}_2\text{NaMg}_3\text{As}_3\text{O}_{12}$ | -3546                      | -3618                       |
| $\text{Ca}_3\text{TiFeSi}_3\text{O}_{12}$ | -5529                      | -5872                       |
| $\text{Ca}_3\text{Ti}_2\text{Fe}_2\text{Si}_2\text{O}_{12}$ | -5061                      | -5424                       |
| $\text{CaZrBAI}_9\text{O}_{18}$ | -9407                      | -9965                       |
| $\text{Ca}_3\text{Zr}_2\text{Al}_2\text{SiO}_{12}$ | -6681                      | -7074                       |
| $\text{Ca}_3\text{Zr}_2\text{Fe}_2\text{SiO}_{12}$ | -5313                      | -5685                       |
| $\text{KN}_2\text{Al}_4\text{Si}_4\text{O}_{16}$ | -6668                      | -7158                       |
| $\text{KN}_3\text{Mg}_4\text{Si}_2\text{O}_{30}$ | -10266                     | -11084                      |
| $\text{Mg}_2\text{Al}_1\text{B}_4\text{Si}_1\text{O}_{37}$ | -18164                     | -19292                      |
| $\text{Mg}_3\text{Al}_4\text{Si}_3\text{BeO}_{16}$ | -8577                      | -9082                       |
| $\text{MgCrAlSiO}_6$      | -2881                      | -3067                       |
| $\text{Na}_2\text{Fe}_2\text{Si}_2\text{O}_{10}$ | -4896                      | -5200                       |
| $\text{Na}_4\text{BaTi}_2\text{Si}_4\text{O}_{12}$ | -5961                      | -6304                       |
| $\text{Na}_3\text{Mg}_3\text{FeTiSi}_3\text{O}_{24}$ | -12497                     | -13330                      |
| $\text{Na}_3\text{Mg}_3\text{FeTiSi}_3\text{O}_{24}$ | -9136                      | -9832                       |

Table 6 - Empirical data of $\Delta G_{emp}^o$ and $\Delta H_{emp}^o$ for senary oxides

| Compound                  | $\Delta G_{emp}^o$ [kJ/mol] | $\Delta H_{emp}^o$ [kJ/mol] |
|---------------------------|----------------------------|-----------------------------|
| $\text{CaMgFe}_2\text{Al}_2\text{SiO}_{10}$ | -4633                      | -4945                       |
| $\text{CaYFeBe}_2\text{Si}_2\text{O}_{10}$ | -4896                      | -5200                       |
| $\text{Na}_4\text{BaTi}_2\text{B}_2\text{Si}_1\text{O}_{30}$ | -12497                     | -13330                      |
| $\text{Na}_3\text{Mg}_3\text{FeTiSi}_3\text{O}_{24}$ | -9136                      | -9832                       |

3. Acknowledgement

The translation of the paper in English by Dr. John Balk, University of Kentucky, is gratefully acknowledged.

4. References

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