

## The use of non-ideal thermodynamic models for sphalerite and pyrrhotite in computer modeling of hydrothermal systems

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Sphalerite is a cubic form of ZnS–FeS solid solution and is the most important mineral of hydrothermal sulfide polymetallic ores. It has been suggested to use the composition of this solid solution as an indicator of physical-chemical conditions of the ore formation (temperature, pressure and S<sub>2</sub> fugacity). The solution of these problems primarily depends on the investigation of thermodynamic properties of the solid solution. The first classic data on the study of Zn–Fe–S ternary system [Barton and Toulmin, 1966] are the basis for sub-regular symmetric model [Fleet, 1975]. It is constructed only for 850 °C and 1 bar and characterized by the maximum positive excess energy of ZnS and FeS mixing at mole fraction  $X_{\text{FeS}} = 0.5$ . The data at  $T = 580\text{--}850$  °C [Barton and Toulmin, 1966] and results at  $T = 331\text{--}524$  °C [Scott and Barnes, 1971] were used to construct the asymmetric model of ZnS and FeS mixing [Hutcheon, 1978]. The cluster variation method (CVM) is also applied, which calls for detailing of the matter structure and sophisticated numerical approach, to the sphalerite solid solution [Balabin and Sack, 2000].

The integrated model of sphalerite mixing [Delgado and Soler, 2005] is supposed to be the most convenient for use. These authors have analyzed the results in the space of P-T variables for pyrite-pyrrhotite-sphalerite and troilite-sphalerite associations on the basis of great set of data (279 experiments according to the published data). The asymmetric model with the calculated values of FeS ( $\gamma_{\text{FeS}}^{\text{sph}}$ ) and ZnS ( $\gamma_{\text{ZnS}}^{\text{sph}}$ ) activity coefficients, excess Gibbs energy ( $G_{\text{ex}}$ ) and Gibbs energy of mixing ( $G_{\text{mix}}$ ) has been constructed. The model, in the view of the authors, has predictive properties in the temperature range 300–850 °C and pressures 1–10000 bar.

If no model of sphalerite non-ideality is available, one can only use the apparatus of the ideal solid solution ZnS–FeS ( $\gamma_{\text{FeS}}^{\text{sph}}$  and  $\gamma_{\text{ZnS}}^{\text{sph}} = 1$ ) for the computer simulation of equilibria in the hydrothermal systems involving sphalerite. We have created “ZnS\_FeS” external module, which works together with Gibbs program and Unitherm thermodynamic database [Shvarov, 2008], to account for non-ideality of the solid solution. It is based on the functional relationships between  $\gamma_{\text{FeS}}^{\text{sph}}$  and  $\gamma_{\text{ZnS}}^{\text{sph}}$  activity coefficients and sphalerite composition [Delgado and Soler, 2005]. The goal of the calculation with “ZnS\_FeS” module was to demonstrate its methodological possibilities and to check the correspondence to the literature experimental data. The obtained data made it possible to forecast the compositional changes of sphalerite in the series of its associations with pyrite and pyrrhotite, pyrite and magnetite, pyrite and barite at 200–300 °C as a function of S<sub>2</sub> fugacity.

### Methodical basis of “ZnS\_FeS” module

The module is used only for the calculation of sphalerite (ZnS–FeS solid solution) properties. It is dynamically linked to the Gibbs program and called if such calculations are required. The module has a common interface with HCh. FeS and ZnS activity coefficients are calculated using the parameters of solid solution (composition, temperature, pressure) according to the adopted equations. The method uses sub-regular model of solid solution [Delgado and Soler, 2005], in which excess energy mixing ( $G_{\text{ex}}$ , J/mol) is given by the following equation:

$$\overline{G}_{\text{ex}} = x_1 x_2 (x_1 W_1 + x_2 W_2),$$

where  $x_1$  and  $x_2$  are FeS and ZnS mole fractions in sphalerite,  $W_1$  and  $W_2$  are interaction energies for FeS and ZnS (J/mol). The values of the last parameters are calculated by the expressions, proposed by the authors of the model:

