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Determination of Components of Cassiterite Surface Free Energy from Contact Angle Measurements

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Measurements of contact angle for water, glycerol, formamide, diiodomethane, and bromoform on cassiterite surface with different initial treatments were conducted. Using the values of contact angle, the total surface free energy of cassiterite, and its components resulting from different kinds of intermolecular interactions were calculated. For this purpose, various approaches to the solid–liquid interfacial free energy have been considered. Next, the usefulness of these approaches for the determination of the cassiterite–water interfacial free energy and of the work of adhesion of water to the cassiterite surface were tested. Thus, it was found that the surface free energy of cassiterite previously dried at 110°C and not treated with HNO_3 is mainly the result of dispersion intermolecular interactions and this energy strongly depends on the amount of OH groups and/or coordinated and physisorbed water molecules on its surface. The presence of OH groups and/or water molecules gives rise to the acid–base components of the cassiterite free energy. It was also found that all the approaches tested for a given sample gave, in many cases, near the same value of the total cassiterite surface free energy; however, their usefulness to predict the cassiterite-water interfacial free energy and the work of adhesion of water to the cassiterite surface was not the same. Using the values of the Lifshitz–van der Waals, electron-acceptor and electron-donor components of the surface free energy for both cassiterite and water, the free energy of interaction between two particles of cassiterite in water was calculated and related with observations of the aggregation process of cassiterite and it was stated that if the energy of interaction is negative the aggregation process of cassiterite particles takes place. © 1993 Academic Press, Inc.

INTRODUCTION

Tin(IV) oxide occurs in nature as cassiterite, with a rutile type structure, but it is also found in rhombic and hexagonal forms. Pure Tin(IV) oxide is white and not soluble in water, it is resistant attacks by acids or alkalis but on fusian dissolves easily with alkali hydroxides to form alkali stannates.

Tin compounds are used in many industrial branches, therefore it is of interest to improve the exploitation of natural cassiterite. With this aim several techniques have been applied, and among them ore flotation is widely used.

As adsorption and adhesion have a predominant role in the flotation processes, a good knowledge of these phenomena is needed. In this sense the study of the surface free energy of cassiterite becomes very helpful. Since it is not possible to measure directly the surface free energy of a solid, its determination is achieved, at present, by many indirect methods. Among others, the methods based on the contact angle measurements for appropriately chosen systems are the most popular (1–24). One of the main problems in using these methods for the evaluation of the solid surface free energy is to express the interfacial solid–liquid free energy in the Young's equation as a function of the surface free energy of the solid and of the liquid involved.

There are two basic approaches to these problems. The first one is based on the assumption that the surface free energy of a solid and a liquid can be divided into components resulting from the different intermolecular interactions (1–15).

Generally, the interfacial solid–liquid or liquid–liquid free energy can be expressed as the sum of the surface free energy of the phases being in contact diminished by the work of adhesion of phase 1 to phase 2.

The work of adhesion can be expressed as a function of the geometric mean or harmonic mean of the dispersion (1–9) and the nondispersion or harmonic mean of the dispersion and geometric mean of the nondispersion (2–9) components of the surface free energy of the phases being in contact.

Recently van Oss and co-workers (10–15) expressed the work of adhesion of phase 1 to phase 2 as a function of the geometric mean of the Lifshitz–van der Waals components and of the geometric mean of the electron-acceptor and electron-donor parts of the acid–base component of both phases.

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The second point of view dealing with interfacial solid–liquid free energy is represented by Neumann and co-workers (16–18). They did not divide the surface free energy of the solid and the liquid into components but expressed the work of adhesion by the geometric mean of the total surface free energy of both contacting phases corrected by a parameter ϕ, which is a unique property of the pair of substances. Since for many solid–liquid systems the calculation of ϕ is impossible or very difficult, Neumann and co-workers (17) assumed the existence of a linear relationship between the interfacial solid–liquid free energy and the ϕ parameter and proposed the so-called equation of state for the calculation of this energy.

In our previous papers (19, 20) we have compared the usefulness of the Fowkes (1, 2) and Owens and Wendt (3), Wu (6–9) and Neumann and co-workers (16–18) approaches for the determination of the surface free energy of polymers and paraffin. Now it can be of interest from a theoretical and a practical point of view to make the comparison between the Fowkes (1, 2) and Owens and Wendt (3), and van Oss and co-workers (10–15), and Neumann and co-workers (16–18) approaches to the evaluation of the interfacial free energy of systems involving such a mineral as cassiterite.

Therefore, we carried out a test to determine the surface free energy of cassiterite and its components using the above-mentioned approaches. This was done on the basis of the measurements of contact angle for five liquids on cassiterite with different surface treatments.

