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CALCULATION OF EQUILIBRIUM COMPOSITION IN A MULTICOMPONENT HETEROGENEOUS SYSTEM¹

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We present an algorithm for calculation of equilibrium composition in a multicomponent heterogeneous system consisting of a solution and solid phases. The test for equilibrium is minimal Gibbs' free energy for the system as a whole.

The mass balance in the system is given by a system of linear equations

$$\begin{aligned} \nu_{11}n_1 + \nu_{12}n_2 + \dots + \nu_{1k}n_k &= M_1, \\ \nu_{21}n_1 + \nu_{22}n_2 + \dots + \nu_{2k}n_k &= M_2, \\ \dots & \dots \\ \nu_{r1}n_1 + \nu_{r2}n_2 + \dots + \nu_{rk}n_k &= M_r \end{aligned} \quad (1)$$

or, in matrix form, $H\bar{n} = \bar{M}$, where M_i is the number of atoms of the i th chemical element, n_j is number of species of the j th kind, and ν_{ij} is stoichiometric coefficient indicating the number of atoms of the i th element in the j th species.

Let $r = \text{rank } H$. Then the solution of system (1) defines a linear manifold Q of dimension $k - r$ in the space $L(n_1, \dots, n_k)$. Let us analyze the subspace L' of space L that is parallel to Q . Let the basis for this subspace be $\bar{e}_1, \dots, \bar{e}_{k-r}$, which is a fundamental system of solutions of the linear system $H\bar{n} = \bar{0}$. Let n_j in the sys-

tem (1) represent solute species for $1 \leq j \leq p$, n_{p+1} the solvent, and n_j the solid phases for $p+1 < j \leq k$. In constructing the basis for L' , we take as coupled variables n_j only those for which $j \leq p$. This can be done because relation $r \leq p$ is always true. With this choice of coupled variables we have

$$\begin{aligned} \bar{e}_1 &= (\varepsilon_{11}, \dots, \varepsilon_{1p}, 0, 0, \dots, 0) \\ \bar{e}_{p-r} &= (\varepsilon_{p-r+1}, \dots, \varepsilon_{p-rp}, 1, 0, \dots, 0) \\ \dots & \dots \\ \bar{e}_{p-r+1} &= (\varepsilon_{p-r+11}, \dots, \varepsilon_{p-r+1p}, 1, 0, \dots, 0) \end{aligned}$$

which are basis vectors of space L that is the region of homogeneous solution, whereas for $p-r+1 < t \leq k-r$ (i.e., for each solid phase)

$$\bar{e}_t = (\varepsilon_{t1}, \dots, \varepsilon_{tp}, 0, 0, \dots, 0, 1, 0, \dots, 0)$$

is the basis vector of the t -th solid phase.

Let the solution be in equilibrium with the solid phases t_1, \dots, t_s ($nt_i > 0$), $s \geq 0$. Then

$$(\bar{e}_i, \text{grad } G) = 0, \quad i=1, 2, \dots, p-r+1, t_1, t_2, \dots, t_s, \quad (2)$$

These are the conditions for minimization of function G in subspace $L_p \oplus \varepsilon_{t_1} \oplus \dots \oplus \varepsilon_{t_s}$. Let us denote this subspace by L_{p, t_1, \dots, t_s} .

Condition (2) is used to minimize the Gibbs free energy function of the chemical system.

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Table 1

Starting information and results of calculation of system MgO-SiO₂-H₂O
at 25° C and 1 atm
(Composition: 1 mole MgSiO₄ + 1000 g H₂O)

Species	Free energy of formation, cal/mole	Equilibrium composition, mol./1000 g
Aqueous solution		
H ⁺	0	0.1768·10 ⁻⁹
OH ⁻	-37 594	0.5838·10 ⁻⁴
H ₄ SiO ₄ ⁰	-313 070	0.5472·10 ⁻⁶
H ₃ SiO ₄ ⁻	-299 740	0.5356·10 ⁻⁶
H ₂ SiO ₄	-281 770	0.2126·10 ⁻⁹
Mg ²⁺	-108 810	0.2923·10 ⁻⁴
MgOH ⁺	-150 000	0.7069·10 ⁻⁶
H ₂ O	-56 687	-
Solid phases		
Mg	-136 100	-
Mg ₂ SiO ₄	-490 760	-
Mg ₂ Si ₂ O ₃	-701 608	-
SiO ₂	-204 710	-
Mg(OH) ₂	-199 230	-
Mg ₃ Si ₄ O ₁₀ (OH) ₂	-1 324 900	0.1667
Mg ₆ Si ₄ O ₁₀ (OH) ₈	-1 930 220	0.0833
Mg ₇ Si ₈ O ₂₂ (OH) ₂	-2 716 200	-
Mg ₅ Si ₈ O ₂₀ (OH) ₂ ·8H ₂ O	-2 885 120	-
Mg ₄ Si ₄ O ₁₅ (OH) ₂ ·6H ₂ O	-2 213 650	-

Homogeneous aqueous solution

For aqueous solutions it is convenient to base the composition of the system on 1000 g H₂O, i. e., to use the molal scale of concentrations of the solutes. Then the system of linear equations (1) takes the form

$$\alpha_{11}m_1 + \dots + \alpha_{1p}m_p = -\alpha_{1p+1} \cdot 55, 51,$$

$$\alpha_{r-11}m_1 + \dots + \alpha_{r-1p}m_p = -\alpha_{r-1p+1} \cdot 55, 51, \quad (1a)$$

where $\alpha_{ij} = v_{ij} - \frac{M_i}{M_r} v_{rj}$ and $m_j = \frac{n_j}{n_{p+1}} \cdot 55.51$.

