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## Comparison of components and parameters of some sulfide minerals surface tension with regards to stability of mineral-air bubble system

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**Abstract:** The measurements of the advancing contact angle of water, glycerol, formamide, ethylene glycol, diiodomethane,  $\alpha$ -bromonaphthalene, 1,2,3-tribromopropane on unoxidized and oxidized galena, pyrite, chalcopyrite, djurleite, bornite and covellite at the temperature equal 293 K were made. Additionally, the measurements of the force air bubble detachment from these sulfide minerals including also chalcocite in water were performed. Using the values of the obtained contact angle of water, glycerol, formamide, ethylene glycol, diiodomethane,  $\alpha$ -bromonaphthalene, 1,2,3-tribromopropane the components and parameters of the unoxidized and oxidized sulfide minerals surface tension were calculated. For this calculation the van Oss et al. method was applied after analysis of the components and parameters of the surface tension of liquids used for contact angle measurements. Taking into account the contact angle of water on the sulfide minerals, the detachment force of air bubble from these minerals in water was determined using our equation and comparing to that of measured one. As follows from the measurements and calculations the wetting properties of sulfide minerals and the stability of mineral-air bubble depends to a larger extent on the degree of sulfide minerals oxidation than on the type of mineral.

**Keywords:** contact angle, wettability, surface tension, detachment force, sulfide minerals

### 1. Introduction

Air bubble adhesion to solids surface plays an important role in flotation beneficiation of ores and minerals (Leja, 1982). Among the minerals, the metal sulfides are often subjected to flotation enrichment. The efficiency of flotation process depends on the stability of the solid-air bubble-liquid system. Such stable system can occur when its total Gibbs free energy is lower than the sum of the total free energy of the solid and bubbles in the liquid before the attachment (Leja, 1982). A measure of the stability of solid-air bubble-liquid system is the value of the force needed to detach the air bubble from the solid surface. This force depends on the radius of the air bubble, the radius of the contact plane, the surface tension of the liquid and the instantaneous contact angle at the detachment moment of air bubble from the solid surface (Jańczuk, 1983; Jańczuk and Białopiotrowicz, 1989). The instantaneous contact angle, at the first approximation, is equal to that of advancing one (Jańczuk, 1983). Thus, on the basis of the contact angle it is possible to predict the stability of the solid-air bubble-liquid system. As it results from the Young equation (Adamson and Gast, 1997), the contact angle depends on the surface tension of liquid and solid as well as the solid-liquid interface tension. As a matter of fact, the liquid surface tension can be directly measured but the solid surface tension and the solid-liquid interface tension are usually determined applying indirect methods. Among different methods those based on the contact angle values are the most frequently used. To determine the solid surface tension from the contact angle measurements on the basis of the Young equation the relationship between the solid-liquid interface tension and the solid and liquid surface tension must be known. In the literature there are two main approaches to this problem. One is based on the assumption that the solid-liquid interface tension is a

function of solid and liquid surface tension as well as not exactly defined of the parameter interactions of liquid and solid through the interface (Li and Neumann, 1992; Kwok and Neumann, 1999; 2000, Chibowski, 2003). The second methods assume that the surface tension of the solid and liquid can be divided into the components resulting from different kinds of intermolecular interactions. Moreover, the solid-liquid interface tension depends on these components of the liquid and solid surface tension (Fowkes, 1964; van Oss, 1994; Owens and Wendt, 1969; Good and Girilaco, 1960; van Oss and Good, 1989; van Oss et al., 1987; 1988; Kloubek, 1992; Wu, 1970). In the literature there are many papers in which these two types of approaches to the interface tension are applied for determination of the solid surface tension from the contact angle measurements (van Oss, 1994). It seems that the van Oss et al. method (van Oss and Good, 1989; van Oss et al., 1987; 1988) is the most useful for this purpose. However, for the calculations of the solid surface tension applying this method the contact angle values of least three liquids are needed under the same condition and in the same state of the solid surface. This can be difficult particularly in the case of sulfide minerals because their surface is very sensitive to the presence of oxygen and moisture. With the influence of minerals oxidation, among others oxygen and -OH group are present changing the hydration of their surface. This fact probably affects the components and parameters of sulfide minerals surface tension. It is also possible that different values of the contact angle of the same liquid on the given sulfide mineral measured by the investigators depend on the degree of mineral oxidation. For this reason, it is difficult to compare the components and parameters of the surface tension of different types of sulfide minerals.

