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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.*

Περίληψη

Στην παρούσα εργασία παρουσιάζονται εμπειρικά θερμοχημικά δεδομένα από μία σειρά υψηλής τάξεως οξειδίων και προτείνεται μεθοδολογία για τον υπολογισμό τους. Η μέθοδος βασίζεται σε πειραματικά δεδομένα.
Λέξεις κλειδιά: *Θερμοχημεία, εμπειρικές τιμές, οξείδια.*

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 ΔG°_{cal} and ΔH°_{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 $C_G = \Delta G^{\circ}_{exp}/\Delta G^{\circ}_{cal}$ and $C_H = \Delta H^{\circ}_{exp}/\Delta H^{\circ}_{exp}$ 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 $\mathbf{C_{G,H} = 1.0658}$.

In order to generate the empirical values for the oxides listed in **Tables 3, 4** and **5**, the quantities ΔG°_{cal} and ΔH°_{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 flnorides, 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. $Ba_2Fe_2O_5 \rightarrow BaO + Fe_2O_3$

ΔG^{o}_{cal} = [-521-743] x [9/7] = -1625 [kJ/mol]; ΔG^{o}_{emp} = (-1625) x 1.066 = -1732 [kJ/mol]

2. $Na_2Mg_2Si_2O_7 \Rightarrow Na_2O + MgO + SiO_2$;

ΔG^{o}_{cal} = [-377-569-853] x [13/8] = -2923 [kJ/mol]; ΔG^{o}_{emp} = (-2923) x 1.066 = -3115 [kJ/mol]

3. $PbCa_3Zn_4Si_4O_{16} \Rightarrow PbO + CaO + ZnO + SiO_2$;

ΔG^{o}_{cal} = [-189-604-321-853] x [28/9] = -6119 [kJ/mol]; ΔG^{o}_{emp} = (-6119) x 1.066 = -6522 [kJ/mol]

4. $CaYFeBe_2Si_2O_{10} \Rightarrow CaO + Y_2O_3 + Fe_2O_3 + BeO + SiO_2$;

ΔG^{o}_{cal} = [-604-1817-743-577-853] x [17/17] = -4594 [kJ/mol]; ΔG^{o}_{emp} = -4897 [kJ/mol]

The values of ΔH^{o}_{emp} were calculated in a similar fashion.

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

Compound	ΔG^{o}_f [kJ/mol]	ΔH^{o}_f	Compound	ΔG^{o}_f [kJ/mol]	ΔH^{o}_f	Compound	ΔG^{o}_f [kJ/mol]	ΔH^{o}_f
AgO	+11	-25	Fe_2O_3	-743	-824	SeO_2	-173	-227
Ag_2O	-11	-31	GeO_2	-498	-559	SiO_2	-853	-909
Al_2O_3	-1578	-1671	HgO	-58	-90	SnO	-257	-286
As_2O_3	-580	-659	MnO	-363	-385	SnO_2	-519	-581
As_2O_5	-779	-921	K_2O	-320	-362	SrO	-564	-594
B_2O_3	-1191	-1270	La_2O_3	-1726	-1824	SrO_2	-582	-638
BaO	-521	-549	Li_2O	-561	-598	Ta_2O_5	-1926	-2058
BeO	-577	-606	MgO	-569	-601	TeO_2	-270	-322
Bi_2O_3	-494	-575	MnO_2	-463	-520	ThO_2	-1168	-1226
CaO	-604	-635	Mn_2O_3	-884	-961	TiO_2	-887	-940
CdO	-228	-257	MoO_3	-670	-747	Ti_2O_3	-1433	-1521
CeO_2	-1025	-1089	Na_2O	-377	-416	UO_2	-1032	-1085
Ce_2O_3	-1707	-1796	Nb_2O_5	-1765	-1898	UO_3	-1146	-1223
CoO	-213	-236	NiO	-212	-240	V_2O_3	-1138	-1227
CrO_3		-589	P_2O_5	-1361	-1506	V_2O_5	-1419	-1551
Cr_2O_3	-1054	-1136	PbO	-189	-218	WO_3	-764	-842
Cs_2O	-297	-332	PbO_2	-217	-276	W_2O_5	-1284	-1413
Cs_2O_3	-360	-465	Rb_2O	-291	-333	Y_2O_3	-1817	-1905
CuO	-127	-156	Rb_2O_3	-387	-488	Yb_2O_3	-1727	-1815
Cu_2O	-147	-169	Sb_2O_5	-844	-987	ZnO	-321	-350
FeO	-250	-271	Sc_2O_3	-1819	-1909	ZrO_2	-1040	-1099