Finally we verified the "working" of surface free energy and its components in the system cassiterite–water.

THEORY

The solid surface free energy can be determined on the basis of the contact angle measurements for properly chosen systems using the Young's equation (25):

$$\gamma_S - \gamma_{SL} - \Pi e_L = \gamma_L \cos\theta_L, \qquad [1]$$

where γ_S is the solid surface free energy; γ_{SL} is the interfacial solid–liquid free energy; γ_L is the liquid surface tension (surface free energy); θ_L is the contact angle in the system solid–liquid–air; and Πe_L, is the film pressure of the liquid on the solid surface.

In Eq. [1] is a major item to find out the correlation between γ_{SL} and γ_L and γ_S.

Fowkes (1, 2) introduced the hypothesis that the surface free energy of a liquid or solid could be subdivided into components due to the London dispersion force, γ^d, to the Debye induction force, γ^i, and to the Keesom dipole–dipole force, γ^p. He also included a component due to hydrogen bonding, γ^h. Then for a given phase,

$$\gamma = \gamma^d + \gamma^i + \gamma^p + \gamma^h. \qquad [2]$$

However, from a practical point of view, the surface free energy is considered as a sum of the dispersion, γ^d, and the nondispersion, γ^n ($\gamma^n = \gamma^i + \gamma^p + \gamma^h$) components:

$$\gamma = \gamma^d + \gamma^n. \qquad [3]$$

Using the geometric mean of the dispersion (1, 2) and the nondispersion (3, 4) components, the solid–liquid interfacial free energy can be expressed in the form:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2(\gamma_S^d \gamma_L^d)^{1/2} - 2(\gamma_S^n \gamma_L^n)^{1/2}. \qquad [4]$$

Another approach was proposed by van Oss and co-workers (10–15). They suggested that the surface free energy of a solid or a liquid can be divided into two parts:

$$\gamma = \gamma^{LW} + \gamma^{AB}. \qquad [5]$$

The γ^{LW} component results from noncovalent long-range Lifshitz–van der Waals interactions and γ^{AB} from Lewis acid–base interactions (10–15).

The γ^{LW} component can be written:

$$\gamma^{LW} = \gamma^d + \gamma^i + \gamma^p. \qquad [6]$$

Moreover, the γ^{AB} component can be expressed as a function of the geometric mean of the electron-acceptor (γ^+) and the electron-donor (γ^-) parts:

$$\gamma^{AB} = 2(\gamma^+\gamma^-)^{1/2} \qquad [7]$$

Using the approach of van Oss and co-workers (10–15) the interfacial free energy, γ_{SL} can be written in the form:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2(\gamma_S^{LW}\gamma_L^{LW})^{1/2} - 2(\gamma_S^+\gamma_L^-)^{1/2} - 2(\gamma_S^-\gamma_L^+)^{1/2}. \qquad [8]$$

Fowkes (1, 2) claims that it is possible to determine the dispersion component of a polar liquid on the basis, for example, of the interfacial tension of polar liquid-saturated hydrocarbon. However, van Oss and co-workers (26) suggest that it is not possible to determine the γ^d component but only the γ^{LW} one, which results from dispersion, dipole–dipole and induced dipole–dipole intermolecular interactions. Simultaneously these authors maintain that the contribution of nondispersion forces to the γ^{LW} value is negligible for many solids or liquids (26, 27). It means that practically the γ^d and the γ^{LW} components differ only by their definition but their numerical values are close.

Thus the values of the γ^d and γ^n components for polar liquids determined on the basis of polar liquid-n-alkane interfacial tension measurements are equal to those of the γ^{LW} and γ^{AB} components, respectively.

Taking this fact into account in Eqs. [4] and [8], we obtain:

$$[(\gamma_{\mathrm{S}}^{+}\gamma_{\mathrm{L}}^{-})(\gamma_{\mathrm{S}}^{-}\gamma_{\mathrm{L}}^{+})]^{1/2} = \frac{\gamma_{\mathrm{S}}^{+}\gamma_{\mathrm{L}}^{-} + \gamma_{\mathrm{S}}^{-}\gamma_{\mathrm{L}}^{+}}{2}. \quad [9]$$

On the basis of Eq. [9] we can state that when $\gamma_{\mathrm{S}}^{+}\gamma_{\mathrm{L}}^{-} = \gamma_{\mathrm{S}}^{-}\gamma_{\mathrm{L}}^{+}$ is fulfilled then $\gamma_{\mathrm{S}}^{\mathrm{d}} = \gamma_{\mathrm{S}}^{\mathrm{LW}}$ and $\gamma_{\mathrm{S}}^{\mathrm{n}} = \gamma_{\mathrm{S}}^{\mathrm{AB}}$.