Since $\partial G / \partial n_j = G_j^0 + RT \ln(m_j \gamma_j) + RT \ln x$, where x is the mole fraction of water, system (2) becomes

$$\sum_{j=1}^p \epsilon_{ij} \ln m_j = - \sum_{j=1}^{p+1} \epsilon_{ij} \frac{G_j^0}{RT} - \sum_{j=1}^{p+1} \epsilon_{ij} \ln(\gamma_j x),$$

$$i=1, 2, \dots, p-r+1. \quad (2a)$$

Simultaneous solution of (1a) and (2a) gives the concentrations m_j at equilibrium. In solving the system by Newton's method it is convenient to convert to new variables $y_j = \ln m_j$ and $m_j = e^{y_j}$, thus avoiding the possibility that the successive approximations exceed the boundaries of the allowed set $m_j > 0$. The values of x and $\ln \gamma_j$ are calculated at every iteration.

Heterogeneous system aqueous solution - solid phase

If the solid phases in equilibrium with the aqueous solution are known, the system of equations for determination of their concentrations is set up as before [(1a) and (2a)], but in this case $\partial G / \partial n_j \text{ solid} = G_j^0$. However, the concentrations of the solid phases, unlike the concentrations of solutes, obey the condition $m_j \text{ solid} \geq 0$, and the conversion to $y_j = \ln m_j$ cannot be made. If the calculated $m_j \text{ solid} < 0$, this solid phase must be eliminated from analysis, as it is completely dissolved. Let us establish the tests for precipitation of a new solid phase from the solution.

Let n_0 be the minimum of function $G(n)$ in L_{pt_1}, \dots, t_s . Let us analyze phase t_{s+1} . Since $n_{t_{s+1}} = 0$, the basis vector $\bar{e}_{t_{s+1}}$ points from point n_0 into the permitted region $L_{pt_1}, \dots, t_s t_{s+1}$. Since the vector $\text{grad } G$ is normal at point n_0 to L_{pt_1}, \dots, t_s , we have that $(\bar{e}_{t_{s+1}}, \text{grad } G) > 0$ if and only if the projection of the gradient on $L_{pt_1}, \dots, t_s t_{s+1}$ is directed from point n_0 into the permitted region ($n_{t_{s+1}} > 0$). Hence the condition for the decrease of function G upon the precipitation of solid phase t_{s+1} is

$$(\bar{e}_{t_{s+1}}, \text{grad } G) < 0. \quad (3)$$

The following algorithm is suggested for determining the set of solid phases at the equilibrium point of the heterogeneous system:

Step 1. We assume no solid phases are present.

Step 2. The minimum of G is found for the system solution - assumed solid phases.

Step 3. Among the excluded phases, we find the solid phase t satisfying condition (3). If there is no such phase, calculation ends. Otherwise:

Step 4. If phase t is linearly independent of the previously assumed solid phases and water, it is now accepted into the set and we go to step 2.

Step 5. All previously accepted phases are assumed "dissolved", and G is minimized for the system solution - phase t.

Step 6. G is minimized for the system: solution remaining after step 5 - accepted solid phases (some of which are thereby dissolved completely), solute phases are eliminated, and we go to step 4.

The program for the Minsk-22 computer, based on this algorithm, permitted computation of phase diagrams for various multicomponent heterogeneous systems, including systems with rock-forming elements and minerals.

The results of calculation of equilibrium composition in the system MgO-SiO₂-H₂O are given in Table 1.

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REDEPOSITION OF POLYMETAL ORES BY AQUEOUS SOLUTIONS¹

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In tests on redeposition of complex ore from the 3rd International deposit we observed differential solution and deposition of ore components, as well as vertical and horizontal zoning in redeposited material, similar to that in natural ores.

Tests were run by the thermal gradient method [1]. The conditions in each of them were as follows. Starting material in the form of small 1- to 5-mm fragments with a total weight of about 25 g, together with 23 mliters of 10 percent NH₄Cl solution, were fed and sealed into an elongated 400- x 15-mm quartz ampoule, which was then placed in a steel autoclave. The latter was heated in a horizontal tube furnace, with temperatures 440° in the hot zone (zone of dissolution) and 365° in the cold zone (where crystallization occurred). The temperature difference between the two zones was maintained at about 75°. The reactor pressure reached 1000 atm. Each test lasted 118 hours. The composition of starting material is shown in Table 1; the relationships between mineral phases are illustrated in Fig. 1a.

The reformed material was deposited in the cold reactor (ampoule) zone as a compositionally and structurally nonuniform sulfide "vein",

Table 1

Composition of starting material *

Mineral	Concentration, vol. %	Element	Concentration, wt. %
Pyrite	52	Fe	28.2
Bornite	32	Cu	21.3
Sphalerite	10	Zn	6.8
Galena	0.7	Pb	0.6
Gray ore	1.9	As	0.24
Chalcopyrite	0.4	Sb	0.16
Gangue minerals	2.5	S	42.7

*Chemical composition was determined by recalculation of mineral composition.

1.5 cm thick and about 12 cm long (see Fig. 1a). The earliest part of this "vein", most remote from the solution zone, consists of minerals of the sphalerite association—sphalerite (78 percent by volume), pyrite (14), idaite (4), galena (2.6), bornite (1) and marcasite (0.1) (Fig. 1c). It is overlain by a zone composed of minerals of the idaite associations—idaite (45 percent by volume), pyrite (30), chalcopyrite (10), bornite (10), covellite (1) (Fig. 1d). This zone,

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