# OXIDE COMPOUNDS LIKE SOLID SOLUTIONS

## APPLICATION TO THE CaO-$Al_2O_3$ AND CaO-$SiO_2$ SYSTEMS

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*A concept of the excess Gibbs energy is adopted for calculation of the Gibbs free energy of oxide compounds. A suitable equation for calculation of the excess Gibbs free energy (as a function of temperature and composition) was suggested. The temperature influence was taken into account through two temperature dependent parameters (A(T) and B(T)) while the composition was represented by total number of constitutive oxides ($n_{tot}$). The parameters were defined as adequate temperature functions, for the CaO-$Al_2O_3$ and CaO-$SiO_2$ systems. This was accomplished by processing the data of following compounds: CaO·$Al_2O_3$, CaO·2$Al_2O_3$, 3CaO·$Al_2O_3$, CaO·6$Al_2O_3$, CaO·$SiO_2$, 2CaO·$SiO_2$, 3CaO·$SiO_2$ and 3CaO·2$SiO_2$. Application of the suggested method to the chosen systems enabled estimation of Gibbs free energy values with relative errors less than 1 % (absolute errors between 0.03 and 30 kJ mol$^{-1}$).*

## INTRODUCTION

Lack of thermodynamic data (especially lack of Gibbs free energy values) has inspired number of scientists to suggest various methods that enable estimation of unknown thermodynamic parameters from known thermodynamic parameters. Such a method, introduced by Fyfe, Turner and Verhoogen [1], concerns oxide systems. They assumed that any stable oxide compound (e.g. CaO·6$Al_2O_3$ ≡ $CA_6$) corresponds to an ideal solid solution formed by components - constitutive oxides (e.g. CaO ≡ C and $Al_2O_3$ ≡ A). Therefore, Gibbs free energy of one compound can be expressed as linear combination of Gibbs free energies of constitutive oxides:

$$G^{id} = \sum_{i=1}^{n_{tot}} n_i G_i + \Delta G^{id}_{mix} = n_{tot} [\sum_{i=1}^{n_{tot}} x_i G_i + RT \sum_{i=1}^{n_{tot}} x_i \ln x_i]$$

(J mol$^{-1}$ of oxide compound) , (1)

where $n_{tot}$ represents total number of oxides in a compound, $n_i$ corresponds to the number of $i$-th oxide, while $x_i$ denotes mole fraction of $i$-th oxide. As for Gibbs energy, $G^{id}$ is Gibbs free energy of a compound treated like ideal solid solution, while $\Delta G^{id}_{mix}$ denotes Gibbs free energy change due to ideal mixing of particular oxides, which is, in fact, a consequence of entropy change due to mixing. Applied to the chosen example ($CA_6$ compound), equation (1) gives:

$$G^{id}_{CA6} = 7\left(\frac{1}{7}G_C + \frac{6}{7}G_A\right) + \\ + 7RT\left(\frac{1}{7}\ln\frac{1}{7} + \frac{6}{7}\ln\frac{6}{7}\right) . \qquad (2)$$

Obviously, approximation (1) fulfils general condition that any stable compound has to have Gibbs free energy value lower than an ordinary sum of Gibbs free energies of particular oxides. The difference is included in the $\Delta G^{id}_{mix}$ term. The precision of an estimation of Gibbs free energy of one compound (equation (1)) is affected by similarity among crystal lattices of compound and its constitutive oxides. An example, where the model (1) was successfully employed, can be found in the reference [2].

Application of solid solution concept was extended to the sulphosalts, when Craig and Barton [3] introduced their "sulphide sum" method. However, they improved ideal mixing model with one correction. It concerns the $\Delta G^{id}_{mix}$ term, which was modified in a way:

$$\Delta G_{mix} = (1.2 \pm 0.8)\, \Delta G^{id}_{mix} = \\ = (1.2 \pm 0.8)\, n_{tot} RT \sum_{i=1}^{n_{tot}} x_i \ln x_i \ . \qquad (3)$$

The correction (1.2 ± 0.8) was suggested after taking into account investigations on sulphosalt ore minerals, conducted by Craig and Lee [4]. The modification (2) was successfully applied to thermodynamic analysis of chemical processes on natural minerals [5, 6].