$$W_1 = -641.280 + 0.572 \cdot P + 12.118 \cdot T,$$

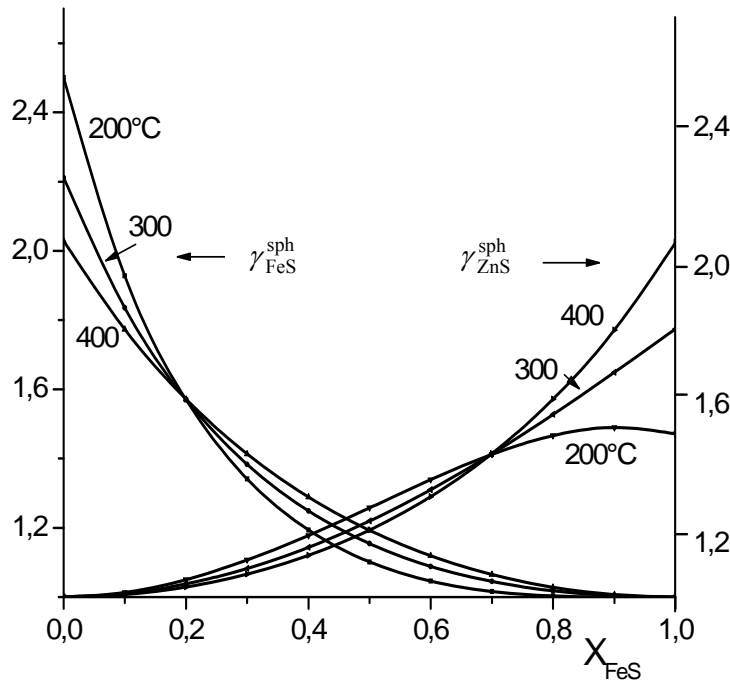
$$W_2 = -3326.356 - 0.052 \cdot P + 1.769 \cdot T.$$

In the sub-regular model the activity coefficients are determined by the following expressions:

$$RT \ln \gamma_{\text{FeS}}^{\text{sph}} = x_2^2 [x_1 (2W_1 - W_2) + x_2 W_2],$$

$$RT \ln \gamma_{\text{ZnS}}^{\text{sph}} = x_1^2 [x_1 W_1 + x_2 (2W_2 - W_1)].$$

The calculated dependences  $\gamma_{\text{FeS}}^{\text{sph}}$  and  $\gamma_{\text{ZnS}}^{\text{sph}}$  versus  $X_{\text{FeS}}$  for 200 - 400 °C and 1 bar are shown (fig. 1)



**Fig. 1.**  $X_{\text{FeS}}$ -dependence of  $\gamma_{\text{FeS}}^{\text{sph}}$  and  $\gamma_{\text{ZnS}}^{\text{sph}}$  in sphalerite for 200, 300 and 400 °C (P=1 bar)

