Study of the Reaction of Dissolution of Sphalerite in the Absence of Oxygen[1]

Abdelhakim Begar[a],*****, **M. Djeghlal**[b], **and M. Ould hamou**[a]

[a]*LGM Laboratory, Department of Mining and Mineral Engneering, National Polytechnic School,
El-Harrach, Algiers, Algeria*
[b]*LSGM Laboratory, Department of Metallurgy, National Polytechnic School, El-Harrach, Algiers, Algeria*
*e-mail: begarabdelhakim@yahoo.fr

Abstract—The present study concerns the dissolution process of sphalerite in synthetic aqueous solution of sulfuric acid in the absence of oxygen, which allows zinc sulfate to be obtained from a sphalerite. The reaction product of the reaction solution in the absence of oxygen is determined using the Pitzer model used to calculate the various activity coefficients. As the leaching experiments of the present study covered the temperature range from 25 to 200°C, it is necessary to consider the expressions giving the coefficients activity of zinc sulfate and sulfuric acid as a function of temperature.

INTRODUCTION

Strict environmental restrictions imposed on the plant of sulfide, the need to utilize small and complex deposits stimulated the development of alternative methods especially process hydrometallurgical that avoid the production of SO_2, a pollutant [1, 5].

During the last decades, attention has been given to the leaching of sphalerite by aqueous sulfuric acid (Forward et Veltman, 1959; Parker, 1961; Demopoulos et Baldwin, 1999, Peng 2005; T. Pecina et al., 2007) [5–9].

Electrolytes are important in many applications that typically occur in the areas of leaching of minerals in the areas of corrosion, the effects of the fight against water pollution, the food processing and oil fields [6, 7–11]. There are many models to represent the thermodynamic propertyes of aqueous solutions of electrolytes. The reaction between ZnS crystallites and aqueous solution can be described by the pseudo-first-order kinetics, which is rationalized in terms of the Langmuir–Hinshelwood model (L–H) modified to accommodate reactions occurring at a solid–liquid interface [12].

Pitzer et al. [13, 14, and 15] have developed a model for calculating the properties of electrolytes from an improved analysis of the Debye–Huckel model and semi-numerical models. This model links the intermolecular forces and the distribution of ions to the osmotic pressure and reflects the influence of short-range forces in binary interactions. The equations obtained are similar to those of Guggenheim.

The terms of the activity coefficient and osmotic coefficient are deduced from the equation of the Gibbs energy molar excess.

The purpose of our work is to describe the equilibrium reaction of dissolution of ZnS without oxygen present over an extensive temperature: range including activity coefficients obtained from the elaborate Pitzer's model adapted to the mixed electrolytes.

THERMODYNAMIC MODEL

In water, sulfuric acid is dissociated according the equilibrium:

$$H_2SO_4 \Leftrightarrow H^+ + HSO_4^- \quad K_1$$

$$HSO_4^- \Leftrightarrow H^+ + SO_4^{-2} \quad K_2$$
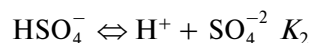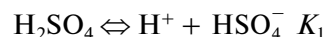
The dissociation constants at 25°C of these reactions are calculated from the values of standard Gibbs energies of the species, that is to say: $K_1 = 80.72$ and $K_2 = 0.0125$

The high value of the equilibrium constant K_1 translated into strong shift in equilibrium towards the formation of HSO_4^- and H^+. We admit later that the first dissociation of sulfuric acid is complete. Only the second dissociation equilibrium will be considered.

Pitzer et al. [13] give a value substantially different for K_2, given the uncertainty associated with various

---

[1] The article is published in the original.

experimental methods: $K_2 = 0.0105$. This value will be used in subsequent calculations.

The law of mass action applied to the dissolution equilibrium of sulfuric acid is then:

$$K_2 = \frac{a_{H^+} \cdot a_{SO_4^{2-}}}{a_{HSO_4^-}}$$

$$= \frac{\gamma_{H^+} \cdot \gamma_{SO_4^{2-}}}{\gamma_{HSO_4^-}} \cdot \frac{m_{H^+} \cdot m_2}{m_1}. \tag{1}$$