Considering experimentally obtained results, it can be stated that the idealisation (1) gives rather approximate values for the Gibbs free energy. Although the relative error of such an assumption does not exceed 20 %, the absolute error is still high (it can reach a few hundreds of kJ mol$^{-1}$). Obviously, a correction should be introduced. Here, an application of excess Gibbs free energy concept is suggested.

## THEORETICAL PART

### Excess Gibbs free energy concept

According to the definition, excess Gibbs free energy $G^E$ expresses the difference between real $G$ and the ideal $G^{id}$ Gibbs free energy of solution:

$$G^E = G - G^{id} \ . \tag{4}$$

Combining with equation (1), it follows:

$$G^E = G - n_{tot}\left[\sum_{i=1}^{n_{tot}} x_i G_i - RT\sum_{i=1}^{n_{tot}} x_i \ln x_i\right] \ , \tag{5}$$

which leads to the following important equation:

$$G^E = \Delta G_{mix} - n_{tot} \ RT\sum_{i=1}^{n_{tot}} x_i \ln x_i \ . \tag{6}$$

Dividing of equation (6) by the term $RT$ and recalling that:

$$\frac{\Delta G_{mix}}{RT} = n_{tot} \sum_{i=1}^{n_{tot}} x_i \ln a_i , \tag{7}$$

one obtains:

$$\frac{G^E}{RT} = n_{tot} \sum_{i=1}^{n_{tot}} x_i \ln \gamma_i \ , \tag{8}$$

where $\gamma_i = a_i / x_i$ is well-known thermodynamic parameter- activity coefficient. In this way, important dimensionless relation is obtained. The remaining problem is to find an equation, suitable in form, for representation of $G^E / RT$ as a function of temperature and composition. Number of authors (Margules, van Laar, Wilson and others [7]) introduced different models, which all have following general form:

$$\frac{G^E}{RT} = g(x_1, x_2, x_3, \dots x_n) \qquad T = \text{const.} \tag{9}$$

Authors of this paper realized that total number of constitutive oxides represents "composition" influence better than mole fractions of particular oxides. So, $n_{tot}$, instead of $x_1$, $x_2$, ... $x_n$, is adopted and following simple mathematical model is suggested:

$$\frac{G^E}{RT} = A(n_{tot} - 1)^B \ , \tag{10}$$

where $A(T)$ and $B(T)$ are temperature dependent parameters, determined by experimental data. In the case of pure component, equation (10) gives:

$$G^E = 0 \ .$$

## EXPERIMENTAL PART

### Application of excess Gibbs free energy concept

The model (10) will be applied to several compounds, from two systems (C-A and C-S), whose thermodynamic data are given in table 1. As is obvious, four compounds were considered like solid solutions in both systems; the system C-A was represented by the compounds: CA ($n_{tot} = 2$), $CA_2$ ($n_{tot} = 3$), $C_3A$ ($n_{tot} = 4$) and $CA_6$ ($n_{tot} = 7$) while the system C-S consists of CS ($n_{tot} = 2$), $C_2S$ ($n_{tot} = 3$), $C_3S$ ($n_{tot} = 4$) and $C_3S_2$ ($n_{tot} = 5$). The data were taken from the references [8] and [9], where they bring sufficiently precise results when calculating phase diagrams in the C-S-A system. The data from table 1 are therefore supposed to enable good assessment of real Gibbs free energies, for all the chosen oxide compounds, as follows:

$$\begin{aligned} G &= H^0 + \int_{298}^{T} C_p(T)\mathrm{d}T - T\left( S^0 + \int_{298}^{T} \frac{C_p(T)}{T}\,\mathrm{d}T \right) \\ &= H^0 + a(T - 298) - c(T^{-1} - 298^{-1}) + 2f(T^{0.5} - 298^{0.5}) + \\ &+ h\ln(T/298) - TS^0 - aT\ln(T/298) + 0.5cT(T^{-2} - 298^{-2}) + \\ &+ 2fT(T^{-0.5} - 298^{-0.5}) + hT(T^{-1} - 298^{-1}) \end{aligned} \tag{11}$$

