

Evaluation of Standard Gibbs Potentials for Copper Hydroxosulfate Hydrates from Solutions of Dual Linear Programming Problems

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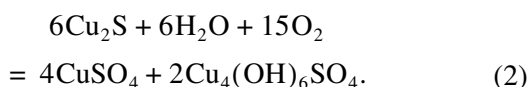
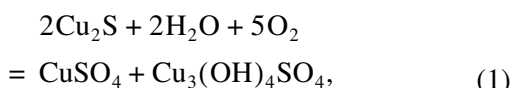
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The study of an oxidation zone at the Udokan deposit has shown that alteration of copper sulfides (chalcopyrite, bornite, and chalcocite) under cryogenic conditions is accompanied by the formation of hydrated complex sulfates (hydroantlerite, hydrobrochantite, udokanite, fibroferrite, K-free jarosite, copper and iron sulfate pentahydrates, and others) [1, 2]. No thermochemical data are available for these minerals. Optimization methods of calculation of geochemical equilibria make it possible to evaluate the thermodynamic functions of compounds [3]. Let us use this possibility to calculate standard Gibbs energy of cryogenic copper hydroxosulfate hydrates [1].

Let us write down two independent chemical reactions in the Cu–S–O–H system:



Calculation of equilibrium compositions x^* in assumption of one-component gas and aqueous phases may be represented as linear programming problems [4]:

$$\text{ming}(x) = \sum_{i=1\dots 5} \Delta_f G_i^0 x_i, \quad Ax = b, \quad x \geq 0, \quad (*)$$

where $\Delta_f G_i^0$ is the standard Gibbs potential of formation of substance i that participates in reactions (1, 2), x_i is its molar quantity, A is the stoichiometric matrix, and b is the vector of material balance.

The direct problem (*) is conjugated with a dual problem [5]:

$$\text{max}d(y) = \sum_{j=1\dots 4} b_j y_j, \quad A'y \leq \Delta_f G^0, \quad (**)$$

where prime designates the index of transposition.

Let us select from problems (**) for reactions (1, 2) a couple of nondegenerate dual solutions $y^* = (y_{\text{H}}^*, y_{\text{S}}^*, y_{\text{O}}^*, y_{\text{Cu}}^*)$:

$$y_1^* = (-45534, -68690, -146114, -8755) \text{ J/mol}$$

and

$$y_2^* = (-46189, -79170, -144804, -3515) \text{ J/mol.}$$

Similarity of the direct and dual problems indicates that components y^* correspond to contributions of chemical elements to Gibbs free energy of the substances that exist at equilibrium in reactions (1, 2). On the basis of this relationship, let us calculate $\Delta_f G^0$ for a number of compounds in the Cu–S–O–H system using formula

$$A'y^* = \Delta_f G^0. \quad (3)$$

The calculation results are presented in the table.

The $\Delta_f G^0$ values taken from literature are given in the upper part of the table. (The range of values published in reference books are shown for some minerals.) The calculated data (3) for reactions (1, 2) are given in the right part of the table. The values used in optimization problems and their equivalents obtained from dual solutions are shown by bold font. Calculations based on (3) for compounds of two elements (sulfides and oxides) yield the greatest relative errors (up to 50% for CuS). However, the error does not exceed 4% for the compounds of three elements (e.g., $\text{Cu}(\text{OH})_2$), <2% for compounds of four elements ($\text{CuSO}_4 \cdot n\text{H}_2\text{O}$), and <1% for copper hydroxosulfates. Thus, we may suppose that errors of the estimates of $\Delta_f G^0$ for copper hydroxosul-

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Values of standard Gibbs potentials of some minerals in the Cu–S–O–H system (after [6–8]) and estimates for reactions (1, 2) (after (3))