Therefore, the aim of the paper was to determine the components and parameters of the surface tension of different sulfide minerals from the contact angle of many liquids under the same condition on the unoxidized and oxidized surfaces of these minerals. For the same minerals the force of air bubble detachment from their surface in water was measured. For our studies water (W), glycerol (G), formamide (F), ethylene glycol (E), diiodomethane (D),  $\alpha$ -bromonaphthalene (B), 1,2,3-tribromopropane (T), unoxidized and oxidized galena, pyrite, chalcopyrite, djurleite, bornite and covellite were used.

## 2. Experimental

### 2.1. Materials

All chemical compounds used for the investigations, namely formamide ( $\geq 99.5\%$ ), glycerol ( $\geq 99.5\%$ ), ethylene glycol (99.8%), diiodomethane ( $> 99\%$ ),  $\alpha$ -bromonaphthalene (97%) and 1,2,3-tribromopropane (97%) were bought from Sigma-Aldrich (Poland). Water obtained from the Milli-Q Plus systems at the resistance equal  $18.2 \Omega$  was next distilled and deionized using the Destamat Bi18E system. Galena, pyrite, chalcopyrite, djurleite, bornite and covellite supplied by the Mining and Metallurgy Academy of Cracow (Poland) were used for contact angle measurements.

The sulfide minerals specimens were cut into plates and next polished with a series of emery papers (Carborundum grit from 400 to 00). Polishing was performed slowly by hand, to avoid local overheating and oxidization. Final polishing was done in the water until reflecting surfaces were obtained. Next only very smooth plates were chosen and washed several times in doubly distilled and deionized water and placed in an ultrasonic bath for 15 min. Afterwards some of the plates were dried at room temperature and placed before measurements in a desiccator filled with a molecular sieve mixture (4 Å and 5 Å) to remove water from the plates surface for 24 hours. As in the natural environment being influenced by oxygen and water oxidation of the surface of sulfide minerals their wettability can change. Therefore, galena plates oxidized by their immersion in the 3% hydrogen peroxide solution for 60 min. After being oxidized the plates were washed several times in doubly distilled and deionized water and dried at room temperature.

To show the influence of natural environment (atmosphere) on the surface properties of unoxidized galena, its plates were placed in desiccator maximal for 10 weeks without molecular sieves. However, some of plates were used for contact angle measurements at the end of the next week. The grains of the sulfide minerals used for the force of air bubble detachment from their surface were prepared in the same way as the plates.

## 2.2. Methods

The advancing contact angles for the above mentioned liquids on the unoxidized and oxidized sulfide minerals were measured using the sessile drop method. For this purpose, the DSA30 measuring system (Krüss) in a thermostated chamber at 293K was applied. Before the contact angle measurements for a given liquid, the chamber was saturated with its vapour placing a cell filled with it for few hours. If the organic liquid was used for the contact angle measurements, at first the water vapour was removed from the apparatus chamber by means of the molecular sieves and next the chamber was saturated with the vapour of this liquid. The contact angle for the given liquid was measured for at least 30 drops and good reproducibility was found. The standard deviation for each set of values was from 1 to 2°. The size of the liquid drop was chosen on the basis of our earlier considerations dealing with the more proper drop size for a given liquid (Zdziennicka et al., 2017). This size was different for each used liquid.

In the case of force of air bubble detachment from the sulfide mineral grain, there was applied the method described elsewhere (Jańczuk, 1983). The detachment force was read under the microscope from the deviation of the quartz rod at the moment of the disruption of the air bubble from the sulfide mineral grain surface. At the same time the instantaneous contact angle was established. The quartz rod used for the detachment force measurements was previously calibrated by means of the cathetometer. The measurements of the detachment force were repeated ten times and the standard deviation was equal to  $\pm 3 \times 10^{-3}$  mN. The diameter of the air bubble used for the measurements was equal to  $4.05 \times 10^{-3}$  m.

## 3. Results and discussion

### 3.1. Contact angle

The values of the contact angle ( $\theta$ ) practically for all studied liquids on the sulfide minerals do not depend on the type of the mineral (Table 1). These values for water on the unoxidized mineral surface are close to its contact angle value on the sulfur surface (Jańczuk, 1983). This suggests that the sulfur atoms decide about the wettability of the unoxidized sulfide minerals.