Table 2 - Experimental and calculated data for ΔG^{o}_{exp}, ΔG^{o}_{cal}, ΔH^{o}_{exp}, ΔH^{o}_{cal} with coefficients $C_G = \Delta G^{o}_{exp}/\Delta G^{o}_{cal}$ and $C_H = \Delta H^{o}_{exp}/\Delta H^{o}_{cal}$ respectively

a. Ternary oxides

Compound	ΔG^{o}_{exp} [kJ/mol]	ΔG^{o}_{cal} [kJ/mol]	C_G	ΔH^{o}_{exp} [kJ/mol]	ΔH^{o}_{cal} [kJ/mol]	C_H
$AgMoO_4$	-822	-659	1.25			
Ag_2CrO_4				-731	-620	1.18
Ag_2MoO_4	-749	-681	1.10	-839	-778	1.08
Ag_2WO_4	-852	-775	1.10	-925	-873	1.06
Al_2SiO_5	-2441	-2431	1.00	-2589	-2580	1.00
$Al_2Si_2O_7$	-3143	-3343	0.94	-3346	-3547	0.94

$Al_6Si_2O_{13}$	-6434	-6381	1.01	-6815	-6772	1.01
$BaMoO_4$	-1442	-1191	1.21	-1548	-1296	1.19
$BaWO_4$	-1546	-1285	1.20	-1681	-1391	1.21
$BaSiO_3$	-1537	-1374	1.12	-1619	-1458	1.11
$BaSi_2O_5$	-2403	-2198	1.09	-2543	-2333	1.09
Ba_2SiO_3	-1969	-1649	1.19	-2079	-1750	1.19
Ba_2SiO_4	-2160	-1924	1.12	-2279	-2041	1.12
$Ba_2Si_3O_8$	-3948	-3572	1.10	-4176	-3791	1.10
Ba_3SiO_5	-2858	-2473	1.16	-3002	-2624	1.14
$BeAl_2O_4$	-2178	-2155	1.01	-2300	-2277	1.01
$BeSiO_3$	-1454	-1430	1.02	-1540	-1515	1.02
Be_2SiO_4	-2038	-2002	1.02	-2153	-2121	1.01
$CaFe_2O_4$	-1413	-1347	1.05	-1520	-1459	1.04
$Ca_2Fe_2O_5$	-2000	-1732	1.15	-2134	-1876	1.14
$CaMoO_4$	-1440	-1274	1.13	-1547	-1382	1.12
$CaSiO_3$	-1547	-1457	1.06	-1632	-1544	1.06
Ca_2SiO_4	-2196	-2040	1.08	-2312	-2162	1.07
Ca_3SiO_5	-2785	-2623	1.06	-2931	-2779	1.05
$Ca_3Si_2O_7$	-3759	-3497	1.07	-3960	-3706	1.07
$CaWO_4$	-1538	-1368	1.12	-1643	-1477	1.11
$CdSiO_3$	-1104	-1081	1.02	-1188	-1166	1.02
$FeAl_2O_4$	-1864	-1828	1.02	-1979	-1942	1.02
$FeCr_2O_4$	-1358	-1304	1.04	-1459	-1407	1.04
$FeMoO_4$	-977	-920	1.06	-1076	-1018	1.06
$FeSiO_3$	-1119	-1103	1.01	-1193	-1180	1.01
Fe_2SiO_4	-1375	-1544	0.89	-1475	-1652	0.89
$FeTiO_3$	-1159	-1137	1.02	-1236	-1211	1.02
$FeWO_4$	-1061	-1014	1.05	-1161	-1113	1.04
K_2SiO_3	-1465	-1173	1.25	-1553	-1271	1.22
$K_2Si_2O_5$	-2335	-1759	1.33	-2483	-1906	1.30
$K_2Si_4O_9$	-4085	-2932	**1.39**	-4330	-3177	**1.36**
$LiAlO_2$	-1128	-1069	1.05	-1190	-1134	1.05
Li_2SiO_3	-1553	-1414	1.10	-1640	-1507	1.09
$Li_2Si_2O_5$	-2396	-2121	1.13	-2540	-2260	1.12
$MgAl_2O_4$	-2179	-2147	1.01	-2304	-2272	1.01
$MgCr_2O_4$	-1669	-1623	1.03	-1773	-1737	1.02
$MgFe_2O_4$	-1326	-1312	1.01	-1437	-1425	1.01
$MgSiO_3$	-1461	-1422	1.03	-1549	-1510	1.02