In the absence of oxygen, the reaction of dissolution of sphalerite in aqueous sulfuric acid is written as:

$$ZnS + 2H^+ + SO_4^{-2} \Leftrightarrow Zn^{+2} + SO_4^{-2} + H_2S.$$
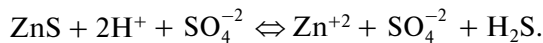
The expression of Pitzer to calculate the activity coefficients of ions H^+, SO_4^{-2} in the presence of HSO_4^- and Zn^{+2}. In this case, the coefficients of B'_{Zn_1} and C_{Zn_1} can be neglected at species interactions Zn^{+2} and SO_4^- as B'_{Zn_1} represents the derivative with respect to the ionic strength of a term $B_{Zn_1}^{(0)}$ which is independent of I and C_{Zn_1} is an adjustable parameter that depends on interactions triples. These parameters are important only for high concentrations (usually greater than 2 mol /kg) which give:

$$\ln(\gamma_H^2 \gamma_{SO_4}) = 6f^\gamma + 4m_2(B_{H_2}^{(0)} + (m_H + 2m_{Zn})C_{H_2})$$
$$+ 4m_1(B_{H_1}) + 2m_{Zn}(B_{Zn_2} + (m_H + 2m_{Zn})C_{Zn_2})$$
$$+ 2m_H(B_{H_2}^{(0)} + (m_H + 2m_{Zn})C_{H_2}) + 6m_1 m_H B'_{H_1} \tag{2}$$
$$+ 4m_2 m_H C_{H_2} + 6m_2 m_{Zn} B'_{Zn_2} + 4m_2 m_{Zn} C_{Zn_2}.$$

Applying the expression of the activity coefficient for a mixture of electrolytes in ion pair H^+, HSO_4^- in the presence of ions SO_4^{-2} and Zn^{+2}, we obtain the following equation:

$$\ln(\gamma_H \gamma_{HSO_4}) = 2f^\gamma + 2m_1 B_{H_1} + 2m_2(B_{H_2}$$
$$+ (m_H + 2m_{Zn})C_{H_2}) + 2m_H B_{H_1} + 2m_1 m_H B'_{H_1} \tag{3}$$
$$+ 2m_2 m_H C_{H_2} + 2m_2 m_{Zn}(B'_{Zn_2} + C_{Zn_2}).$$

As the difference between (2) and (3), we obtain the term $\ln(\gamma_H^2 \gamma_{SO_4}/\gamma_{HSO_4})$ which is used to calculate the molarity of H^+ ions by applying eq. (1). The calculation is done by the numerical method using as an initial value of molality mH slightly higher than the initial molality of sulfuric acid.

$$\ln\left(\frac{\gamma_H^2 \gamma_{SO_4}}{\gamma_{HSO_4}}\right) = 4f^\gamma + 2m_2(B_{H_2}^{(0)} + (m_H + 2m_{Zn})C_{H_2})$$
$$+ 2m_1(B_{H_1}) + 2m_{Zn}(B_{Zn_2} + (m_H + 2m_{Zn})C_{Zn_2}) \tag{4}$$
$$+ 2m_H(B_{H_2}^{(0)} - B_{H_2}^{(1)} + (m_H + 2m_{Zn})C_{H_2}) + 4m_1 m_H B'_{H_1}$$
$$+ 2m_2 m_H C_{H_2} + 4m_2 m_{Zn} B'_{Zn_2} + 2m_2 m_{Zn} C_{Zn_2}.$$

For all these expressions the terms f^γ, A^γ, B'_{H_1}, $B_{H_1}^{(0)}$, $B_{H_2}^{(0)}$, $B_{H_1}^{(1)}$, C_{H_2} are given by the following formulas:

$$f^\gamma = A^\gamma\left(\frac{I^{0.5}}{1 + 1.2I^{0.5}} + \frac{2}{1.2}\ln(1 + 1.2I^{0.5})\right), \tag{5}$$

with

$$A^\gamma = 0.0000043 T^2 + 0.002709 T + 0.583022. \tag{6}$$

Pitzer et al. [15] gives the equations $B_{H_1}^{(0)}$, $B_{H_2}^{(0)}$, $B_{H_1}^{(1)}$, C_{H_2} and K_2 as a function of temperature:

$$B_{H_1}^{(0)} = 0.05584 + \frac{46.040}{T}, \quad B_{H_1}^{(1)} = -0.65758$$
$$+ \frac{336.514}{T}, \quad B_{H_2}^{(0)} = -0.32806 + \frac{98.607}{T}, \tag{7}$$
$$C_{H_2} = 0.25333 - \frac{63.124}{T}, \quad k_2 = e^{-14.0321 + \frac{2825.2}{T}}$$