The oxidation of the sulfide minerals results in an increase of oxygen atoms and/or -OH group influence on the contact angle values. The presence of oxygen and -OH group on the sulfide minerals

Table 1. The values of the contact angle of water ( $\theta_W$ ), glycerol ( $\theta_G$ ), formamide ( $\theta_F$ ), ethylene glycol ( $\theta_E$ ), diiodomethane ( $\theta_D$ ),  $\alpha$ -bromonaphthalene ( $\theta_B$ ) and 1,2,3-tribromopropane ( $\theta_T$ ) on the unoxidized and oxidized sulfide minerals surface at the temperature equal 293 K

Solid	$\theta_W$	$\theta_G$	$\theta_F$	$\theta_E$	$\theta_D$	$\theta_B$	$\theta_T$
	in degree						
Unoxidized chalcocite	80.2	66.9	54.8	47.7	46.4	36.2	38.1
Oxidized chalcocite	40.0	27.0	5.0	0.0	37.3	23.0	26.0
Unoxidized galena	82.3	69.6	58.2	51.0	46.4	36.3	38.2
Oxidized galena	41.6	39.0	37.0	0.0	39.5	26.6	29.2
Unoxidized pyrite	79.0	66.0	53.1	47.0	44.0	33.0	35.0
Oxidized pyrite	36.0	34.5	33.4	0.0	39.8	26.8	29.6
Unoxidized chalcopyrite	78.0	64.0	52.0	45.0	45.0	34.2	36.2
Oxidized chalcopyrite	37.0	35.4	34.2	0.0	40.0	27.2	29.6
Unoxidized djurleite	79.0	64.8	55.0	47.0	45.7	35.3	37.2
Oxidized djurleite	38.0	36.2	34.8	0.0	40.5	28.0	30.5
Unoxidized bornite	81.0	67.0	56.0	48.0	44.5	33.8	35.8
Oxidized bornite	38.0	36.0	34.4	0.0	39.5	26.5	29.2
Unoxidized covellite	78.6	67.0	56.5	48.7	44.8	34.0	36.0
Oxidized covellite	38.0	36.0	34.4	0.0	40.0	27.0	29.8

surface increases their degree of hydration which causes that the contact angles of different liquids on such surface are close to those on the oxides surface. To show the influence of the sulfide mineral oxidation degree the measurements of the contact angle for water, formamide and diiodomethane on the galena surface, as example, were carried out at different time after the galena plates preparation (Table 2, Fig. 1). The contact angle of the studied liquids decreases to the constant value which is obtained after 8 weeks of galena contact with atmosphere. It appeared that the real contact angle of water changed from 82.3 to 39.0°. The initial contact angle for water is close to its contact on the pure sulfur surface (Jańczuk, 1983) and final that on a type of quartz (Zdziennicka et al., 2017a). The highest values of contact angle were obtained for water. According to van Oss (1994) the contact angle of particular liquids depends on the values of the components and parameters of liquids and solids surface tension.

Table 2. The contact angle values of water ( $\theta_W$ ), formamide ( $\theta_F$ ) and diiodomethane ( $\theta_D$ ) on the galena surface as well as the values of the Lifshitz-van der Waals ( $\gamma_S^{LW}$ ) and Lewis acid-base ( $\gamma_S^{AB}$ ) components of the galena surface tension ( $\gamma_S$ ) and electron-acceptor ( $\gamma_S^+$ ) and electron-donor ( $\gamma_S^-$ ) parameters of the acid-base component at the temperature equal 293K calculated from Eq. (6)

Number of weeks	$\theta_W$	$\theta_F$	$\theta_D$	$\gamma_S^{LW}$	$\gamma_S^+$	$\gamma_S^-$	$\gamma_S^{AB}$	$\gamma_S$
	[in degree]			[mN/m]				
0	82.3	58.2	46.4	36.26	0.76	1.52	2.14	38.40
1	67.0	50.4	44.5	37.28	0.34	11.43	3.93	41.20
2	57.0	46.8	42.7	38.23	0.04	23.6	1.83	40.06
3	51.3	43.0	41.3	38.95	0.03	29.44	1.84	40.79
4	47.4	40.6	40.4	39.41	0.02	33.75	1.61	41.01
5	43.8	38.3	39.5	39.86	0.01	37.61	1.44	41.30
6	41.9	37.5	39.3	39.96	0.01	40.1	1.02	40.98
7	40.2	37.2	39.0	40.11	0.00	42.85	0.02	40.13
8	39.8	36.6	38.8	40.21	0.00	42.83	0.38	40.59
9	39.4	36.4	38.6	40.31	0.00	43.32	0.22	40.53
10	39.0	36.3	38.5	40.36	0.00	43.93	0.01	40.36

It is interesting that the changes of the contact angle of water, formamide and diiodomethane on the galena surface as a function of the weeks number ( $x$ ) in which the galena surface was in contact with air including oxygen and water vapour can be described by the exponential function of the second order. The equations for water, formamide and diiodomethane are respectively as follows:

$$\theta_W = 42.026 \cdot \exp\left(\frac{x}{2.586}\right) + 2.372 \cdot \exp\left(\frac{x}{0.589}\right) + 37.911 \quad (1)$$

$$\theta_F = 11.287 \cdot \exp\left(\frac{x}{2.639}\right) + 11.267 \cdot \exp\left(\frac{x}{2.639}\right) + 36.531 \quad (2)$$

$$\theta_D = 4.25 \cdot \exp\left(\frac{x}{3.14}\right) + 4.25 \cdot \exp\left(\frac{x}{3.14}\right) + 38.07 \quad (3)$$

From Eqs. (2) and (3) it results that the changes of contact angle for formamide and diiodomethane can be described also by the exponential function of the first order.