Mg_2SiO_4	-2055	-1991	1.03	-2175	-2114	1.03
$MgTiO_3$	-1484	-1456	1.02	-1572	-1541	1.02
$MnSiO_3$	-1241	-1216	1.02	-1320	-1294	1.02
Mn_2SiO_4	-1631	-1702	0.96	-1729	-1812	0.95
$MnWO_4$	-1204	-1127	1.07	-1305	-1227	1.06
Na_2SiO_3	-1468	-1230	1.19	-1560	-1325	1.18
Na_2UO_4	-1773	-1523	1.16	-1959	-1639	1.19
$NiAl_2O_4$	-1819	-1790	1.02	-1928	-1911	1.01
$NiFe_2O_4$	-972	-955	1.02	-1080	-1064	1.01
$NiSiO_3$	-1128	-1065	1.06			
Ni_2SiO_4	-1294	-1491	0.87	-1408	-1609	0.87
$PbMoO_4$	-956	-859	1.11	-1071	-965	1.11
$PbSiO_3$	-1061	-1042	1.02	-1134	-1129	1.00
Pb_2SiO_4	-1253	-1459	**0.86**	-1336	-1578	**0.85**
$PbWO_4$	-1020	-953	1.07	-1122	-1060	1.06

$SrSiO_3$	-1560	-1417	1.10	-1634	-1503	1.09
Sr_2SiO_4	-2212	-1984	1.11	-2313	-2104	1.10
Sr_3SiO_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
$ZnAl_2O_4$				-2065	-2021	1.02
$ZnSiO_3$	-1175	-1174	1.00	-1265	-1259	1.00
Zn_2SiO_4	-1525	-1644	0.93	-1638	-1763	0.93
Zn_2TiO_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	ΔG^o_{exp} [kJ/mol]	ΔG^o_{cal}	C_G	ΔH^o_{exp} [kJ/mol]	ΔH^o_{cal}	C_H
$CaAl_2SiO_6$	-3122	-3035	1.03	-3293	-3215	1.02
$CaAl_2Si_2O_8$	-3999	-3945	1.01	-4226	-4179	1.01
$Ca_2Al_2SiO_7$	-3791	-3642	1.04	-3989	-3858	1.03
$Ca_3Al_2Si_3O_{12}$	-6277	-6070	1.03	-6639	-6430	1.03
$CaFeSi_2O_6$	-2676	-2438	1.10	-2840	-2593	1.09
$Ca_3Fe_2Si_3O_{12}$	-5416	-4400	**1.23**	-5760	-4736	**1.22**
$CaMgSiO_4$	-2143	-2026	1.06	-2262	-2145	1.05
$CaMgSi_2O_6$	-3032	-2894	1.05	-3206	-3064	1.05
$Ca_2MgSi_2O_7$	-3678	-3473	1.06	-3875	-3677	1.05
$CaTiSiO_5$	-2455	-2344	1.05	-2590	-2484	1.04
$Fe_2Al_4Si_5O_{18}$	-7961	-7775	1.02	-8450	-8268	1.02
$Fe_3Al_2Si_3O_{12}$	-4970	-5362	**0.93**	-5302	-5702	**0.93**
$FeMgSi_2O_6$	-2593	-2388	1.08	-2756	-2544	1.08
$KAlSiO_4$	-2000	-1751	1.14	-2115	-1872	1.13
$KAlSi_2O_6$	-2866	-2501	1.14	-3028	-2674	1.13
$KAlSi_3O_8$	-3729	-3251	1.15	-3960	-3477	1.14
$LiAlSiO_4$	-2007	-1904	1.05	-2121	-2022	1.05
$LiAlSi_2O_6$	-2868	-2720	1.05	-3038	-2889	1.05
$Mg_2Al_4SiO_{10}$	-4982	-5100	0.98	-5278	-5408	0.97
$Mg_2Al_4Si_5O_{18}$	-8666	-8700	1.00	-9161	-9225	0.99
$Mg_3Al_2Si_3O_{12}$	-5949	-6000	0.99	-6275	-6362	0.99
$NaAlSiO_4$	-1970	-1787	1.10	-2085	-1906	1.09
$NaAlSi_2O_6$	-2833	-2553	1.11	-3023	-2724	1.11
$NaAlSi_3O_8$	-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 ΔG°_{emp} and ΔH°_{emp} for ternary oxides