B_{Zn_2} is a function expressing the binary interaction between Zn^{+2} ions and sulfate ions SO_4^{-2}, its expression is given by:

$$B_{Zn_2} = B_{Zn_2}^{(0)} + \frac{2B_{Zn_2}^{(1)}}{\alpha_2^2 I}(1 - (1 + \alpha_1 I^{0.5})\exp(-\alpha_1 I^{0.5})$$
$$+ \frac{2B_{Zn_2}^{(2)}}{\alpha_2^2 I}(1 - (1 + \alpha_2 I^{0.5})\exp(-\alpha_2 I^{0.5}) \tag{8}$$

B'_{Zn_2} is the derivative of B_{Zn_2} compared to ionic strength, as:

$$B'_{Zn_2} = \frac{2B_{Zn_2}^{(1)}}{\alpha_1^2 I^2}\left(-1 + \left(1 + \alpha_1 I^{0.5} + \frac{1}{2}\alpha_1^2 I\right)\exp(-\alpha_1 I^{0.5})\right)$$
$$+ \frac{2B_{Zn_2}^{(2)}}{\alpha_2^2 I^2}\left(-1 + \left(1 + \alpha_2 I^{0.5} + \frac{1}{2}\alpha_2^2 I\right)\exp(-\alpha_2 I^{0.5})\right). \tag{9}$$

In the case of the electrolyte 2-2 ($ZnSO_4$), it was necessary to introduce an additional factor $B(2)$ com-

pared to the analogous expressions valid for electrolytes 1-1 and 1-2. $B_{Zn_2}^{(0)}$, $B_{Zn_2}^{(1)}$, $B_{Zn_2}^{(2)}$ are parameters dependent on temperature.

Pitzer and Mayorga [14] give the values of these parameters at 25°C:

$$B_{Zn_2}^{(0)} = 0.1949, \quad B_{Zn_2}^{(1)} = 2.883,$$

$$B_{Zn_2}^{(2)} = 32.81,$$

$$\frac{\partial B_{Zn_2}^{(0)}}{\partial T} = -3.68 \times 10^{-3}, \quad \frac{\partial B_{Zn_2}^{(1)}}{\partial T} = 2.33 \times 10^{-2}, \quad (10)$$

$$\frac{\partial B_{Zn_2}^{(2)}}{\partial T} = -3.33 \times 10^{-1}.$$

The term C_{Zn_2} corresponding to the ternary interactions here is equal to:

$$C_{Zn_2} = \frac{3}{2} C_{Zn_2}^{\delta}.$$

The general expression giving the Pitzer activity coefficient for a mixture of electrolytes can be applied to zinc sulfate in the presence of sulfuric acid. In this case we obtain:

$$\ln[(\gamma_{Zn^{+2}})(\ln\gamma_{SO_4})] = 8f^{\gamma} + 2m_2[B_{Zn_2}$$
$$+ (m_H + 2m_{Zn})C_{Zn_2}] + 2m_{Zn}[B_{Zn_2}$$
$$+ (m_H + 2m_{Zn})C_{Zn_2}] + 2m_H[B_{H_2} \quad (11)$$
$$+ (m_H + 2m_{Zn})C_{H_2}] + 2m_2 m_{Zn}[4B'_{Zn_2} + 2C_{Zn_2}]$$
$$+ 2m_2 m_H[2C_{H_2}] + 2m_1 m_H[4B'_{H_1}],$$

with $B_{Zn_2} = B_{Zn_2}^{\gamma} - B_{Zn_2}^{\varphi}$ et $B'_{Zn_2} = (2B'_{Zn_2} - B_{Zn_2}^{\gamma})/I$ and C_{Zn_2} expressed according to $C_{Zn_2}^{\varphi}$ or $C_{Zn_2}^{\gamma}$:

$$C_{Zn_2} = \frac{C_{Zn_2}^{\varphi}}{4} = \frac{C_{Zn_2}^{\gamma}}{6}. \quad (12)$$

The activity coefficient using the zinc sulfate, will be expressed as below by expanding the terms f^{γ}, B^{γ} et C^{γ}:

$$\ln\gamma_{ZnSO_4} = -4A^{\varphi}\left(\frac{I^{0.5}}{I + bI^{\frac{1}{2}}} + \frac{2}{b}\ln(I + bI^{0.5})\right)$$

$$\quad (13)$$

$$+ \frac{3}{2}m^2 C_{ZnSO_4}^{\varphi} + m\left\{B_{ZnSO_4}^{(0)} + 2\frac{B_{ZnSO_4}^{(1)}}{\alpha_1^2 I}[1 - (1 + \alpha_1 I^{0.5})\right.$$

$$\times \exp(-\alpha_1 I^{0.5})] + 2\frac{B_{ZnSO_4}^{(2)}}{\alpha_2^2 I}[(1 + \alpha_2 I^{0.5})\exp(-\alpha_2 I^{0.5})]\right\}.$$

As the leaching experiments of this study cover the temperature range from 25°C to 200°C, it was necessary to supplement the expressions giving the coefficients of activity of zinc sulfate at 25°C, introducing the dependence with respect to temperature.