Girifalco and Good (28) described the solid–liquid interfacial free energy as a function of the geometric mean of the total surface free energy of the contacting phases corrected by a parameter ϕ, whose value resulted from unique properties of these two phases (28–30):

$$\gamma_{\mathrm{SL}} = \gamma_{\mathrm{S}} + \gamma_{\mathrm{L}} - 2\phi(\gamma_{\mathrm{S}}\gamma_{\mathrm{L}})^{1/2}. \quad [10]$$

Since for many solid–liquid systems the calculation of ϕ is impossible or very difficult, Neumann *et al.* (17) taking into account the values of contact angle measured by Zisman and co-workers (31–33) found a linear relationship between the interfacial solid–liquid free energy and the ϕ parameter (17):

$$\phi = -\alpha\gamma_{\mathrm{SL}} + \beta. \quad [11]$$

They also found that $\alpha = 0.0075$ and $\beta = 1$.

Introducting Eq. [11] into Eq. [10] it is possible to obtain the so-called equation of state for the interfacial free energy (17):

$$\gamma_{\mathrm{SL}} = \frac{[(\gamma_{\mathrm{S}})^{1/2} - (\gamma_{\mathrm{L}})^{1/2}]^2}{1 - 0.015(\gamma_{\mathrm{S}}\gamma_{\mathrm{L}})^{1/2}}. \quad [12]$$

Now we assume that Eqs. [4], [8] and [12] are true and comparable. In such case from Eqs. [4] and [12] results that

$$\gamma_{\mathrm{SL}} = 133.3333\left[1 - \frac{(\gamma_{\mathrm{S}}^{\mathrm{d}}\gamma_{\mathrm{L}}^{\mathrm{d}})^{1/2} + (\gamma_{\mathrm{S}}^{\mathrm{n}}\gamma_{\mathrm{L}}^{\mathrm{n}})^{1/2}}{(\gamma_{\mathrm{S}}\gamma_{\mathrm{L}})^{1/2}}\right]. \quad [13]$$

Combining Eq. [8] with [12], yields:

$$\gamma_{\mathrm{SL}} = 133.3333\left[1 - \frac{\begin{array}{c}(\gamma_{\mathrm{S}}^{\mathrm{LW}}\gamma_{\mathrm{L}}^{\mathrm{LW}})^{1/2} \\ + (\gamma_{\mathrm{S}}^{+}\gamma_{\mathrm{L}}^{-})^{1/2} + (\gamma_{\mathrm{S}}^{-}\gamma_{\mathrm{L}}^{+})^{1/2}\end{array}}{(\gamma_{\mathrm{S}}\gamma_{\mathrm{L}})^{1/2}}\right]. \quad [14]$$

Knowing the correlation between γ_{SL} and γ_{S} and γ_{L} and their components, the Young's equation can be solved against the surface free energy components of the solid or its total surface free energy.

Thus introducing Eq. [4] into Eq. [1] or [8] into [1] or [12] into [1], respectively, gives

$$\gamma_{\mathrm{L}}(\cos\theta_{\mathrm{L}} + 1) + \Pi e_{\mathrm{L}} = 2(\gamma_{\mathrm{S}}^{\mathrm{d}}\gamma_{\mathrm{L}}^{\mathrm{d}})^{1/2} + 2(\gamma_{\mathrm{S}}^{\mathrm{n}}\gamma_{\mathrm{L}}^{\mathrm{n}})^{1/2} \quad [15]$$

$$\gamma_{\mathrm{L}}(\cos\theta_{\mathrm{L}} + 1) + \Pi e_{\mathrm{L}} = 2(\gamma_{\mathrm{S}}^{\mathrm{LW}}\gamma_{\mathrm{L}}^{\mathrm{LW}})^{1/2} + 2(\gamma_{\mathrm{S}}^{+}\gamma_{\mathrm{L}}^{-})^{1/2} + 2(\gamma_{\mathrm{S}}^{-}\gamma_{\mathrm{L}}^{+})^{1/2} \quad [16]$$

$$\gamma_{\mathrm{S}} - \frac{[(\gamma_{\mathrm{S}})^{1/2} - (\gamma_{\mathrm{L}})^{1/2}]^2}{1 - 0.015(\gamma_{\mathrm{S}}\gamma_{\mathrm{L}})^{1/2}} = \gamma_{\mathrm{L}}\cos\theta_{\mathrm{L}} + \Pi e_{\mathrm{L}}. \quad [17]$$

If the Πe_{L} value is known it is possible to determine, from Eq. [15] the surface free energy components of a solid from the measurements of the contact angle of two liquids by solving a system of two equations in the unknowns $\gamma_{\mathrm{S}}^{\mathrm{d}}$ and $\gamma_{\mathrm{S}}^{\mathrm{n}}$.