In the equation (11), $H^0$ and $S^0$ represent enthalpy and entropy of formation of a compound at 298.15 K and 1 bar, while $a$, $c$, $f$ and $h$ are parameters of a heat capacity ($C_p$) correlation (table 1).

Real Gibbs free energy values calculated from equation (11) are given in tables 2-3 (first column). It is, also, possible to calculate Gibbs free energies ($G^{id}$) by applying the ideal solid solution concept [1], with $G_i$ values of oxides as the components (lime, corundum and β-trydimite, from table 1). These values can be seen in the second column of tables 2-3. The differences between the pairs of $G$ and $G^{id}$ values correspond to $G^E$ values, which will be denoted as "experimental" throughout the text. So called experimental excess Gibbs energies are presented in the third column of tables 2-3. The experimental excess Gibbs energies were correlated by equation (10) for the temperature interval: 298-1500 K, and $A(T)$ and $B(T)$ functions were defined as follows:

for the system C-A:

$$A(T) = -506(\ln T)^{-4.47} \ , \tag{12}$$

$$B(T) = 0.4518 - 5.5\times10^{-4}\ T + 1.3902\times10^{-7}\ T^2 \ , \tag{13}$$

for the system C-S:

$$A(T) = -13220(\ln T)^{-6.77} \ , \tag{14}$$

$$B(T) = 0.7 \ . \tag{15}$$

Table 1. Thermodynamic data for oxides and oxide compounds [8].

| compound (abbreviation) | $n_{tot}$ | enthalpy* | entropy** | | heat capacity*** | | |
|---|---|---|---|---|---|---|---|
| | | (J mol$^{-1}$) | (J mol$^{-1}$ K$^{-1}$) | $a$ | $c$ | $f$ | $h$ |
| lime<br>(C) | 1 | -635990 | -104.5 | 57.1 | -103034 | | -3103.7 |
| corundum<br>(A) | 1 | -1674411 | -313.5 | 152.7 | -852486 | -522.6 | -10068 |
| β-tridymite<br>(S) | 1 | -909466 | -182 | 86.6 | -1495314 | -434.3 | |
| calcium aluminate<br>(CA) | 2 | -2330292 | -393.3 | 220.7 | -1372400 | -1461.3 | |
| calcium dialuminate<br>(CA$_2$) | 3 | -4007413 | -698 | 345.5 | -1199855 | -672.4 | -27883.6 |
| tricalcium aluminate<br>(C$_3$A) | 4 | -3606151 | -589.3 | 304.5 | | | -28244.7 |
| calcium hexaluminate<br>(CA$_6$) | 7 | -10724605 | -1961.8 | 973.4 | -5517950 | -3135.5 | -63511.2 |
| pseudowollastonite<br>(CS) | 2 | -1626056 | -280 | 138.6 | | | -15533.5 |
| α'-larnite<br>(C$_2$S) | 3 | -2309060 | -385 | 252.6 | | -2183 | |
| tricalcium silicate<br>(C$_3$S) | 4 | -2943382 | -491 | 322.7 | | -2409.2 | -3383 |
| rankinite<br>(C$_3$S$_2$) | 5 | -3940436 | -667.4 | 339.5 | -3384403 | -772.2 | -12621.2 |

* Enthalpy of formation from elements at 298.15 K and 1 bar

** Entropy of formation at 298.15 K and 1 bar

*** Heat capacity equation: $C_p = a + cT^{-2} + fT^{-0.5} + hT^{-1}$ (J mol$^{-1}$ K$^{-1}$)

The values of Gibbs energy estimated from (10) with parameters $A(T)$ and $B(T)$ (cf. equations (12-15)), will be denoted as "calculated" ($G^E_{cal}$) throughout the text. These values can be found in the fourth column of tables 2-3.