In this expression the coefficients $B_{ZnSO_4}^{(0)}$, $B_{ZnSO_4}^{(1)}$, $B_{ZnSO_4}^{(2)}$, $C_{ZnSO_4}^{\varphi}$ and A^{φ} are temperature dependent. The partial derivative of the activity coefficient of zinc sulfate in relation to temperature is:

$$\frac{\partial \ln\gamma_{ZnSO_4}}{\partial T} = -4\left(\frac{\partial A^{\varphi}}{\partial T}\right)_p\left(\frac{I^{0.5}}{(I + bI^{0.5})} + \frac{2}{b}\ln(1 + bI^{0.5})\right)$$

$$+ m\left\{2\left(\frac{\partial B_{ZnSO_4}^{(0)}}{\partial T}\right) + \left(\frac{2}{\alpha_1^2 I}\right)\left(\frac{\partial B_{ZnSO_4}^{(1)}}{\partial T}\right)[1 - (1 + \alpha_1 I^{0.5})\right.$$

$$\quad (14)$$

$$\times \exp(-\alpha_1 I^{0.5})] + \left(\frac{2}{\alpha_2^2 I}\right)\left(\frac{\partial B_{ZnSO_4}^{(2)}}{\partial T}\right)[1 - (1 + \alpha_2 I^{0.5})$$

$$\left. \times \exp(-\alpha_2 I^{0.5})]\right\} + \frac{3}{2}m^2\left(\frac{\partial C_{ZnSO_4}^{\varphi}}{\partial T}\right).$$

Solving this equation requires knowledge of the partial derivatives of the A^{φ} with respect to temperature:

$$\frac{A_H}{RT} = 4I\frac{\partial A^{\varphi}}{\partial T}. \quad (15)$$

Bradley and Pitzer [15] provide the values of the apparent molar enthalpy reduced A_H/RT for temperatures ranging from 0 to 350°C.

For the convenience of numerical calculation, the apparent molar enthalpy is expressed as a function of temperature and pressure equal to the saturation vapor pressure in the form:

$$\frac{A_H}{RT} = 11.0679053 - 0.145798089\,T$$

$$+ 6.95581035\,T^2 - 1.414944867 \times 10^{-6}\,T^3 \quad (16)$$

$$+ 1\,012\,268\,758 \times 10^{-9}\,T^4.$$

OPTIMIZATION OF MODEL PARAMETERS

The Pitzer model was applied to calculate the activity coefficients and the average H^+ ion molality in aqueous solution of sulfuric acid We have developed for this purpose as a machine code in Fortran that allowing the calculation of the H^+ ion molality in aqueous solution of sulfuric acid and the activity coefficients.
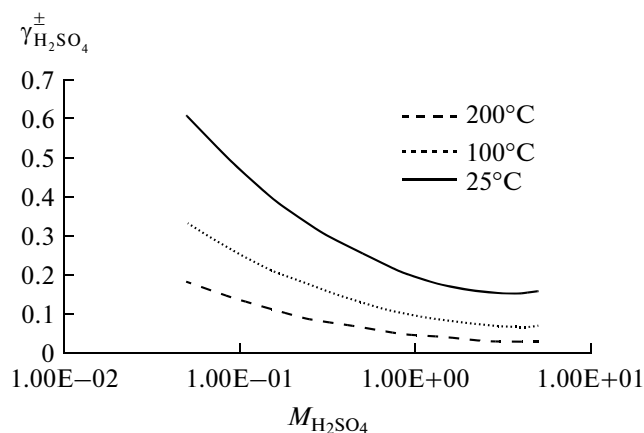
Fig. 1. Activity coefficient of sulfuric ad din the presence of zinc sulfate as a function of molality of sulfuric add at 25, 100 and 200°C.
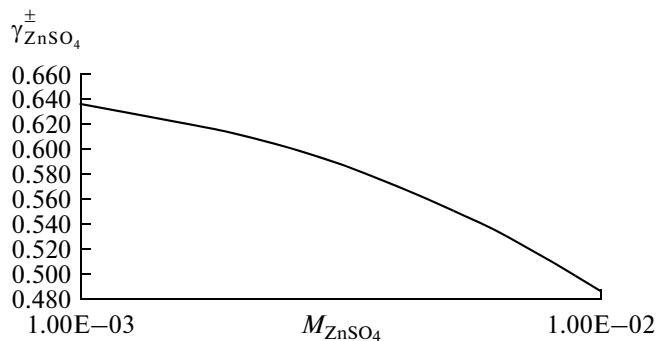

Fig. 2. Stoichiometric activity coefficient of zinc sulfite in the presence of sulfuric acid as a function of molality in zinc sulfate at 25°C.