Moreover, introducing into Eq. [16] the contact angle values measured for three different liquids on a given solid surface, the values of $\gamma_{\mathrm{S}}^{\mathrm{LW}}$, γ_{S}^{+} and γ_{S}^{-} can be determined if Πe_{L} is known.

In the case of Eq. [17] the γ_{S} value can be calculated on the basis of the measurement of the contact angle of one liquid only, if the pressure of the liquid film is negligible.

Commonly it is assumed that for such systems for which $\theta_{\mathrm{L}} > 0$ the $\Pi e_{\mathrm{L}} = 0$ (1–15); however, studies carried out by Adamson and co-workers (34, 35) indicate that even on polymeric solids the liquid film can be present and play an important role in the interfacial systems.

EXPERIMENTAL

The cassiterite sample came from Bolivia (Huanuni Mine). The mineralogical specimens of cassiterite were cut into plates, which were polished using abrasive-paper of various grades and by rubbing one plate against other. The composition of the cassiterite plate has been analyzed with the aid of a scanning electron microscope with an elemental microanalysis attachment (Zeiss DSM-950). It shows that the sample has more than 99% of SnO_2 and more than 0.7% of Fe_2O_3, although small traces of other impurities, as Si, B, or Al can be present. Plates were washed several times in doubly distilled and deionized water, cleaned in an ultrasonic bath for 15 minutes, and dried at room temperature or at 110°C for 1 h. These plates are denoted as cassiterite Ia and Ib, respectively.

Before the contact angle measurements the plates dried at room temperature were placed in a closed chamber filled with saturated water vapor, and those dried at 110°C placed in a desiccator with molecular sieves.

After polishing, some plates were boiled in HNO_3 60% for some minutes, then washed several times in doubly distilled and deionized water, cleaned in an ultrasonic bath for 15 min, and then dried at room temperature, or at 110°C for 1 h, or at 200°C for 1 h. These plates are denoted as cassiterite IIa, IIb, and IIc, respectively. A few plates were dried at 200°C for a time longer than 1 h.

TABLE 1

Measured Values of Contact Angle for Water (θ_W), Glycerol (θ_G), Formamide (θ_F), Diiodomethane (θ_D), and Bromoform (θ_B) on the Cassiterite Surface, in Degrees

Plate of cassiterite	θ_W	θ_G	θ_F	θ_D	θ_B
Ia	72	55	44	41	14
Ib	91	72	63	42	18
IIa	0	14	0	39	0
IIb	26	28	12	30	0
IIc	58	47	36	38	0

Note. Ia, plate dried at room temperature. Ib, plate dried at 110°C for 1 h. IIa, plate boiled in the HNO_3 60% and dried at room temperature. IIb, plate boiled in the HNO_3 60% and dried at 110°C. IIc, plate boiled in the HNO_3 60% and dried at 200°C.

The advancing contact angle measurements were made by the sessile drop method (36) using water (doubly distilled and deionized), glycerol anhydrous (Fluka, pure > 99,5%), formamide (Fluka, pure > 99%), diiodomethane (Fluka, pure > 98%), and bromoform (Aldrich, pure > 99%). For each system of solid–liquid–air at least 10 plates were used and the mean value of not less than 30 contact angle determinations was taken for calculations. A good reproducibility was found for contact angle measurements. The standard deviation for each set of values was less than 1.4°.

All measurements were carried out with the aid of a goniometer–camera–computer system made in the physics department (Extremadura University, Spain). This device was checked comparing measurements with those done with a Model 100-00 goniometer (Rame-Hart, Inc.) with a thermostated environment chamber Model 100-07 (Rame-Hart, Inc) at 20 ± 1°C in the physics department (Granada University).

RESULTS

The results obtained from the contact angle measurements are shown in Table 1. From this Table it appears that the contact angle for cassiterite depends on plate preparation before measurements. For each liquid studied the highest contact angle is found for cassiterite Ib, and for this sample the highest value is observed for water (91°) and the lowest for bromoform (18°). In the other hand, water, formamide, and bromoform spread completely over cassiterite IIa surface. In the case of diiodomethane the lowest value of contact angle is measured for cassiterite IIb. For the cassiterite IIb contact angles are comprised between 30° for diiodomethane and 0° for bromoform, and it is interesting to note that for this sample the contact angle for water is lower than for glycerol. It is also worthwhile to emphasize that the contact angle for all polar liquids tested increases in the series of cassiterite: IIa, IIb, IIc, Ia, and Ib.