The data presented in Fig. 1 explain why different values of the contact angle for the same liquid on the given sulfide mineral surface were obtained. Thus, to compare the wettability of the particular sulfide minerals under the same conditions the contact angle of different liquids should be measured.

### 3.2. Components and parameters of the sulfide minerals surface tension

The contact angle is a very important parameter which determines the wetting properties of the liquid in the given phase system. In the solid-liquid-air system the contact angle depends on the solid ( $\gamma_S$ ) and liquid ( $\gamma_L$ ) surface tension as well as the solid-liquid interface tension ( $\gamma_{SL}$ ). This dependence is expressed by the Young equation (Adamson and Gast, 1997):

$$\gamma_S - \gamma_{SL} = \gamma_L \cos\theta \quad (4)$$

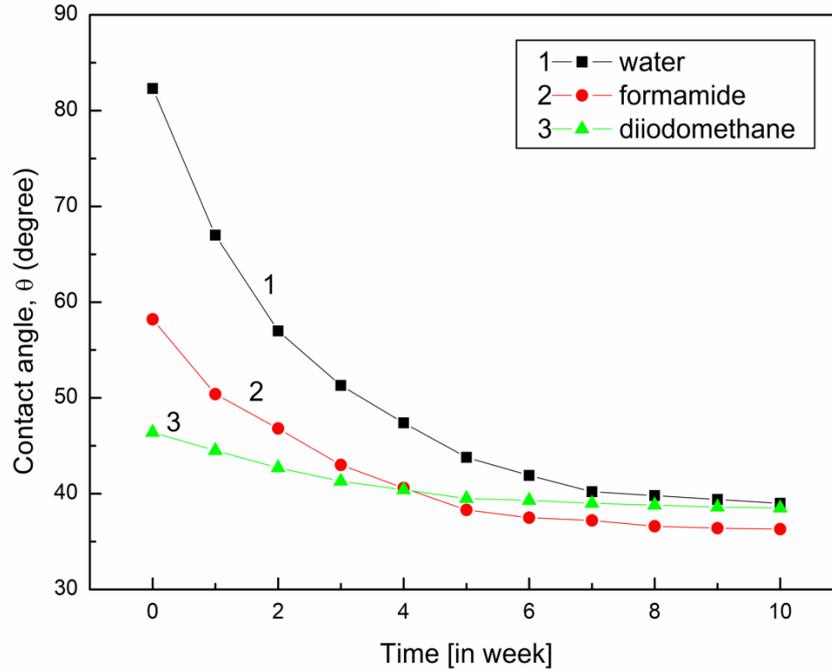


Fig. 1. A plot of the contact angle of the water (curve 1) formamide (curve 2) and diiodomethane (curve 3) on the galena surface versus the number of weeks at which the galena plates were contacting with the air and water vapour

Eq. (4) allows to determine the surface tension of solid which decides about its wetting as well as stability of the solid-air bubble-liquid system which plays an important role, among others, in the flotation process (Leja, 1982).

To solve Eq. (4) against  $\gamma_s$  the dependence between the solid-liquid interface tension and the solid and liquid surface tension must be known. In the literature there are many approaches to this dependence which allows to determine  $\gamma_s$  on the basis of the Young equation (Eq. (4)). Among the approaches to  $\gamma_{SL}$  those of the Owens and Wendt (Owens and Wendt, 1969), van Oss et al. (van Oss, 1994; van Oss and Good, 1989; van Oss et al., 1987; 1988) and Neumann et al. (Li and Neumann, 1992; Kwok and Neumann, 1999; 2000) are the most frequently used for the solid surface tension determination. From the Owens and Wendt (Owens and Wendt, 1969) concept and the Young equation it results:

$$\gamma_L(\cos\theta + 1) = 2\sqrt{\gamma_L^d \gamma_S^d} + 2\sqrt{\gamma_L^p \gamma_S^p} \quad (5)$$

where the superscripts  $d$  and  $p$  refer to the dispersion and polar components of the solid and liquid surface tension, respectively.

In turn van Oss et al. (van Oss, 1994; van Oss and Good, 1989; van Oss et al., 1987; 1988) proposed that:

$$\gamma_L(\cos\theta + 1) = 2\sqrt{\gamma_L^{LW} \gamma_S^{LW}} + 2\sqrt{\gamma_L^+ \gamma_S^-} + 2\sqrt{\gamma_L^- \gamma_S^+} \quad (6)$$

where the superscripts  $LW$ ,  $+$  and  $-$  refer to the Lifshitz van der Waals component, electron-acceptor and electron-donor parameters of the solid and liquid surface tension, respectively.