EXPERIMENTAL

Zinc analysis in the leach liquor was made volumetrically by EDTA titration

Knowing the number of moles of hydrogen sulfide introduced, liquid and gaseous volumes as well as initial and final pressures, allows the calculation of the coefficient of Henry.

The measurements were carried out in a glass reactor with agitation placed in an enclosure regulated at 25°C. Hydrogen sulfide is initially introduced into a reactor vessel isolated Annex. At temperature equilibrium, the reactor containing the aqueous solution and the stirred vessel containing hydrogen sulfide are communicated.

The raised pressure and the initial temperature and the curve representing the kinetics of dissolution of the gas, allows the calculation of the coefficient HENRY. The steps were conducted in the autoclave used for the leaching experiments zinc sulfide.

Experiments were carried out in function of time in the absence of oxygen and sulfur aqueous medium.

For temperatures from ambient to 200°C, the autoclave head of the initial air is filled with two nitrogen atmosphere at room temperature, the initial mass of 5 g sphalerite is introduced into 400 mL of sulfuric solution 0.125 M.

RESULTS AND DISCUSSION

The curves in (Fig. 1) which gives the activity coefficient of sulfuric acid molality for between 0.01 and 5 mol kg^{-1} at 25°C, and molality of 0.01, 0.05 and 0.1 mol kg^{-1} in zinc sulfate, can say that the presence of zinc sulfate affects the average ionic activity coefficient $\gamma_{H_2SO_4}$ in the lower bound, especially at low stoichiometric molality of sulfuric acid. This molality of zinc sulfide is of the order of magnitude of those we find in the solution from the dissolution of zinc sulfide in sulfuric acid medium. The attack of 5 g of zinc sulfide in 400 mL of sulfuric acid solution corresponds to a 0.128 M solution of zinc sulfate to total dissolution.

The curves corresponding to temperatures from 50 to 200°C, show that the presence of zinc sulfate resulted in lower average activity coefficients of sulfuric acid, regardless of temperature. This influence becomes negligible at low molality zinc sulfate and sulfuric acid molality important.

The change in the activity coefficient of sulfuric acid depending on the temperature data for molality of zinc sulfate and sulfuric acid is comparable to those obtained in the absence of zinc sulfide. It may be noted that the coefficient $\gamma_{H_2SO_4}^{\pm}$ of a solution without zinc sulfate at 190°C is greater than the coefficient $\gamma_{H_2SO_4}^{\pm}$ of the solution containing zinc sulfate.

The values of activity coefficients of zinc sulfate at room temperature are slightly higher between 10^{-3} and 10^{-2} mol/kg the values of 50°C. At a given temperature, the activity coefficient using the zinc sulfate passes through a minimum which is located in a zinc sulfate molality between 1 mol/kg at 25°C and 0.01 mol/kg at 200°C (Figs. 2–4).

The curve (Fig. 5) allows giving an experimental average value equal to 547.105 Pa by mole fraction for the Henry coefficient of hydrogen sulfide in water at 25°C.

For aqueous sulfuric solution, the Henry coefficient increases as a function of the concentration, and reached 1080.105 Pa value for a concentration of 8.8 M.