CALCULATIONS

As the contact angle for cassiterite has been measured for five liquids, there are ten different combinations to calculate the γ_S^d and γ_S^n components from Eq. [15] and the γ_S^{LW}, γ_S^+, and γ_S^- components from Eq. [16]. In the case of Eq. [17] there are five possibilities to calculate γ_S.

It was found by Panzer (5) that when the contact angle values for two apolar or two polar liquids are used for the γ_S^d and γ_S^n estimation the biggest error is occurred. Therefore the calculations of γ_S^d and γ_S^n for cassiterite were made from Eq. [15] from the values of contact angle for apolar–polar pair of liquids only, on the assumption that $\Pi e_L = 0$.

The values of the dispersion (γ_L^d) and nondispersion (γ_L^n) components of the liquid surface tension used in Eq. [15] were taken from literature (1, 15, 19) (Table 2). In Table 3 are shown the values of the cassiterite surface free energy and its components obtained from Eq. [15], labeled with the first letter of each of the two liquids used for its determination. As the contact angle for bromoform on cassiterite IIa, IIb, and IIc is zero, and also the contact angle for water on cassiterite IIa was assumed strictly equal to zero, there are only two combinations of apolar–polar liquids to calculate γ_S^d and γ_S^n for cassiterite IIa, and three for cassiterite IIb and IIc.

From Table 3 it appears that there is a good agreement in most cases, among the γ_S^d and the γ_S^n values obtained from different groups of liquids for cassiterite Ia as well as for Ib.

The γ_S^d values for cassiterite IIa, IIb and IIc calculated from the contact angle of water and diiodomethane are close but the γ_S^n values are higher than those obtained from contact angle for two organic liquids.

The values of the dispersion component for the different cassiterite plates only slightly change but those of the nondispersion component increase in the series of cassiterite samples Ib, Ia, IIc, IIb, and IIa.

Introducing in Eq. [16] the values of γ_L^{LW}, γ_L^+, and γ_L^- for water, glycerol, formamide, diiodomethane, or bromoform, as needed, taken from literature (15, 37) (Table 4), the components of the surface free energy γ_S^{LW}, γ_S^+ and γ_S^- were calculated on the assumption that $\Pi e_L = 0$. In Table

TABLE 2

Values of the Dispersion (γ_L^d) and Nondispersion (γ_L^n) Components of Liquid Surface Tension Taken from the Literature (1, 15, 19)

Liquid	γ_L^d	γ_L^n	γ_L	Ref.
Water	21.8	51	72.8	(1)
Glycerol	34	30	64	(15)
Formamide	39	19	58	(15)
Diiodomethane	50.42	0.38	50.8	(19)
Bromoform	40.55	0.95	41.5	(19)

TABLE 3

Values of the Dispersion (γ_S^d) and Nondispersion (γ_S^n) Components of the Cassiterite Surface Free Energy (γ_S) Calculated from Eq. [15] on the Basis of γ_L^d and γ_L^n Values Taken from the Literature (1, 15, 19), in mJ/m^2

plate of cassiterite	Liquids	γ_S^d	γ_S^n	γ_S	γ_{SW}	$\gamma_{SW}(1)$	$W_A(1)$
Ia	DW	36.49	7.41	43.90	21.41	20.96	95.29
	DG	36.44	7.66	44.10	21.00	20.50	95.90
	DF	36.41	7.80	44.22	20.77	20.24	96.24
	BW	35.99	7.56	43.55	21.06	20.51	95.29
	BG	35.87	7.94	43.81	20.44	19.80	96.17
	BF	35.77	8.24	44.01	19.96	19.26	96.85
Ib	DW	37.82	0.98	38.80	40.03	43.56	71.57
	DG	37.69	1.24	38.92	38.50	41.62	73.23
	DF	37.97	0.71	38.68	41.90	45.92	69.58
	BW	38.60	0.90	39.49	40.73	44.36	71.57
	BG	38.40	1.10	39.50	39.45	42.77	72.85
	BF	39.02	0.52	39.54	43.71	48.05	68.63
IIa	DW	33.65	40.98	74.63	1.83	1.64	145.60
	DG	34.85	27.32	62.17	5.19	4.73	129.78
IIb	DW	38.26	31.74	70.00	4.57	4.24	138.23
	DG	39.72	18.42	58.14	10.79	10.21	120.15
	DF	39.92	16.88	56.80	11.92	11.33	117.68
IIc	DW	36.76	14.70	51.46	12.88	12.02	111.38
	DG	37.30	11.06	48.36	16.63	15.89	104.53
	DF	37.35	10.76	48.10	16.99	16.27	103.92

Note. γ_{SW}, interfacial cassiterite – water free energy calculated from Eq. [4]. $\gamma_{SW}(1)$, interfacial cassiterite – water free energy calculated from Eq. [13]. $W_A(1)$, work of adhesion of water to cassiterite surface calculated from Eq. [18].