Compound	ΔG°_{emp} [kJ/mol]	ΔH°_{emp}	Compound	ΔG°_{emp} [kJ/mol]	ΔH°_{emp}	Compound	ΔG°_{emp} [kJ/mol]	ΔH°_{emp}
Al_2ZnO_4	-2024	-2154	**$LaVO_4$**	-1676	-1798	$Pb_3V_2O_8$	-2476	-2723
$Ba_2Fe_2O_5$	-1732	-1881	$Li_2Ge_7O_{15}$	-4515	-4932	$SbFeO_4$	-845	-964
$BaTiO_3$	-1501	-1587	Li_2SiO_3	-1507	-1606	$Sc_2Si_2O_7$	-3916	-4130
$BaSi_2O_5$	-2343	-2486	$Li_2Si_2O_5$	-2260	-2409	$ScTaO_4$	-1995	-2113
$BaZrO_3$	-1664	-1756	Li_4SiO_4	-2260	-2409	$SnPb_2O_4$	-1056	-1193
$Bi_4Si_3O_{12}$	-3409	-3756	Li_2WO_4	-1412	-1535	$Sn_2Ta_2O_7$	-2843	-3053
$Bi_2Sn_2O_7$	-1485	-1693	$Mg_2B_2O_5$	-2412	-2564	$SrAl_{12}O_{19}$	-10436	-11035
$BiVO_4$	-1019	-1133	$Mg_3B_2O_6$	-2948	-3133	$SrFe_{12}O_{19}$	-6368	-6908
CaB_2O_4	-1913	-2030	$MgGeO_3$	-1137	-1236	SrB_2O_4	-1870	-1987
$CaGeO_3$	-1174	-1273	Mg_2GeO_4	-1592	-1731	$SrTiO_3$	-1546	-1635
Ca_2GeO_4	-1644	-1782	$MgNb_2O_6$	-2487	-2663	$SrZrO_3$	-1709	-1804
$CaMn_2O_4$	-1586	-1701	$MgSb_2O_6$	-1506	-1692	$ThSiO_4$	-2154	-2275
$Ca_2Ta_2O_7$	-3295	-3507	$MgTi_2O_5$	-2483	-2628	$ThTi_2O_6$	-3285	-3463
$CeAsO_4$	-1325	-1447	Mg_2TiO_4	-2172	-2299	$TiBO_3$	-1398	-1487
$CeVO_4$	-1666	-1783	$MgWO_4$	-1421	-1538	Ti_2MgO_4	-2134	-2262
$Co_2B_2O_5$	-1924	-2063	$MnGeO_3$	-918	-1006	UMo_2O_8	-2851	-3068
$Co_3B_2O_6$	-2351	-2523	Mn_2GeO_4	-1284	-1409	UTe_3O_8	-2775	-2999