Contrary to Owens-Wendt (Owens and Wendt, 1969) and van Oss et al. (van Oss, 1994; van Oss and Good, 1989; van Oss et al., 1987; 1988). Neumann et al. (Li and Neumann, 1992; Kwok and Neumann, 1999; 2000) suggested that the value of the contact angle of a given liquid on the solid surface depends only on the total surface tension of liquid and solid and contribution of different kinds of intermolecular interactions to the surface tension is insignificant. They proposed the following equation for the calculation of the solid surface tension:

$$\frac{\cos\theta + 1}{2} = \sqrt{\frac{\gamma_S}{\gamma_L} \exp[-\beta(\gamma_L - \gamma_S)^2]} \quad (7)$$

where  $\beta$  is the constant which does not depend on the kind of solid and is assumed to be equal to  $0.000115 \text{ (m}^2/\text{mJ)}^2$ .

Equations (5) - (7) can be applied for the calculation of the solid surface tension from the contact angle measurements if the solid surface is flat and smooth as well as the liquid vapour does not change the solid surface tension around of a liquid drop settles on the solid surface. In the case of Eqs. (5) and (6) the additional condition must be fulfilled, namely the components and parameters of the model liquids used for the contact angle measurements should not depend on the type of solid.

Some authors (Fowkes, 1964; Hu and Adamson, 1977; van Oss, 1994; Kwok and Neumann, 1999) suggest that the vapour of the liquids for which the surface tension is higher than that of the solid does not change its surface tension. This fact does not consider the solutions. Equations (5) - (7) can be used for the solid surface tension calculations if other conditions are fulfilled. From the suggestions made by some authors it results that model liquids used for the contact angle measurements for the solid surface tension determination should have high values of their surface tension. The liquids chosen by us for the contact angle measurements on the sulfide minerals surface fulfill such a condition.

Based on the contact angle values of many apolar and polar liquids on different polymers Zdziennicka et al. (Zdziennicka et al., 2017b) proved that the calculated values of  $\gamma_s$  depend on the kind of the liquid whose contact angle values were taken into calculations. One reason may be that the  $\beta$  parameter in equation (7) depends on the type of solid. Therefore the  $\gamma_s$  values calculated from Eq. (7) may not be certain.

To apply equations (5) and/or (6) for determination of components and parameters of the solid surface tension, the component and/or parameters of the liquids surface tension must be independent of the solid type being in contact with the liquid. On the other hand, the values of the components and parameters of the liquids surface tension which are used for the components and parameters of solid surface tension determination must be established in a proper way.

The components and parameters of the liquid surface tension can be determined by two ways. The first is based on the liquid-liquid interface tension (Jańczuk et al., 1993) and the second on the contact angle values of liquid on the apolar and monopolar solids (van Oss, 2004; Zdziennicka et al., 2017b). It appeared that the components and parameters determined by these two ways for the same model liquid are different. However, if for the determination of  $\gamma_L^d$  and  $\gamma_L^{LW}$  of a given liquid, the same method was used then  $\gamma_L^d = \gamma_L^{LW}$ . This indicates that the dispersion component differs from the Lifshitz-van der Waals one only by definition (Jańczuk et al., 1993).

In the concept of the van Oss et al. (van Oss, 1994; van Oss and Good, 1989; van Oss et al., 1987; 1988) water is treated as a reference liquid. They assumed that for water the Lifshitz-van der Waals component of its surface tension is equal to 21.8 mN/m at 293 K. This value was determined by Fowkes (Fowkes, 1964) based on water-n-alkane interface tension and was treated as a dispersion component of water surface tension. To determine the electron-acceptor and electron-donor parameters of the Lewis acid-base component of other liquids van Oss et al. (van Oss, 1994; van Oss and Good, 1989; van Oss et al., 1987; 1988) assumed their values for water are identical and equal to 25.5 mN/m at 293 K. Taking into account the parameters values of water surface tension and Lifshitz-van der Waals component equal to 21.8 mN/m as well as the contact angle of water, apolar and bipolar liquids on the monopolar polymer surface (for example polymethyl methacrylate, PMMA) the electron-acceptor and electron-donor parameters of polar liquids were determined. Indeed, the Lifshitz-van der Waals component was established from the contact angle on the apolar solid (for example polytetrafluoroethylene, PTFE). However, it appeared that the Lifshitz-van der Waals component of water obtained from the contact angle on polytetrafluoroethylene and polyethylene is higher than 21.8 and equal to 26.85 mN/m. Based on this Zdziennicka et al. (Zdziennicka et al., 2017b) determined new values of the electron-acceptor and electron donor-parameters of glycerol, formamide and ethylene glycol surface tension (Table 3). They were used for determination of the components and parameters of the sulfide minerals surface tension (Table 4 and 5).