5 are shown the values obtained, labeled with the first letter of each of the three liquids used for its determination. For the systems of three liquids including diiodomethane, the calculations of γ_S^{LW}, γ_S^+ and γ_S^- were also made on the assumption that γ_L^+ for diiodomethane is equal zero (Table 6).

For cassiterite IIb and IIc there are only four instead of ten combinations to calculate because their contact angle for bromoform is zero and for cassiterite IIa only were used the values of contact angle for water, glycerol, and diiodomethane, on the assumption that the contact angle for water is strictly equal to zero for this sample.

From Table 5 it appears to be a good agreement among the values of γ_S^{LW}, γ_S^+, and γ_S^- obtained with different groups of liquids for cassiterite IIb and also for cassiterite IIc. For these samples the γ_S^- values are considerably higher than the γ_S^+. In the case of cassiterite Ia, for the groups of liquids in which one of them is polar and two are apolar the γ_S^+ values are higher than the γ_S^- ones and the γ_S^{LW} values obtained are about 2–3 mJ / m^2 higher than those obtained from other groups of liquids.

For cassiterite Ib the values of γ_S^{LW}, γ_S^+, and γ_S^- obtained from FDG, FBG, and FGW strongly differ from those cal-

TABLE 4

Values of the Lifshitz–van der Waals (γ_L^{LW}), Electron Acceptor (γ_L^+) and Electron Donor (γ_L^-) Components of Liquid Surface Tension (γ_L) Taken from the Literature (15, 37), in mJ · m^{-2}

Liquids	γ_L^{LW}	γ_L^+	γ_L^-	γ_L	Ref.
Water	21.8	25.5	25.5	72.8	(15)
Glycerol	34	3.92	57.4	64	(15)
Formamide	39	2.28	39.6	58	(15)
Diiodomethane	50.8	0.72	0	50.8	(37)
Bromoform	41.5	1.72	0	41.5	(37)

TABLE 5

Values of the Components of the Cassiterite Surface Free Energy, Cassiterite–water Interfacial Free Energy and the Work of Adhesion of Water to Cassiterite Surface Calculated from Eqs. [16], [8], and [18], Respectively, in mJ · m^{-2}

Plate of cassiterite	liquids	γ_S^{LW}	γ_S^+	γ_S^-	γ_S^{AB}	γ_S	γ_{SW}	$\gamma_{SW}(1)$	$W_A(1)$
Ia	WDB	37.48	7.15	1.21	5.88	43.36	20.88	20.27	95.28
	GDB	37.48	2.71	1.21	3.62	41.10	29.00	29.85	84.90
	FDB	37.48	2.51	1.21	3.49	40.97	29.49	30.45	84.28
	GDW	35.43	1.97	6.39	7.10	42.53	20.04	19.17	95.29
	FDW	35.44	1.99	6.35	7.11	42.55	20.06	19.19	95.29
	GBW	33.95	2.23	6.53	7.63	41.58	19.08	17.86	95.30
	FBW	34.05	2.34	6.30	7.68	41.73	19.24	18.08	95.29
	FDG	35.58	2.03	5.85	6.89	42.47	20.75	20.01	94.52
	FBG	35.16	2.40	4.19	6.34	41.50	22.61	22.12	91.69
	FGW	35.70	1.93	6.36	7.01	42.71	20.21	19.40	95.30
Ib	WDB	37.33	0.33	0.73	0.98	38.31	39.63	43.09	71.48
	GDB	37.33	0.36	0.73	1.03	38.36	39.41	42.83	71.74
	FDB	37.33	0.19	0.73	0.74	38.07	40.79	44.58	70.09
	GDW	37.39	0.37	0.67	1.00	38.39	39.68	43.16	71.51
	FDW	37.06	0.17	1.09	0.86	37.92	39.17	42.54	71.56
	GBW	37.42	0.37	0.67	1.00	38.42	39.68	43.16	71.53
	FBW	36.87	0.18	1.09	0.89	37.76	39.03	42.38	71.53
	FDG	32.32	0.00	19.59	0.00	32.32	7.33	-1.07	97.79
	FBG	31.23	0.11	11.69	0.27	33.50	16.23	11.75	90.07
	FGW	28.66	1.33	0.96	2.26	30.92	32.19	32.82	71.53
IIa	GDW[a]	30.12	5.03	50.38	31.84	61.96	-10.83	-11.18	145.59
IIb	GDW	34.49	2.99	42.63	22.58	57.07	-8.38	-9.65	138.25
	FDW	34.48	2.96	42.72	22.49	56.97	-8.45	-9.75	138.22
	FDG	34.33	2.91	44.14	22.67	57.00	-9.24	-10.56	139.04
	FGW	34.21	3.04	42.71	22.79	57.00	-8.43	-9.72	138.23
IIc	GDW	34.65	2.28	16.62	12.31	46.96	8.37	6.33	111.39
	FDW	34.67	2.31	16.52	12.35	47.02	8.44	6.42	111.38
	FDG	34.90	2.36	15.24	11.99	46.89	9.59	7.70	110.11
	FGW	35.08	2.20	16.56	12.07	47.15	8.56	6.59	111.39