$CoGeO_3$	-758	-847	$MnNb_2O_6$	-2268	-2433	**UTi_2O_6**	-3067	-3237
Co_2SiO_4	-1590	-1708	$MnSb_2O_6$	-1286	-1462	VBO_3	-1241	-1330
$CoWO_4$	-1041	-1149	$Mn_6Sb_2O_{15}$ [5]	-3412	-3737	V_2FeO_4	-1479	-1596
Cr_2CuO_4	-1259	-1377	Mn_7SiO_{12} [6]	-4476	-4807	**$Y_3Al_5O_{12}$**	-7237	-7623
Cr_2MnO_4	-1510	-1621	$MnTa_2O_6$	-2440	-2604	$YAsO_4$	-1383	-1506
Cr_2NiO_4	-1349	-1466	$MnTiO_3$	-1332	-1412	YBO_3	-1603	-1691
$CuAs_2O_4$	-753	-869	Mn_2ZnO_4	-1284	-1397	$YNbO_4$	-1909	-2026
$CuFeO_2$ [1]	-402	-455	Na_2GeO_3	-932	-1039	$Y_2Si_2O_7$	-3912	-4123
$CuFeO_2$ [2]	-474	-529	$NaNbO_3$	-1141	-1233	$YTaO_4$	-1994	-2111
Fe_3BO_5 [3]	-1746	-1891	$Na_2Si_2O_5$	-1966	-2118	$ZnCr_2O_4$	-1465	-1584
$FeGeO_3$	-797	-885	$NaTaO_3$	-1227	-1318	$ZnFe_2O_4$	-1134	-1251
Fe_2MnO_4	-1179	-1288	$Na_2U_2O_7$	-2550	-2745	Zn_2GeO_4	-1222	-1357
$FeNbO_4$	-1336	-1450	$NiAs_2O_4$	-844	-958	$ZnNb_2O_6$	-2223	-2396
$FeNb_2O_6$	-2147	-2312	$NiWO_4$	-1040	-1153	$ZnSb_2O_6$	-1242	-1425
$FeSb_2O_6$	-1166	-1341	$PbCu_6O_8$	-1100	-1381	$ZnTa_2O_6$	-2395	-2566
$Fe_5Si_3O_{12}$ [4]	-3935	-4272	$PbSeO_3$	-386	-474	$ZrTiO_4$	-2054	-2173
Fe_2ZnO_4	-1134	-1251	$PbSeO_4$	-416	-536	$Zr_5Ti_7O_{24}$	-12323	-13039
Hg_2TeO_4	-489	-615	$PbTiO_3$	-1147	-1234	ZrV_2O_7	-2621	-2824
K_2CrO_4		-1014	$Pb_2V_2O_7$ [7]	-2094	-2304	$ZnWO_4$	-1156	-1270
			$Pb_2V_2O_7$ [8]	-1985	-2203	ZrW_2O_8	-3021	-3251