As a matter of fact, to determine  $\gamma_s^{LW}$ ,  $\gamma_s^+$ ,  $\gamma_s^-$  and next  $\gamma_s^{AB}$  ( $\gamma_s^{AB} = 2\sqrt{\gamma_s^+ \cdot \gamma_s^-}$ ) the contact angle values of three liquids are needed. The calculations of  $\gamma_s^{LW}$ ,  $\gamma_s^+$  and  $\gamma_s^-$  were made for all possible combinations of three liquids (see for example Table 4).

The average values of the components and parameters of the sulfide minerals surface tension are presented in Table 5 with chalcocite whose data are taken from our previous paper (Jańczuk and Zdziennicka, 2018).

Table 3. The average values of the Lifshitz-van der Waals ( $\gamma_{LV}^{LW}$ ) and Lewis acid-base ( $\gamma_{LV}^{AB}$ ) components of water (W), glycerol (G), formamide (F), ethylene glycol (E), diiodomethane (D),  $\alpha$ -bromonaphthalene (B) and 1,2,3-tribromopropane (T) surface tension ( $\gamma_{LV}$ ) components as well as the electron-acceptor ( $\gamma_{LV}^+$ ) and electron-donor ( $\gamma_{LV}^-$ ) parameters of the acid-base component ( $\gamma^{AB}$ ) at the temperature equal to 293 K taken from the literature (Zdziennicka et al., 2017b)

Liquid	$\gamma_{LV}$	$\gamma_{LV}^{LW}$	$\gamma_{LV}^{AB}$	$\gamma_{LV}^+$	$\gamma_{LV}^-$
	[mN/m]				
Water	72.80	26.85	45.95	22.975	22.975
Glycerol	64.00	34.00	30.00	9.43	23.87
Formamide	58.00	39.00	19.00	3.67	24.61
Ethylene glycol	48.00	29.00	19.00	4.70	19.20
Diiodomethane	50.80	50.80	0.00	0.00	0.00
$\alpha$ -Bromonaphthalene	44.40	44.40	0.00	0.00	0.00
1,2,3-Tribromopropane	45.40	49.70	0.00	0.00	0.00

Table 4. The average values of the Lifshitz-van der Waals ( $\gamma_s^{LW}$ ) and Lewis acid-base ( $\gamma_s^{AB}$ ) components of the unoxidized and oxidized galena surface tension ( $\gamma_s$ ) components as well as the electron-acceptor ( $\gamma_s^+$ ) and electron-donor ( $\gamma_s^-$ ) parameters of the acid-base component at the temperature equal to 293K calculated from Eq. (6)

Liquids	Unoxidized galena					Oxidized galena				
	$\gamma_s^{LW}$	$\gamma_s^+$	$\gamma_s^-$	$\gamma_s^{AB}$	$\gamma_s$	$\gamma_s^{LW}$	$\gamma_s^+$	$\gamma_s^-$	$\gamma_s^{AB}$	$\gamma_s$
	[mN/m]					[mN/m]				
W-G-F	40.76	0.14	1.79	1.00	41.76	35.75	0.36	38.51	7.48	43.24
W-G-E	5.53	155.28	1.71	-32.0	-27.0					
W-F-E	1135.76	1374.22	85.56	-685	449.98					
G-F-E	4842.88	10801.39	367.06	-398	860.5					
W-G-D	36.26	0.77	1.51	2.15	38.4	39.86	0.02	39.78	1.77	41.63
W-F-D	36.26	0.76	1.52	2.14	38.4	39.86	0.02	39.98	1.58	41.44
W-E-D	36.26	0.92	1.31	2.19	38.45	39.86	0.00	41.44	0.13	39.99
G-F-D	36.26	0.75	1.53	2.15	38.41	39.86	0.01	40.28	1.47	41.33
G-E-D	36.26	1.15	0.84	1.96	38.22	39.86	0.03	46.24	-2.30	37.56
F-E-D	36.26	0.51	2.68	2.34	38.59	39.86	0.11	33.51	3.83	43.7
W-G-B	36.2	0.78	1.50	2.16	38.36	39.82	0.02	39.77	1.82	41.65
W-F-B	36.2	0.77	1.51	2.16	38.36	39.82	0.02	39.97	1.63	41.45
W-E-B	36.2	0.93	1.31	2.20	38.41	39.82	0.00	41.43	0.18	40.01
G-F-B	36.2	0.76	1.53	2.16	38.36	39.82	0.01	40.27	1.52	41.34
G-E-B	36.2	1.16	0.84	1.97	38.17	39.82	0.03	46.23	-2.25	37.58
F-E-B	36.2	0.52	2.68	2.36	38.56	39.82	0.11	33.5	3.88	43.70
W-G-T	36.2	0.78	1.50	2.16	38.36	39.81	0.02	39.77	1.84	41.65
W-F-T	36.2	0.77	1.51	2.16	38.36	39.81	0.02	39.96	1.64	41.46
W-E-T	36.2	0.93	1.31	2.20	38.4	39.81	0.00	41.43	0.20	40.01
G-F-T	36.2	0.76	1.53	2.16	38.36	39.81	0.01	40.27	1.53	41.35
G-E-T	36.2	1.16	0.84	1.97	38.17	39.81	0.03	46.22	-2.23	37.58
F-E-T	36.2	0.52	2.67	2.36	38.56	39.81	0.11	33.49	3.89	43.71
Average	36.22	0.82	1.56	2.16	28.38	39.83	0.017	40.01	1.64	41.48