## DISCUSSION

Suggested model (10) fits the excess Gibbs free energy, for two examined systems, as it can be seen in figure 1, where experimental $G^E$ and calculated $G^E_{cal}$ values are presented comparatively.

Compared with Fyfe's ideal solution model [1], application of the excess Gibbs energy (10) as a correction gives more precise Gibbs free energy value. This statement corresponds to comparative presentation of real $G$, ideal $G^{id}$ and corrected $G_{corr}$ in tables 2-3. It should be emphasised that $G_{corr}$ presents the corrected Gibbs free energy, according to our suggestion:

$$G_{corr} = G^{id} + G^E_{cal} \ , \qquad (16)$$

where $G^E_{cal}$ is estimated by the model (10).

Figure 2 compares relative deviations of ideal and corrected Gibbs free energy values defined as follows:

$$\sigma^{id} = \frac{G - G^{id}}{G} \, 100 \quad \text{and} \quad \sigma_{corr} = \frac{G - G^{corr}}{G} \, 100 \ . \qquad (17)$$

As is obvious, the deviations of ideal Gibbs free energies reach 1.5 % (for the C-A system) and 5.5 % (for the C-S system). However, it is less than 0.2 % (for the C-A system) and less than 1 % (for the C-S system) using the corrected values.

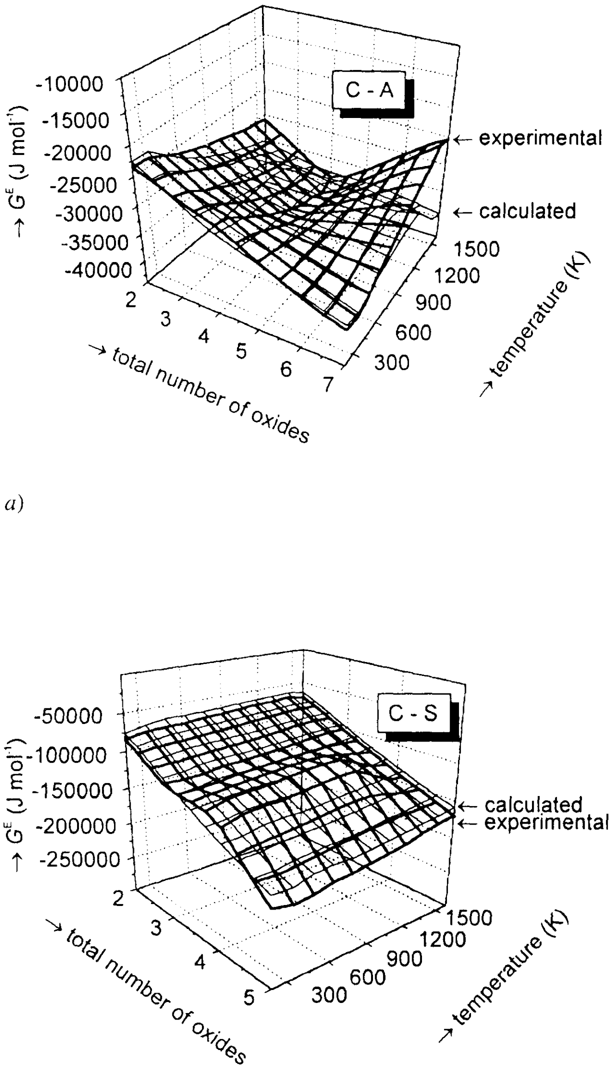
Parameters of the model (10), given by equations (12-15), were determined using experimental values of Gibbs energies for four compounds for each of two systems. However, the model should cover all other compounds from these systems. The C$_{12}$A$_7$ compound is taken as a simple example . Relative deviations from experimental $G$ values [10] were calculated in two ways. The first, the compound was considered like ideal solid solution; the second , the correction suggested here was applied. Although the equation (10) had been extrapolated to very large extent ($n_{tot}$ = 19), it brings the deviations of the Gibbs free energy values being almost twice lower than those of the ideal solution model.