The solubility of the hydrogen sulfide thus decreases as a function of sulfuric acid concentration but for the relatively low acid solutions used. The Solubility varies little as the Henry coefficient only changing from 547 to 590.105 Pa by molar fraction when the sulfuric acid concentration passing of 0.125 and 0.5 M.
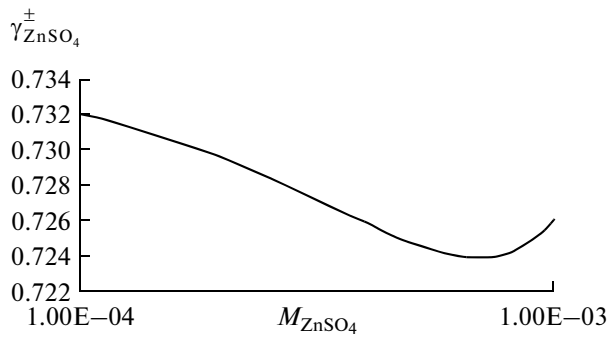
Fig. 3. Stoichiometric activity coefficient of zinc sulfate in the presence of sulfuric acid as a function of molality in zinc sulfate at 100°C.
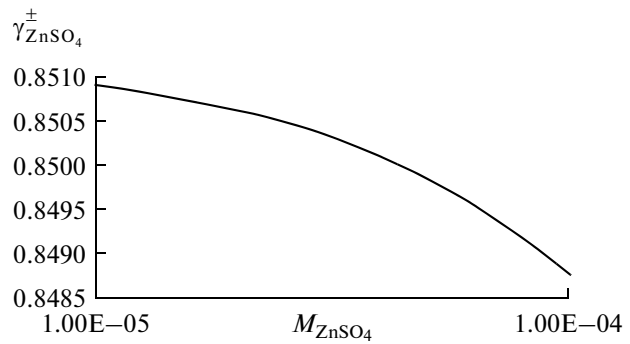

Fig. 4. Stoichiometric activity coefficient of zinc sulfate in the presence of sulfuric acid as a function of molality in zinc sulfate at 200°C.
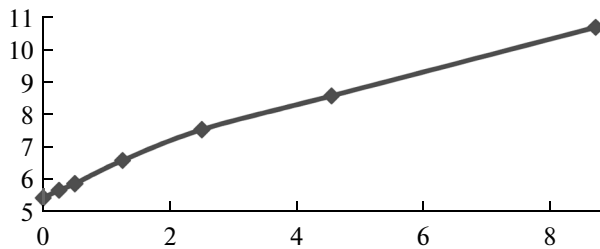

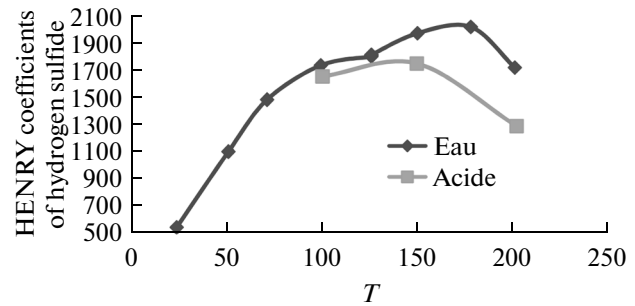**Fig. 5.** HENRY coefficients of hydrogen sulfide as a function of sulfuric acid concentration.

Fig. 6. HENRY coefficients of hydrogen sulfide as a function of temperature for the water and an aqueous sulfuric solution 0.125 M.

The solubility of hydrogen sulfide in aqueous sulfuric media is accompanied above 150°C of a formation of elemental sulfur and sulfur acid according to the reaction:

$$H_2S + H_2SO_4 \Leftrightarrow S^+ + H_2SO_3^- + H_2O.$$
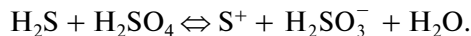
The sulfur formation increases with the temperature, and at 200°C, 22% of hydrogen sulfide introduced is converted into sulfur.

In sulfuric medium 0.125 M the few experimental points obtained is a consequence of the very rapid corrosion observed on the head of the autoclave and the pressure sensor. At high temperatures, hydrogen sulfide is extremely corrosive. The results for the coefficient of HENRY in water and sulfuric aqueous solution are generally tainted with a positive error can be estimated at 22% maximum. In aqueous sulfuric medium, HENRY coefficient for hydrogen sulfide is lower than in water at temperatures above 100°C, the solubility of the gas is therefore important in the weakly dilute sulfuric acid in the water.

The dissolution reaction of sphalerite in aqueous sulfuric medium is written:

$$ZnS + 2H^+ + SO_4^{-2} \Leftrightarrow Zn^{+2} + SO_4^{-2} + H_2S_{gas}.$$
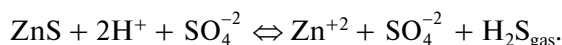
Experiments were carried out in function of time in the absence of oxygen and sulfuric aqueous medium. For temperatures from 25 to 200°C, the autoclave rid of the initial air, is filled with two nitrogen atmosphere at room temperature, the initial mass of 5 g of sphalerite is introduced into 400 mL of sulfuric solution 0.125 M.

The curves of (Fig. 7) show that the dissolution is fast, it varies very little after 15 minutes especially below 160°C.

The system will be considered in balance after two hours of experience.

The final concentrations of carried acid were transformed into molality.