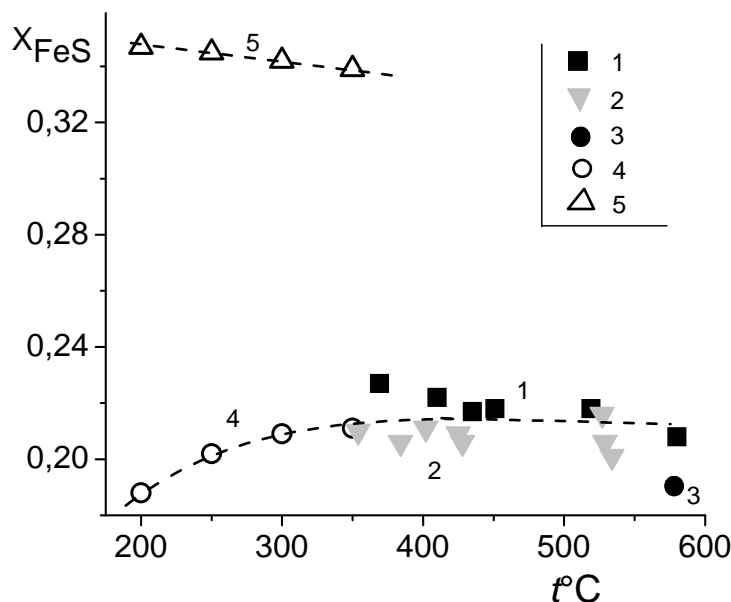
### Results of calculations

Computer simulation has been carried out for hydrothermal systems in the conditions wherein the formation of pyrite and sphalerite associated with pyrrhotite (1), magnetite (2) or barite (3) occur. In the ideal model cubic modification of pure sphalerite ZnS and hexagonal troilite FeS have been taken as the standard state of the ZnS–FeS solid solution end-members. In the improved model of the non-ideal solid solution, troilite has been replaced by FeS with formal sphalerite structure. This is an ordinary approach in the description of the solid solution models of substitution type [Hutcheon, 1978; Delgado and Soler, 2005]. This fact evidences that equilibrium exists in the system with two solid solutions (sphalerite and pyrrhotite):  $\text{FeS}_{\text{po}} \leftrightarrow \text{FeS}_{\text{sph}}$  with the constant  $K_1 = a_{\text{FeS}}^{\text{sph}} / a_{\text{FeS}}^{\text{po}}$ . The standard free energy of the reaction is:  $\Delta G_R = 2226.696 + 0.288 \cdot P + 1.434 \cdot T$ , J/mol [Delgado and Soler, 2005].

Basic equilibrium, which determines sphalerite composition, is as follows:  $\text{FeS}_{\text{sph}} + 0.5\text{S}_{2(\text{gas})} = \text{FeS}_2$  with the constant  $K_2 = 1/[x_{\text{FeS}}^{\text{sph}} \times \gamma_{\text{FeS}}^{\text{sph}} \times (f_{\text{S}_2})^{0.5}]$ . The  $f_{\text{S}_2}$  change in these associations makes it possible to show how the non-ideal model of ZnS-FeS solid solution affects its composition. The calculations have been carried out for 200, 250, 300 (P = 100 bars) and 350 °C (P = 150 bars).

Pure sphalerite ZnS, pyrite  $\text{FeS}_2$  and troilite FeS have been taken as the initial excessive phases in the system with sphalerite–pyrite–pyrrhotite. The solution contained 0.1m  $\text{H}_2\text{S}$  and 0.17m NaCl. The problem to determine sphalerite composition by “ZnS\_FeS” module has been first solved in these calculations with regard to the non-ideal model of pyrrhotite solid solution [Shvarov, 2011]. Experimental data in the Zn–Fe–S system for the temperatures below 600 °C have been taken to correlate the calculation results and

experiments on sphalerite composition in the presence of pyrite and pyrrhotite (fig 2). It is seen that in the non-ideal model of ZnS–FeS solid solution the calculated sphalerite composition at 350 °C coincides well with average experimental values in the range 350–580 °C ( $X_{\text{FeS}} = 0.215$ ). Lowering of the temperature from 350 to 200 °C at the excepted model parameters [Delgado and Soler, 2005] must cause the decrease of  $X_{\text{FeS}}$  up to 0.19. The comparative calculations carried out according to the ideal sphalerite and pyrrhotite models cause the elevation of  $X_{\text{FeS}}$  mole fraction in sphalerite up to 0.34–0.345. Very high  $X_{\text{FeS}}$  values by the ideal model are evidence that it does not correspond to the experimental data.