[a] Values of γ_S^{LW}, γ_S^+ and γ_S^- calculated from Eq. [5] under assumption that θ_W is strictly equal to zero.

culated from WDB, GDB, FDB, GDW, FDW, FBW, and GBW groups of liquids.

The value of γ_S^{LW} increases and those of γ_S^+ and γ_S^- decrease in the series of cassiterite samples IIa, IIb, IIc, Ia, and Ib. It is worthwhile to note the very low values of γ_S^+ and γ_S^- for cassiterite Ib. However, if we assumed that γ_L^+ for diiodomethane is equal to zero the values of γ_S^{LW} for the studied cassiterite samples change in quite different way. As it is seen from Table 6 in this case the γ_S^{LW} value increases in the series Ib, Ia, IIa, IIc, and IIb. For the FDG group of liquids there is not solution of Eq. [16] against γ_S^+ and γ_S^- for cassiterite Ib, IIb, and IIc. For a given cassiterite sample it is observed significant differences among the γ_S^+ and the γ_S^- values. Comparing the values of γ_S^{LW}, γ_S^+ and γ_S^- presented in Tables 5 and 6 for the same cassiterite sample a big disagreement is evident. However, in many cases the γ_S values differ no more than 1–2 mJ/m^2 and they are quite similar to those obtained from Eq. [15] (Table 3).

It is possible from Eq. [17] to plot the relationship between γ_S and θ_L for a given value of γ_L on the assumption that $\Pi e_L = 0$. Such graphical representation is shown in Fig. 1 for the γ_L values of water, glycerol, formamide, diiodomethane and bromoform. From this figure it appears that Eq. [17] behaves in a quite different way for water and for organic liquids. If the contact angle of water ranges between 17.5 and 65.2° the equation has not solution for γ_S.

The values of the total surface free energy obtained from Eq. [17] from the measurements of contact angle of water, glycerol, formamide, diiodomethane, and bromoform are listed in Table 7. In the case of cassiterite IIb and IIc, as their contact angle with water are 26 and 58°, only approximated values are listed. From Table 7 it appears that there are big

TABLE 6

Values of the Components of the Cassiterite Surface Free Energy Calculated from Eq. [16], in mJ · m^{-2} on the Assumption That $\gamma_D^+ = 0$ and the Cassiterite–Water Interfacial Free Energy and the Work of Adhesion of Water to Cassiterite Surface Calculated from Eqs. [8] and [18], Respectively

Plate of cassiterite	liquids	γ_S^{LW}	γ_S^+	γ_S^-	γ_S^{AB}	γ_S	γ_{SW}	$W_A(1)$
Ia	WDB	39.10	10.21	0.21	2.93	42.03	19.54	95.29
	GDB	39.10	2.94	0.21	1.57	40.67	33.14	80.34
	FDB	39.10	2.59	0.21	1.47	40.57	34.10	79.27
	GDW	39.10	1.42	6.07	5.87	44.97	22.46	95.31
	FDW	39.10	1.22	6.49	5.63	44.73	22.25	95.28
	FDG	39.10	0.18	29.08	4.58	43.68	-0.66	117.34
Ib	WDB	38.59	0.97	0.13	0.71	39.30	40.50	71.60
	GDB	38.59	0.43	0.13	0.47	39.06	43.59	68.27
	FDB	38.59	0.20	0.13	0.32	38.91	45.54	66.17
	GDW	38.59	0.29	0.64	0.86	39.45	40.72	71.53
	FDW	38.59	0.08	1.12	0.60	39.19	40.43	71.55
	FDG	38.59	3.40[b]	98.32	-	-	-	-
IIa	GDW[a]	40.11	2.69	47.90	22.70	62.81	-9.99	145.60
IIb	GDW	44.22	1.37	40.55	14.91	59.13	-6.30	138.23
	FDW	44.22	0.87	43.63	12.32	56.54	-8.89	138.23
	FDG	44.22	[b] 1.11	221.21	-	-	-	-
IIc	GDW	40.60	1.35	15.80	9.24	49.84	11.26	111.38
	FDW	40.60	1.06	16.85	8.45	49.05	10.56	111.36
	FDG	40.60	[b] 0.007	76.38	-	-	-	-