As follows from the calculations of the values of components and parameters of the sulfide minerals surface tension the most possible values of parameters and components were obtained when the data for two polar and one apolar liquids were taken into account in the calculations. However, if for the polar liquids the contact angle values were close to zero, then not real values of the  $\gamma_S^{LW}$ ,  $\gamma_S^+$ ,  $\gamma_S^-$  and next  $\gamma_S^{AB}$  were obtained.

Table 5. The average values of the Lifshitz-van der Waals ( $\gamma_S^-$ ) and Lewis acid-base ( $\gamma_S^{AB}$ ) components of the unoxidized and oxidized sulfide minerals surface tension ( $\gamma_S$ ) components as well as the electron-acceptor ( $\gamma_S^+$ ) and electron-donor ( $\gamma_S^-$ ) parameters of the acid-base component at the temperature equal to 293K calculated from Eq. (6)

Sulfide minerals	Unoxidized					Oxidized				
	$\gamma_S^{LW}$	$\gamma_S^+$	$\gamma_S^-$	$\gamma_S^{AB}$	$\gamma_S$	$\gamma_S^-$	$\gamma_S^+$	$\gamma_S^-$	$\gamma_S^{AB}$	$\gamma_S$
	[mN/m]					[mN/m]				
Chalcocite	36.25	1.36	1.47	2.83	39.08	40.93	3.25	22.00	16.91	57.85
Galena	36.22	0.82	1.56	2.16	28.38	39.83	0.017	40.01	1.64	41.48
Pyrite	37.54	1.31	1.60	2.53	40.07	39.71	0.039	45.33	2.61	42.33
Chalcopyrite	37.04	1.54	2.13	3.25	40.30	39.64	0.030	44.57	2.38	42.01
Djurleite	36.62	0.98	3.33	3.02	39.64	39.35	0.04	43.49	2.68	42.03
Bornite	37.24	0.95	1.97	2.50	39.74	39.84	0.033	43.14	2.46	42.30
Covellite	37.13	0.494	3.29	2.55	39.68	39.63	0.046	43.07	2.77	42.39

This may result from the fact that the contact angle was not strictly equal to zero and/or that during liquid spreading at first the liquid film was formed decreasing the solid surface tension and in this case Eq. (6) can not be applied. If the data of three polar liquids were used in Eq. (6) for  $\gamma_S^{LW}$ ,  $\gamma_S^+$ ,  $\gamma_S^-$  and next  $\gamma_S^{AB}$  determination, then only in some cases real values of components and parameters of sulfide surface tension were obtained. It should be noted that if the contact angle values of three polar liquids are used for calculations of components and parameters of solid surface tension, changes of the contact angle of one value of one of the three liquids causes a very large error in the calculations of  $\gamma_S^{LW}$ ,  $\gamma_S^+$  and  $\gamma_S^-$  (Zdziennicka et al., 2017b). For this reason, the components and parameters of sulfide minerals calculated from the contact angle of three polar liquid are not reliable (Fu et al., 2015). Therefore for calculations of the average values of  $\gamma_S^{LW}$ ,  $\gamma_S^+$ ,  $\gamma_S^-$  and next  $\gamma_S^{AB}$  as well as  $\gamma_S$ , the values of the component and parameters of the sulfide minerals obtained from the contact angle of three polar liquids as well as when for one liquid the contact angle was zero were not taken into account (Table 5). Table 5 shows that the  $\gamma_S^{LW}$ ,  $\gamma_S^+$ ,  $\gamma_S^-$ ,  $\gamma_S^{AB}$  and  $\gamma_S$  values practically do not depend on the type of sulfide mineral. For unoxidized sulfide minerals the  $\gamma_S^+$  values are only insignificantly lower than the  $\gamma_S^-$  ones. This suggests that not only sulfur and also metal influence on the surface properties of sulfide minerals. The increase in the degree of sulfide minerals oxidation (Tables 2 and 5) causes  $\gamma_S^{LW}$  increase to the value close to  $\gamma_S^{LW}$  obtained for PMMA and quartz (Zdziennicka et al., 2017a; 2017b, Zdziennicka et al., 2009) and  $\gamma_S^+$  decreases to the value close to zero. However,  $\gamma_S^-$  strongly increases to the value close to that for quartz (Zdziennicka et al., 2009). This indicates that the oxygen atoms and -OH groups may play main role in the surface properties of sulfide minerals. It is also possible that the oxidized mineral surface can be strongly hydrated.