The curve (Fig. 8) shows that the equilibrium constant grows rapidly as the temperature after 150°C, indicating that this reaction of dissolution are endothermic. The temperature increase causes an increase of the dissolution in the endothermic direction which opposes the increase of this temperature.

The result obtained for the experimental equilibrium constant: 1.05×10^{-4} is of the same order of magnitude as that obtained from the standard enthalpies of formation and standard entropies.
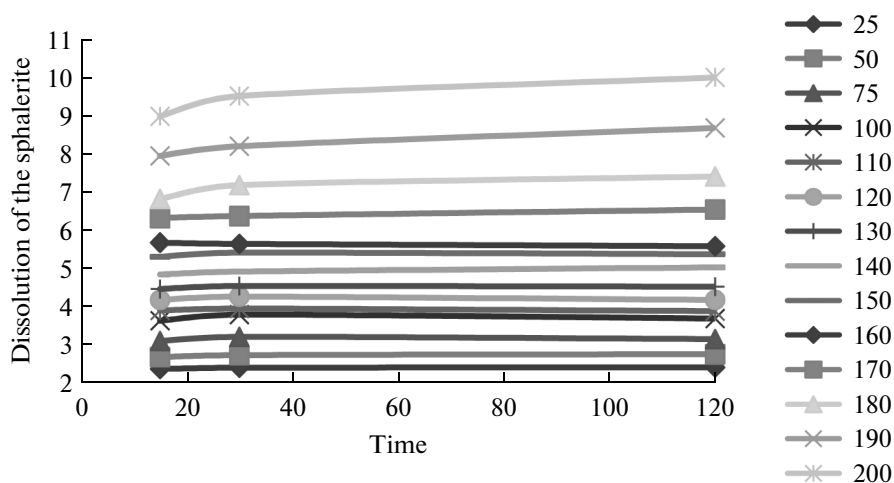
Fig. 7. Dissolution of the sphalerite as function of time for different temperatures.
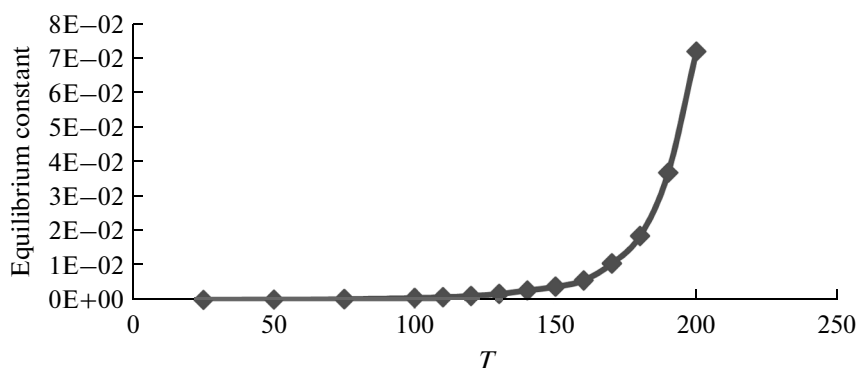

Fig. 8. Equilibrium constant in function of the temperature.

This experimental value of the equilibrium constant is leads to a standard free enthalpy to 22.7 kJ mol^{-1}.

The curve (Fig. 8) shows three distinct areas: between 25 and 100°C, the alignment of the points is not perfect, the reaction enthalpy is $\Delta H = 23.2$ kJ mol^{-1}, between 110 and 150°C the reaction enthalpy is $\Delta H = 50.82$ kJ mol^{-1}; between 160 and 200°C enthalpy is 106.9 kJ mol^{-1}. The enthalpy of the reaction calculated from thermodynamic data $\Delta H_{298} = 13.43$ kJ mol^{-1} has a value relatively close to that found below 100°C.

This temperature of 160°C is important in the study of the liquid sulfur. Indeed, above 120°C, the sulfur melting temperature, the liquid sulfur is present mainly in two allotropic, sulfur λ and sulfur μ.

Sulfur λ corresponds to an octagonal left ring inter atomic distance equal to 2.07 Å; it is especially predominant (85%) below 160°C. Its proportion decreases above this temperature, but still remains above 50%.

The sulfur μ, which is metastable at room temperature and is transformed into sulfur λ corresponds to chains of sulfur atoms to S8 units of varying lengths. The interatomic distance of 1.8 Å, this species is generally below 160°C in a proportion of 0.1 to 5%, which then increases up to 40% above 160°C.