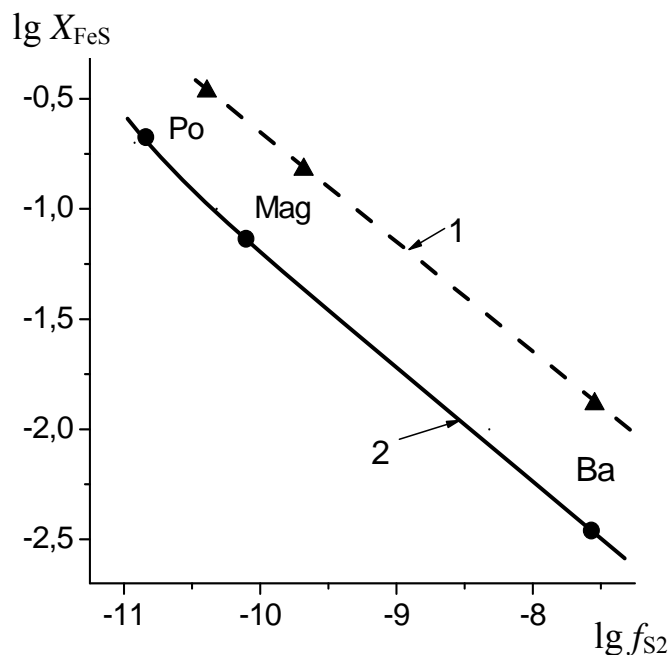


**Fig. 2.** Experimental data on the  $X_{\text{FeS}}$  mole fraction in ZnS–FeS solid solution correlated with the results of our calculations for sphalerite-pyrite-pyrrhotite equilibrium in relation to the temperature. Experiment: 1 – [Lusk and Calder, 2004]; 2- [Scott and Barnes, 1973]; 3 – [Barton and Toulmin, 1966]. Our calculations: 4 – ZnS\_FeS module with regard for FeS and ZnS activity coefficients; 5 – without regard for FeS and ZnS activity coefficients

Higher  $f_{\text{S}_2}$  (as compared to the pyrrhotite association) occurs in the system with sphalerite, pyrite and magnetite in chloride-sulfide solutions (1 m NaCl,  $10^{-2}$ – $10^{-4}$  m  $\text{H}_2\text{S}$ , pH 6–7) at 200–350 °C. According to the equation for constant  $K_2$  increase of  $f_{\text{S}_2}$  in the calculations by the non-ideal model causes the decrease of  $X_{\text{FeS}}$  up to 0.08–0.11. Significant  $X_{\text{FeS}}$  increase up to the maximal values 0.31 is observed in the calculations for the ideal model. It is 3 times higher than the calculation results made by the non-ideal model.

The equilibrium of sphalerite with pyrite and barite occurs in the near neutral sulfide-sulphate solutions (0.17 m NaCl, 0.1 m  $\text{H}_2\text{S}$ , 0.01 m  $\text{H}_2\text{SO}_4$ , pH 6–7) with maximal  $f_{\text{S}_2}$ . According to the equation for constant  $K_2$ , this causes low  $X_{\text{FeS}}$  values in sphalerite, which increase with increasing temperature from 200 to 300 °C within the range  $10^{-4.5}$ – $10^{-2.5}$  by the non-ideal model. Triple increase is observed according to the ideal model.

Fig.3 demonstrates general functional dependences of  $\lg X_{\text{FeS}}$  versus  $\lg f_{\text{S}_2}$ , constructed with regard to the calculations for the ideal and non-ideal sphalerite models for three discussed associations at  $t = 300$  °C. According to the ideal model (line 1) the data strictly correspond to the linear dependence as a consequence of this function expressed through equilibrium constant  $K_2$ :  $\lg a_{\text{FeS}} = \lg X_{\text{FeS}} + \lg \gamma_{\text{FeS}} = -\lg K_2 + \lg a_{\text{FeS}_2} - 0.5 \lg f_{\text{S}_2}$ , where  $a_{\text{FeS}_2} = 1$ , and  $\lg X_{\text{FeS}}$  at  $\gamma_{\text{FeS}} = 1$  equal  $\lg a_{\text{FeS}}$ . According the non-ideal model (curve 2), the dependence differs from the linear one due to the change of the activity coefficient as FeS mole fraction in sphalerite is different (fig. 1). Curve 2 is lower than line 1 due to  $\gamma_{\text{FeS}} > 1$ , that corresponds to smaller  $X_{\text{FeS}}$  according to the non-ideal model.



**Fig. 3.** Calculated dependences of the  $\lg X_{\text{FeS}}$  mole fraction in sphalerite composition, which correspond to its equilibria with pyrite and pyrrhotite (Po), pyrite and magnetite (Mag), pyrite and barite (Ba), versus the  $\lg f_{\text{S}_2}$  at 300 °C. Line 1 and curve 2 – our calculations according to the ideal and non-ideal sphalerite model, correspondingly

### Conclusions

It is shown that thermodynamic modeling of hydrothermal processes with the use of the ideal model of sphalerite solid solution becomes a foolproof method. The deviations from the ideal model correspond to a triple decrease of Fe content in the “real” sphalerite in the studied temperature (200–350 °C) and composition ( $X_{\text{FeS}} = n \cdot 10^{-4} - 0.34$ ) range. The suggested use of “ZnS\_FeS” module in the variant of sphalerite solid solution model by [Delgado and Soler, 2005] can be further corrected on the basis of new experimental data and theory.

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