### 3.3. Force of air bubble detachment from the sulfide mineral in water

The measured values of the force of air bubble detachment from sulfide minerals in water indicate that for the unoxidized minerals the stability of mineral grain-air bubble system practically does not depend on the type of sulfide mineral (Table 6).

However, in the case of oxidized sulfides there are some differences between particular sulfides. It is possible that the grains of particular sulfides were oxidized to a different degree and/or hydration of the grain surface depends insignificantly on the type of sulfide mineral. Our previous studied (Jańczuk and Białopiotrowicz, 1989) proved that the maximal force of air bubble detachment from the solid

surface in water, apart of water surface tension, depends on the radius of air bubble, radius of the contact plane of the air bubble to the solid surface and the instantaneous contact angle at the moment of grain-air bubble system disruption. The equation describing this dependence has the form (Jańczuk and Białopiotrowicz, 1989):

$$F_{0(\max)} = \frac{\pi R \sin^2 \theta_l}{2} \sqrt[3]{\frac{4}{2 + 1.5\sqrt{4 - \sin^2 \theta_l} - 0.125\sqrt{(4 - \sin^2 \theta_l)^3}}} \quad (8)$$

where  $F_{0(\max)}$  is the maximal force of air bubble detachment from grain in water (for the grain at the surface larger or equal to the contact plane at the time of grain-air bubble disruption),  $R$  is the radius of air bubble and  $\theta_l$  is the instantaneous contact angle at the time of grain-air bubble system disruption. It appeared that the instantaneous contact angle is, at the first approximation, equal to that of the advancing contact angle (Jańczuk, 1983; Jańczuk and Białopiotrowicz, 1989). If this takes place, it is possible to calculate the force of air bubble detachment from the sulfide minerals in water based on the measured values of advancing contact angle for water on the minerals surface. The  $F_{0(\max)}$  values calculated from Eq. (8) are listed in Table 6. As can be seen the values of  $F_{0(\max)}$  calculated from Eq. (8) are similar to those measured directly.

Table 6. The values of the force of air bubble detachment from the sulfide minerals in water measured and calculated from Eq. (8)

Sulfide mineral	Unoxidized		Oxidized	
	$F_0$ measured $\times 10^{-2}$ mN	$F_0$ calculated $\times 10^{-2}$ mN	$F_0$ measured $\times 10^{-2}$ mN	$F_0$ calculated $\times 10^{-2}$ mN
Chalcocite	2222.41	22.58	9.49	9.57
Galena	22.73	22.84	10.09	10.22
Pyrite	22.35	22.40	7.85	8.00
Chalcopyrite	22.21	22.24	8.31	8.39
Djurleite	22.21	22.40	8.69	8.78
Bornite	22.62	22.68	8.65	8.78
Covellite	22.31	22.34	8.72	8.78

## Conclusions

From our studies there can be drawn the following conclusions:

- The contact angle of polar and apolar liquids on the unoxidized and oxidized surface of some sulfide minerals practically does not depend on the type of sulfide minerals.
- The contact angle changes of water, formamide and diiodomethane as a function of the time of the air and water vapour contact with the galena surface can be described by the exponential function of the first and/or second order but the constant in these functions depends on the kind of liquid.
- The Lifshitz-van der Waals component and electron-donor as well as the electron-acceptor parameters of the sulfide minerals surface tension depends insignificantly on the type of mineral.
- The oxidation of sulfide mineral surface causes the increase in the Lifshitz-van der Waals component and electron-donor parameters and decrease of the electron-acceptor parameter of the sulfide mineral surface tension.
- The force of air bubble detachment from the grain of the sulfide mineral in water depends largely on oxidation of the grain surface.
- The force of air bubble detachment from the grain surface in water can be predicted based on the air bubble radius, surface tension of water and contact angle of water on the sulfide mineral surface.

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