Table 2. Gibbs free energies for the C-A system (J mol$^{-1}$ K$^{-1}$).

| $T$ (K) | system | $G$ | $G^{id}$ | $G^E$ | $G^E_{cal}$ | $G_{corr}$ |
|---|---|---|---|---|---|---|
| 298 | CA | -2213084 | -2190005 | -23079 | -21759 | -2211764 |
| | $CA_2$ | -3799417 | -3772846 | -26572 | -26861 | -3799707 |
| | $C_3A$ | -3430540 | -3402196 | -28344 | -30383 | -3432579 |
| | $C_6A$ | -10139990 | -10101400 | -38588 | -37507 | -10138907 |
| 500 | CA | -2141130 | -2116040 | -25090 | -25170 | -2141210 |
| | $CA_2$ | -3670992 | -3641898 | -29090 | -28970 | -3670869 |
| | $C_3A$ | -3324256 | -3292817 | -31440 | -31454 | -3324271 |
| | $C_6A$ | -9776797 | -9740623 | -36174 | -36204 | -9776827 |
| 800 | CA | -2056203 | -2028854 | -27349 | -29161 | -2058015 |
| | $CA_2$ | -3517527 | -3485540 | -31988 | -31137 | -3516677 |
| | $C_3A$ | -3202729 | -3167448 | -35282 | -32355 | -3199803 |
| | $C_6A$ | -9337346 | -9304755 | -32591 | -34548 | -9339303 |
| 1000 | CA | -2010515 | -1982055 | -28460 | -31194 | -2013249 |
| | $CA_2$ | -3433880 | -3400488 | -33393 | -32066 | -3432554 |
| | $C_3A$ | -3139407 | -3102121 | -37286 | -32586 | -3134708 |
| | $C_6A$ | -9095011 | -9064810 | -30201 | -33497 | -9098307 |
| 1200 | CA | -1971785 | -1942445 | -29340 | -32844 | -1975289 |
| | $CA_2$ | -3362099 | -3327660 | -34440 | -32672 | -3360332 |
| | $C_3A$ | -3087195 | -3048295 | -38901 | -32572 | -3080870 |
| | $C_6A$ | -8885038 | -8857226 | -27812 | -33293 | -8890520 |
| 1500 | CA | -1924584 | -1894246 | -30339 | -34740 | -1928986 |
| | $CA_2$ | -3272952 | -3237525 | -35427 | -36455 | -3273981 |
| | $C_3A$ | -3026102 | -2985413 | -40689 | -37498 | -3022911 |
| | $C_6A$ | -8620757 | -8596528 | -24229 | -39349 | -8635777 |

Table 3. Gibbs free energies for the C-S system (J mol$^{-1}$ K$^{-1}$).