[1] $Cu^{2+}Fe^{2+}O_2$ [2] $Cu^{1+}Fe^{3+}O_2$ [3] $Fe^{2+}{}_2Fe^{3+}BO_5$ [4] $Fe^{2+}{}_3Fe^{3+}{}_2Si_3O_{12}$ [5] $Mn^{2+}{}_2Mn^{4+}{}_4Sb_2O_{15}$ [6] $Mn^{2+}{}_4Mn^{4+}{}_3SiO_{12}$ [7] $Pb^{2+}{}_2V^{5+}{}_2O_7$ [8] $Pb^{4+}{}_2V^{3+}{}_2O_7$

Table 4 - Empirical data of ΔG^{o}_{emp} and ΔH^{o}_{emp} for quaternary oxides

Compound	ΔG^{o}_{emp} [kJ/mol]	ΔH^{o}_{emp}	Compound	ΔG^{o}_{emp} [kJ/mol]	ΔH^{o}_{emp}	Compound	ΔG^{o}_{emp} [kJ/mol]	ΔH^{o}_{emp}
$Al_{16}B_6Si_2O_{37}$	-18113	-19254	$Ca_3Mn_2Si_4O_{14}$	-5738	-6140	$LaBSiO_5$	-2473	-2625
Al_4MgBeO_8	-4516	-4772	$Ca_2MnSi_2O_8$	-3325	-3575	$LiAlSiO_4$	-2029	-2155
$Al_2Be_3Si_6O_{18}$	-9297	-9847	$CaNiSi_2O_6$	-2541	-2717	$LiAlSi_2O_6$	-2899	-3079
$BaAl_2Ge_2O_8$	-3598	-3851	**$CaSnB_2O_6$**	-2466	-2650	$LiAlSi_4O_{10}$	-4638	-4926
$BaAl_2Si_2O_8$	-4090	-4336	**$CaSnSiO_5$**	-2106	-2265	Li_2BeSiO_4	-2122	-2252
$BaBe_2Si_2O_7$	-3565	-3771	$Ca_3Ti_2Si_3O_{12}$	-6160	-6533	$LiFeSi_2O_6$	-2090	-2258
$BaCa_2Si_3O_9$	-4518	-4780	$CaTiZr_3O_9$	-4720	-4987	$LiSbWO_6$	-1486	-1663
$BaCuSi_4O_{10}$	-3657	-3932	$Ca_3V_2Si_3O_{12}$	-5531	-5907	$Li_3ScMo_3O_{12}$	-5147	-5492
$BaFeSi_4O_{10}$	-3956	-4212	$CaZn_2Ti_8O_{19}$	-8277	-8793	$LiScSiO_4$	-2192	-2317
$BaSnSi_3O_9$	-3531	-3803	$Ca_2ZnSi_2O_7$	-3248	-3461	$LiScSi_2O_6$	-3132	-3309
$BaTiGe_3O_9$	-3554	-3820	$CaZrTi_2O_7$	-3709	-3919	Mg_2AlBO_5	-2668	-2831
$BaTiSi_3O_9$	-4217	-4472	$CaYAl_3O_7$	-4262	-4488	$MgAl_2SiO_6$	-3197	-3390
$Ba_2TiSi_2O_8$	-3916	-4153	$Cd_3Al_2Si_3O_{12}$	-5668	-6047	$Mg_2Al_4SiO_{10}$	-5436	-5764
$BeMg_2Al_6O_{12}$	-6774	-7157	$Cd_3V_2Si_3O_{12}$	-4730	-5101	$Mg_2Al_4Si_5O_{18}$	-9272	-9832
$BeMg_3Al_8O_{16}$	-9033	-9543	$CeBSiO_5$	-2460	-2607	$Mg_2Al_4Si_{11}O_{30}$	-15028	-15935
$Ca_3Al_2Si_3O_{12}$	-6469	-6853	$CeNbTiO_6$	-2787	-2963	$Mg_3Al_2Si_3O_{12}$	-6395	-6781
$Ca_3Al_2Si_{15}O_{36}$	-18114	-19189	$Co_3Al_2Si_3O_{12}$	-5636	-6003	$Mg_3Cr_2Si_3O_{12}$	-5278	-5640
$CaB_2Si_2O_8$	-3668	-3899	$CsFeSi_2O_6$	-1834	-2000	**Mg_2FeBO_5**	-2000	-2254
$Ca_2BeSi_2O_7$	-3716	-3928	$Cs_3Mn_3V_4O_{16}$	-4803	-5254	$Mg_3Fe_2GeO_8$	-2701	-2961
$CaBi_2Nb_2O_9$	-3051	-3312	$Cs_3ScSi_8O_{19}$	-8917	-9461	$MgFeSiO_4$	-1782	-1898