| Chemical formula (mineral) | $\Delta_f G^0$, J/mol | | | $\Delta_f G^0$ (after (3)) for reactions (1, 2), J/mol | |
|---|------------------------|-----------------------------|----------------------|---|-----------------|
| | [6] | [7] | [8] | (1) | (2) |
| Cu ₂ S (chalcocite) | -86200 | -86900 -85600 | | -86200 | -86200 |
| CuS (covellite) | -53600 | -49000 -53900 | | -77445 | -82685 |
| Cu ₂ O (cuprite) | -146000 | -146000 -148000 | -168600 -170883 | -163624 | -151834 |
| CuO (tenorite) | -129500 | -129700 -125100 | -129700 -127897 | -154869 | -148319 |
| CuSO ₄ (chalcocyanite) | -661900 | -661700 -662300 | -661700 -662310 | -661900 | -661900 |
| CuSO ₄ · H ₂ O (potevinitite) | -918220 | -917100 -918100 | -918110 -918042 | -899081 | -899081 |
| CuSO ₄ · 3H ₂ O (bonattite) | -1400170 | -1400000 | -1399884 -1399960 | -1373443 | -1373443 |
| CuSO ₄ · 5H ₂ O (chalcantinite) | -1880060 | -1879900 -1879600 | -1879578 -1879796 | -1847805 | -1847805 |
| Cu ₃ (OH) ₄ SO ₄ (antlerite) | | -1446600 -1445600 | | -1446600 | -1432900 |
| Cu ₄ (OH) ₆ SO ₄ (brochantite) | | -1818400 -1817100 | | -1838050 | -1818400 |
| Cu ₄ (OH) ₆ SO ₄ · H ₂ O (posnjakite) | -2044300 | -2044000 | | -2075231 | -2055581 |
| CuOCuSO ₄ (dolerophanite) | -801198 | | | -816769 | -810219 |
| Cu(OH) ₂ (spertiniite) | -372200 | -356900 | -359018 | -392050 | -385500 |
| Cu ₂ SO ₄ | | -652700 | | -670655 | -665415 |
| H ₂ O (liq.) | | | -237181 | -237181 | -237181 |
| Cu ₈ (OH) ₁₀ (SO ₄) ₃ · H ₂ O (udokanite) | | | | -4183131 | -4150381 |
| Cu _{2.72} (OH) _{3.44} SO ₄ · 2.44H ₂ O (cryogenic antlerite) | | | | -1914948 | -1903681 |
| Cu _{2.84} (OH) _{3.87} SO ₄ · 3.16H ₂ O (the same) | | | | -2169177 | -2157000 |
| Cu _{2.91} (OH) _{3.82} SO ₄ · 3.03H ₂ O (the same) | | | | -2129374 | -2116863 |
| Cu _{2.94} (OH) _{3.88} SO ₄ · 3.33H ₂ O (the same) | | | | -2212290 | -2199583 |
| Cu ₁₅ (OH) ₂₂ (SO ₄) ₄ · 6.6H ₂ O (cryogenic brochantite) | | | | -8525544 | -8453495 |
| Cu ₁₅ (OH) ₂₂ (SO ₄) ₄ · 5.24H ₂ O (the same) | | | | -8202978 | -8130928 |
| Cu ₄ (OH) ₆ SO ₄ · 2H ₂ O (langite, wroewolfeite) | | | | -2312412 | -2292762 |
| Cu ₃ (OH) ₄ SO ₄ · 2H ₂ O (ktenasite) | | | | -1920362 | -1907262 |
| CuSO ₄ · 7H ₂ O (boothite) | | | | -2322167 | -2322167 |

fate hydrates and boothite presented in the lower part of the table do not exceed the uncertainty of the respective classes of compounds (i.e., 1 and 2%, respectively).

In order to obtain information on the stability of the considered method, we elaborated an algorithm that computes the interval of variation of dual solutions caused by uncertainty of the input $\Delta_f G^0$ values at arbitrary b values. The program based on this algorithm allows us to choose the most plausible input data for y^* estimates and determine them, for example, from variation ranges of vector components or by comparison of calculations with high-reliable thermochemical data.

The obtained $\Delta_f G^0$ values may be applied to the analysis (at a first approximation) of some geochemical processes with participation of these minerals. For instance, $\Delta G^0 = -2925 \pm 83$ kJ/mol for reaction

Cu_3FeS_4 (bornite) + $18.7\text{H}_2\text{O}$ (ice) + $9.25\text{O}_2 = 3.4\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (chalcantite) + $0.2\text{Cu}_8(\text{OH})_{10}(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ (udokanite) + FeOOH (goethite). This estimate indicates that the reaction can proceed in the cryogenic mineralization zone. Such a process of the formation of

mineral assemblages observed in ores of the Udokan deposit is likely related to the above reaction.

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