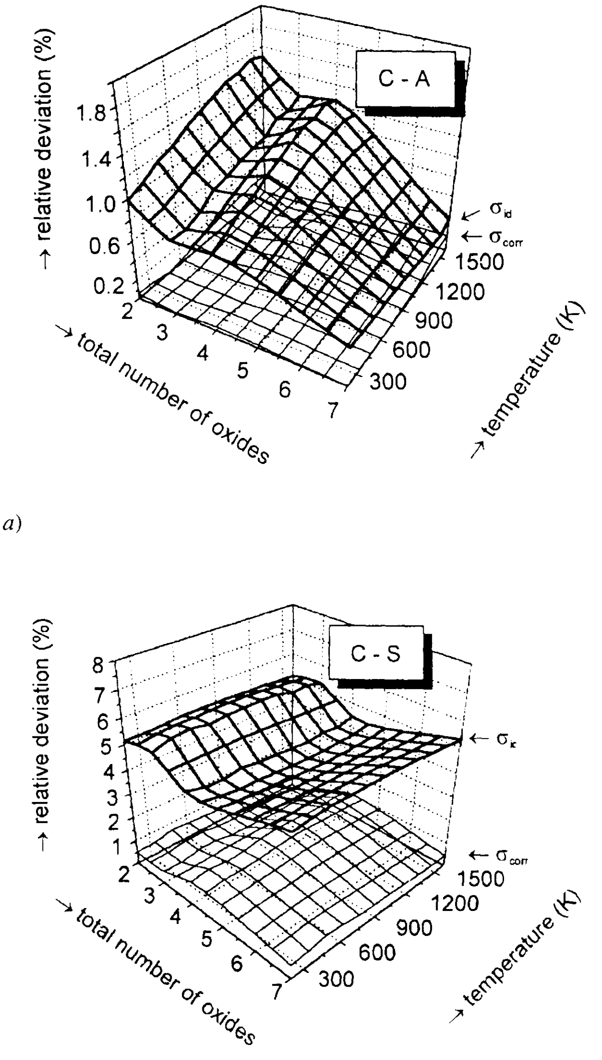
| $T$ (K) | system | $G$ | $G^{id}$ | $G^E$ | $G^E_{cal}$ | $G_{corr}$ |
|---|---|---|---|---|---|---|
| 298 | CS | -1542664 | -1464091 | -78573 | -70741 | -1534832 |
| | $C_2S$ | -2194351 | -2070414 | -123937 | -114919 | -2185333 |
| | $C_3S$ | -2797116 | -2676282 | -120834 | -152636 | -2828918 |
| | $C_3S_2$ | -3741544 | -3534676 | -206868 | -186687 | -3721363 |
| 500 | CS | -1491511 | -1414413 | -77098 | -66317 | -1480730 |
| | $C_2S$ | -2124357 | -2003182 | -121174 | -107732 | -2110915 |
| | $C_3S$ | -2708491 | -2591189 | -117301 | -143090 | -2734280 |
| | $C_3S_2$ | -3620090 | -3417883 | -202207 | -175012 | -3592896 |
| 800 | CS | -1431270 | -1356757 | -74513 | -66770 | -1423397 |
| | $C_2S$ | -2043137 | -1926664 | -116473 | -108257 | -2034921 |
| | $C_3S$ | -2607413 | -2495351 | -112062 | -143786 | -2639138 |
| | $C_3S_2$ | -3478614 | -3283882 | -194732 | -175863 | -3459745 |
| 1000 | CS | -1398922 | -1326292 | -72630 | -64937 | -1391229 |
| | $C_2S$ | -2000449 | -1887088 | -113361 | -105490 | -1992578 |
| | $C_3S$ | -2555294 | -2446358 | -108936 | -140111 | -2586470 |
| | $C_3S_2$ | -3403418 | -3213955 | -189463 | -171368 | -3385323 |
| 1200 | CS | -1371519 | -1300849 | -70670 | -63367 | -1364216 |
| | $C_2S$ | -1965136 | -1854689 | -110447 | -102940 | -1957629 |
| | $C_3S$ | -2512949 | -2406698 | -106250 | -136725 | -2543423 |
| | $C_3S_2$ | -3340250 | -3156229 | -184021 | -167227 | -3323456 |
| 1500 | CS | -1338120 | -1270484 | -67636 | -61371 | -1331855 |
| | $C_2S$ | -1923803 | -1817212 | -106591 | -99698 | -1916910 |
| | $C_3S$ | -2464797 | -2361651 | -103145 | -132419 | -2494070 |
| | $C_3S_2$ | -3264155 | -3088560 | -175595 | -161960 | -3250520 |