$Ca_3Cr_2Ge_3O_{12}$	-4596	-4967	$CuZn_2As_2O_8$	-1545	-1794	**$Mg_3Fe_2Si_3O_{12}$**	-4615	-4975
$Ca_3Cr_2Si_3O_{12}$	-5352	-5713	$Fe_2Al_4Si_5O_{18}$	-8286	-8812	Mg_2MnBO_5	-2113	-2264
$CaCuSi_4O_{10}$	-3859	-4142	$Fe_3Al_2Si_3O_{12}$	-5715	-6077	$MgScBO_4$	-2225	-2350
$CaFeSiO_4$	-1819	-1934	$Fe_2Ba_3Ge_3O_{12}$	-3756	-4118	$MnAl_2Si_2O_8$	-3871	-4107
$CaFeSi_2O_6$	-2599	-2764	$FeCoBO_4$	-1334	-1448	$Mn_2Al_4Si_5O_{18}$	-8636	-9164
$Ca_2Fe_3Si_3O_{12}$ [i]	-4352	-4684	$Fe_3Cr_2Si_3O_{12}$	-4598	-4937	$Mn_3Al_2Si_3O_{12}$	-5956	-6320
$CaK_2As_2O_7$	-1815	-2044	$Fe_2MgTi_3O_{10}$	-3749	-4033	$Mn_3Cr_2Si_3O_{12}$	-4839	-5180
$CaLa_4Si_3O_{13}$	-7124	-7538	$KAlGeO_4$	-1625	-1757	$Mn_3Fe_2Si_3O_{12}$	-4176	-4515
$CaMgAl_{14}O_{23}$	-12705	-13426	$KAlTi_3O_8$	-3507	-3744	$NaBSi_3O_8$	-3049	-3269
$CaMg_2Al_{16}O_{27}$	-14986	-15836	$KFeSiO_4$	-1299	-1421	$NaCrSi_2O_6$	-2213	-2384
$CaMgGeO_4$	-1781	-1913	$KFeSi_2O_6$	-1857	-2029	$NaFeGe_2O_6$	-1568	-1742
$Ca_3MgSi_2O_8$	-4319	-4572	$KFeSi_3O_8$	-2413	-2639	$NaFeSi_2O_6$	-1912	-2082
$CaMnSiO_4$	-1940	-2056	$K_2TiSi_4O_{11}$	-4391	-4713	$NaFe_6Si_6O_{20}$ [ii]	-6014	-6547
$CaMnSi_2O_6$	-2771	-2937	$K_2ZrSi_3O_9$	-3931	-4210	$Na_2FeSi_2O_6$	-2169	-2338
$CaMn_4Si_5O_{15}$	-6928	-7342	$K_2ZrSi_6O_{15}$	-6289	-6736	$NaLa_9Ge_6O_{26}$	-10584	-11390
$Na_2Mg_2Si_2O_7$	-3115	-3336	$Na_2ZrSi_2O_7$	-3226	-3360	$Rb_2ZnSi_5O_{12}$	-3903	-4242
$NaMnSi_2O_6$	-2048	-2436	$Ni_3Al_2SiO_8$	-3943	-4208	$Sc_2Be_3Si_6O_{18}$	-10042	-13229
$Na_3Mn_5Si_8O_{24}$ [iii]	-8122	-8759	$PbAl_2Si_2O_8$	-3630	-3876	$SrAl_2Si_2O_8$	-4149	-4397
$NaNbAl_2O_6$	-2643	-2832	$Pb_3BiAs_3O_{12}$	-2114	-2479	$SrCuSi_4O_{10}$	-3761	-4041
$NaSbBe_4O_7$	-2076	-2319	$Pb_3BiV_3O_{12}$	-3041	-3390	$Sr_2V_2Si_4O_{14}$ [iv]	-5658	-5904
$NaScSi_2O_6$	-2954	-3133	$PbCu_2Se_3O_9$	-1117	-1373	$YAl_3B_4O_{12}$	-6517	-6886
$Na_2TiSi_2O_7$	-3009	-3219	$Pb_2Fe_2Si_2O_9$	-2853	-3118	$YNbTiO_6$	-2857	-3033
$Na_2TiSi_4O_{11}$	-4512	-4828	$Pb_2Mn_2Si_2O_9$	-3079	-3338	$Y_2SiBe_2O_7$	-4152	-4374
$Na_2Ti_2Si_2O_9$	-3760	-4023	$Pb_8MnSi_6O_{21}$	-7701	-8288	**$YTiTaO_6$**	-2961	-3135
$Na_2ZrSi_4O_{11}$	-4839	-5167	$PbZnSiO_4$	-1453	-1574	$ZrK_2Si_3O_9$	-3931	-4210