The autoclave tests, which allowed the determination of the Henry coefficient for hydrogen sulfide in aqueous solutions of sulfuric acid, resulted in the production of sulfur, which is in yellow compact form above 160°C, and increases with temperature. Produce the quantity, expressed in moles, if it is considered as pure sulfur is substantially equal to the sulfuric acid concentration of the solution decreased. However, in concentrated sulfuric medium at room temperature, hydrogen sulfide reacts with the acid:

$$H_2S + H_2SO_4 \rightleftharpoons H_2SO_3^- + S^\cdot + H_2O.$$
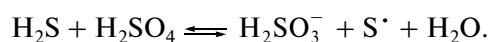
The sulfurous acid as written here probably does not exist in this form, but is a complex mixture of SO_2, H_3O^+, $S_2O_5^{2-}$ et HSO_3^-.

CONCLUSIONS

The values of activity coefficients of zinc sulfate in the presence of sulfuric acid show that at a given temperature, the presence of sulfuric acid lowers the activity coefficient of zinc sulfate. It decreases as the molality increases in zinc sulfate which results in a weak sulfuric acid molality.

The study area is divided into three distinct parts: 25°C and 100°C, 110°C and 150°C and 160°C and 200°C. These areas appear to be related to the structure of sulfur, the melting temperature of crystalline sulfur of between 110°C and 120°C while the temperature of 160°C corresponds to the transition $S\lambda \rightarrow Sp$.

NOMENCLATURE

m_i	molality of the species considered
A^φ	Debye−Huckel parameter
I	ionic strength
T	temperature
R	gas constant
f^γ	term describing the effect of electrostatic forces
K	equilibrium constant
B	function expressing the binary interaction
C_x	function expressing the triple interactions
B'_x	derivative with respect to the ionic strength
b	adjustable parameter that was optimized and set equal to 1.2 kg$^{1/2}$ mol$^{-1/2}$ for all temperatures
$\alpha_1 = 2$	for most electrolytes
$\alpha_2 = 12$	for electrolytes 2-2
γ	activity coefficient of the body considered

REFERENCES

1. Peng, P., Xie, H., and Lu, L., *Hydrometallurgy*, 2005, vol. 80, pp. 265−271.

2. Pecina, T., Franco, T., Castillo, P., and Orrantia, E., *Miner. Eng.,* 2008, pp. 23−30.

3. Forward, F.A. and Veltman, H., *J. Met.*, 1959, vol. 11, pp. 836−840.

4. Parker, E.G., *CIM Bull.,* 1961, vol. 74, pp. 145−150.

5. Demopoulos, G.P. and Baldwin, S.A., Stoichiometric and kinetic aspects on the pressure leaching of zinc concentrates, in EPD Congress 1999, Mishra, Brajendra, Ed., *Proceedings of Sessions and Symposia held at the TMS Annual Meeting, San Diego, 1999*, pp. 567−583.

6. Wadsworth, M.E., *Hydrometallurgical Processes in Rate Processes of Extractive Metallurgy*, New York: Plenum Press, 1979, pp. 133−197.

7. Wang, P., Anderko, A., Springer, R.D., and Young, R.D., *J. Mol. Liq.,* 2006, vol. 125, pp. 37−44.

8. Xing-Mei Lu, Wei-Guo Xu, Xiao-Hong Chang, Dianzhen Lu, and Jia-zhen Yang, *J. Chem. Thermodynam.*, 2004, vol. 36, pp. 253−257.

9. Marion, G.M., *Geochim. Cosmochim. Acta*, 2002, Issue 14, 15, pp. 2499−2516.

10. Pitzer, K.S., *Activity Coefficients in Electrolyte Solutions*, 2nd ed., USA Boca Raton: CRC, 1991.

11. Zemaitis, J.F., Clark, D.M., Rafal, M., and Scrivner, N.C., *Handbook of Aqueous Electrolyte Thermodynamics*, New York: Design Institute for Physical Property Data-AIChE, 1986.

12. Liu, L.L., Huang, J.F., Cao, L.Y., Wu, J.P., Fei, J., et al., Influence of temperature on the morphology and photocatalytic activity of ZnGa$_2$O$_4$ crystallites prepared by hydrothermal method, *Ceram. Int.*, 2013, vol. 39, pp. 3165−3171.

13. Pitzer, K.S., Roy, R.N., and Silvester, L.F., *J. Am. Chem. Soc.*, 1977, vol. 99, no. 15, pp. 4930−4936.

14. Pitzer, K.S. and Mayorga, G., *J. Sol. Chem.*, 1974, vol. 3, no. 7, pp. 539−546.

15. Bradley, D.J. and Pitzer, K.S., *J. Phys. Chem.*, 1979, vol. 83, no. 12, pp. 1599−1603.