*a)*

*b)*

Figure 1. Comparison of calculated and experimental values of Gibbs free energy.
*a)* C-A system; *b)* C-S system



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*b)*

Figure 2. Relative deviations ideal and corrected Gibbs free energy values.
*a)* C-A system; *b)* C-S system

This paper considers two systems: C-A and C-S. However, the same concept can be applied to any other oxide system (such as building ceramics, cement and concrete, glass, etc.). A preliminary consideration was performed on the following systems: $BaO-SiO_2$, $B_2O_3$-CaO, $K_2O-SiO_2$, $Na_2O-SiO_2$, $Li_2O-SiO_2$, at the standard state ($T$ = 298.15 K and $p$ = 1 bar). Relative deviations between ideal solution estimations and experimental Gibbs energies are lower than 5.5 % , while the maximal deviation is 20 %, in the case of $Li_2O-SiO_2$ system. This fact indicates that the Fyfe's model should be corrected. One of the possible ways is suggested in this paper.

## CONCLUSION

Investigations presented in this paper leads to the following conclusions:

Multioxide compounds can be treated like solid solutions with constitutive oxides as components.

Gibbs free energies of the compounds can be estimated by applying ideal solution model, which was suggested by other authors.

More reliable estimation will be achieved by applying the excess Gibbs free energy as a correction, which was suggested by authors of this paper.

A simple mathematical model for correlating of the $G^E/RT$- quantity, in terms of composition of the solution and its temperature, was offered. Instead of mole fractions of particular components (oxides), total number of oxides was suggested.

Applying experimental data to the model, the excess Gibbs free energies for the C-A system and the C-S system were estimated.

When compared with the ideal solution model, the excess Gibbs free energy concept brings higher precision of calculated values.

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# SLOUČENINY OXIDŮ JAKO TUHÉ ROZTOKY

## PŘÍKLAD SYSTÉMŮ $CaO-Al_2O_3$ A $CaO-SiO_2$

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Neznalost hodnoty Gibbsovy volné energie některých sloučenin vedla některé badatele k návrhu způsobů odvozování neznámých termodynamických parametrů ze známých termodynamických hodnot. Například Fyfe, Turner a Verhoogen [1] předpokládali, že Gibbsovu volnou energii oxidické sloučeniny lze vyjádřit jako lineární kombinaci Gibbsových volných energií příslušných konstitučních oxidů:

$$G^{\mathrm{id}} = \sum_{i=1}^{n_{tot}} n_\mathrm{i} G_\mathrm{i} + \Delta G^{\mathrm{id}}_{\mathrm{mix}} = n_{\mathrm{tot}} [\sum_{i=1}^{n_{tot}} x_\mathrm{i} G_\mathrm{i} + RT \sum_{i=1}^{n_{tot}} x_\mathrm{i} \ln x_\mathrm{i}]$$

(J $\mathrm{mol}^{-1}$ kyslíkatých sloučenin) , (1)

kde $G^{\mathrm{id}}_{\mathrm{mix}}$ je změna Gibbsovy volné energie způsobená ideálním smísením příslušných oxidů, zatímco *n* jsou počty molů a *x* jsou molární zlomky příslušných oxidů. Aproximace (1) zřejmě splňuje obecnou podmínku, že totiž jakákoliv stabilní sloučenina musí mít hodnotu Gibbsovy volné energie nižší, než je součet Gibbsových volných energií příslušných oxidů. Příslušný rozdíl je obsažen ve členu $\Delta G^{\mathrm{id}}_{\mathrm{mix}}$. Nakolik správně rovnice (1) stanovuje Gibbsovu volnou energii určité sloučeniny, závisí na podobnosti krystalové mřížky příslušné sloučeniny a krystalových mřížek příslušných oxidů, ze kterých se sloučenina skládá.