i $Ca_2Fe^{2+}Fe^{3+}{}_2Si_3O_{12}$; ii $NaFe^{2+}{}_3Fe^{3+}{}_3Si_6O_{20}$; iii $Na_3Mn^{3+}{}_3Mn^{2+}{}_2Si_8O_{24}$; iv $Sr^{2+}Sr^{4+}V^{3+}{}_2Si_4O_{14}$

Table 5 - Empirical data of ΔG^{o}_{emp} and ΔH^{o}_{emp} for quinary oxides

Compound	ΔG^{o}_{emp} [kJ/mol]	ΔH^{o}_{emp}	Compound	ΔG^{o}_{emp} [kJ/mol]	ΔH^{o}_{emp}
$BaFe_2TiSi_2O_9$	-4014	-4266	$Ca_3Zr_2Al_2SiO_{12}$	-6681	-7074
$BaMg_2Al_6Si_9O_{30}$	-15011	-15902	$Ca_3Zr_2Fe_2SiO_{12}$	-5313	-5685
$BaNa_2Al_4Si_4O_{16}$	-7369	-7847	$KNa_3Al_4Si_4O_{16}$	-6668	-7158
$BaSr_2Mn_2Si_4O_{14}$	-5765	-6155	$KNa_3Mg_4Si_{12}O_{30}$	-10266	-11084
$CaAlFeSiO_6$	-2685	-2870	$Mg_2Al_{14}B_4Si_4O_{37}$	-18164	-19292
$CaCrAlSiO_6$	-2905	-3092	$Mg_3Al_4Si_3BeO_{16}$	-8577	-9082
$Ca_2FeB_2Si_2O_{10}$	-4375	-4657	$MgCrAlSiO_6$	-2881	-3067
$Ca_6Mg_5MnB_{12}O_{30}$	-14268	-15126	**$NaMg_2CrSi_3O_{10}$**	-3976	-4267
$CaMn_2Be_3Si_3O_{12}$	-5961	-6304	**$Na_2BaTi_2Si_4O_{14}$**	-5879	-6271
$CaNa_2Al_4Si_4O_{16}$	-7552	-8037	$Na_2Fe_5TiSi_6O_{20}$	-7797	-8354
$Ca_2NaMg_2As_3O_{12}$	-3546	-3618	$PbCa_3Zn_4Si_4O_{16}$	-6522	-7003
$Ca_3TiFeSi_3O_{12}$	-5529	-5872	$SrMg_2Al_6Si_9O_{30}$	-15194	-16093
$Ca_3Ti_2Fe_2SiO_{12}$	-5061	-5424	$Y_2FeBe_2Si_2O_{10}$	-5280	-5573
$CaZrBAl_9O_{18}$	-9407	-9965			

Table 6 - Empirical data of ΔG^{o}_{emp} and ΔH^{o}_{emp} for senary oxides

Compound	ΔG^{o}_{emp} [kJ/mol]	ΔH^{o}_{emp}
$CaMgFe_2Al_2SiO_{10}$	-4633	-4945
$CaYFeBe_2Si_2O_{10}$	-4896	-5200
$Na_4BaTi_2B_2Si_{10}O_{30}$	-12497	-13330
$Na_3Mg_3FeTiSi_8O_{24}$	-9136	-9832

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4. References

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