Na základě experimentálních výsledků lze konstatovat, že rovnice (1) poskytuje dosti přibližné hodnoty Gibbsovy volné energie. I když relativní chyba takového výpočtu nepřesahuje 20%, absolutní chyba je přesto vysoká (může činit až několik stovek kJ $\mathrm{mol}^{-1}$). Je zřejmě záhodno zavést určitou korekci. V této práci se navrhuje uplatnění koncepce přebytečné Gibbsovy volné energie, která vyjadřuje rozdíl mezi skutečnou a ideální Gibbsovou energií roztoku: $G^{\mathrm{E}} = G - G^{\mathrm{id}}$.

Lze prokázat, že

$$\frac{G^{\mathrm{E}}}{RT} = n_{\mathrm{tot}} \sum_{i=1}^{n_{tot}} x_\mathrm{i} \ln \gamma_\mathrm{i} \ , \tag{8}$$

kde $\gamma_\mathrm{i} = a_\mathrm{i}/x_\mathrm{i}$ je známý termodynamický parametr, koeficient aktivity.

Autoři této práce zvolili následující jednoduchý matematický model pro ověření experimentálních hodnot:

$$\frac{G^{\mathrm{E}}}{RT} = A(n_{\mathrm{tot}} - 1)^{\mathrm{B}} \ , \tag{10}$$

kde *A*(*T*) a *B(T)* jsou teplotně závislé parametry. V případě čisté složky dává rovnice (3) hodnotu $G^{\mathrm{E}} = 0$. Je-li model (3) uplatňován na několik sloučenin, získáme pro systém C-A:

$$A(T) = -506 \ (\ln T)^{-4{,}47} \tag{4}$$

$$B(T) = 0{,}4518 - 5{,}5 \times 10^{-4} \ T + 1{,}3902 \times 10^{-0{,}7} \ \mathrm{T}^2 \tag{5}$$

a pro systém C-S:

$$A(T) = -13220(\ln T) -6.77 \tag{6}$$

$$B(T) = 0{,}7 \ . \tag{7}$$

V porovnání s Fyfeho modelem ideálního roztoku (1) poskytuje korekce pomocí přebytečné Gibbsovy volné energie přesnější hodnoty Gibbsovy volné energie. Tato skutečnost byla v této práci prokázána porovnáním dvou druhů relativních odchylek stanovených Gibbsových volných energií od jejich experimentálních hodnot: i) v případě, kdy byl výpočet proveden podle ideálního modelu (1), a ii) v případě, že byl výpočet proveden na základě koncepce přebytečné Gibbsovy volné energie (3). Parametry dle modelu 3, dané rovnicemi (4) - (7), byly stanoveny na základě experimentálně stanovených hodnot Gibbsovy volné energie čtyř sloučenin obou systémů (C-A a C-S). Daný model však platí pro všechny ostatní sloučeniny těchto systémů. Koncepci přebytečné Gibbsovy volné energie lze teoreticky aplikovat na jakýkoliv oxidický systém významný v oborech stavební keramiky, cementu a betonu, skla, atd. Předběžně byla tato možnost sledována na systémech $BaO-SiO_2$, $B_2O_3-CaO$, $K_2O-SiO_2$, $Na_2O-SiO_2$, $Li_2O-SiO_2$, a to za normálních podmínek ($T = 298{,}15$ K a $p = 1$ bar). Relativní odchylky mezi výpočty dle ideálního roztoku a experimentálně stanovenými hodnotami Gibbsovy volné energie nebyly nižší než 5,5 %, zatímco maximální odchylka činila 20 % v případě systému $Li_2O-SiO_2$. Tato skutečnost svědčí pro nutnost korigovat Fifův model. Jeden z možných způsobů korekce je navržen v této práci.