[a] Values of γ_S^{LW}, γ_S^+ and γ_S^- calculated from Eq. [16] under the assumption that θ_W is strictly equal to zero.

[b] Negative square root.

differences among the γ_S values for the same cassiterite sample. For cassiterite IIa, IIb, and IIc, the γ_S values obtained from the contact angles for polar liquids are higher than from diiodomethane. In the case of cassiterite Ib the γ_S values obtained from contact angles for polar liquids are lower than those from the apolar ones. For cassiterite Ia the γ_S values obtained from θ_D and θ_B are almost the same and about 5 mJ/m^2 lower than those from θ_W, θ_G, and θ_F. The γ_S values increase in the series of cassiterite Ib, Ia, IIc, IIb, and IIa.

Using the components of the cassiterite surface free energy determined in the above-described ways, the values of the interfacial free energy of cassiterite–water (γ_{SW}) were calculated from the Eqs. [4] and [8] and presented in Tables 3, 5, and 6, respectively. This energy was also evaluated from the equation of state (Eq. [12]), and the values obtained listed in Table 7.

It is seen that using the geometric mean approach (1–4) (Table 3) for a given cassiterite sample very similar results for γ_{SW} are obtained. These values increase in the series of cassiterite IIa, IIb, IIc, Ia, and Ib. In the case of the van Oss and co-workers (10–15) approach (Table 5) the γ_{SW} values for cassiterite IIa and IIb are negative and for cassiterite Ia, Ib, and IIc positive and close to those in Table 3. If for the evaluation of γ_{SW} in Eq. [8] were used the values of γ_S^{LW}, γ_S^+, and γ_S^- from Eq. [16] on the assumption that $\gamma_L^+ = 0$ for diiodomethane (Table 6), the value of γ_{SW} for a given system is different than that obtained in the case $\gamma_L^+ = 0.72$ mJ/m^2 for diiodomethane (Table 5); however, in both circumstances γ_{SW} increases for the cassiterite series IIa, IIb, IIc, Ia, and Ib in the same direction.

The values of γ_{SW} determined from the equation of state (Eq. [12]) (16–18) (Table 7) in many cases differ from those obtained using the geometric mean (1–4) or the van Oss and co-workers (10–15) approaches (Tables 3, 5, and 6). Even the direction of the γ_{SW} changes for the studied series of cassiterite differs from those from geometric and van Oss and co-workers (10–15) approaches.

To compare the geometric mean (1–4) and the van Oss

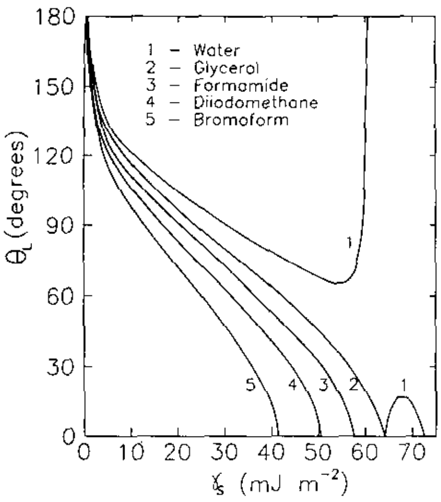

FIG. 1. Relationship between contact angle (θ_L) for water, glycerol, formamide, diiodomethane, and bromoform and the solid surface free energy (γ_S) calculated from Eq. [17] on the assumption that $\Pi e_L = 0$.

and co-workers (10–15) approaches with the equation of state (16–18), the calculations of $\gamma_{SW}(1)$ values from Eqs. [13] and [14] were made and the results are shown in Tables 3 and 5, respectively. From these Tables it appears that for cassiterite Ia, IIa, IIb, and IIc the $\gamma_{SW}(1)$ values do not differ, in most cases, more than 1 mJ/m^2 from those calculated from Eqs. [4] and [8], respectively. However, for cassiterite Ib the differences between the values of γ_{SW} and $\gamma_{SW}(1)$ are larger (more than 3 mJ/m^2).

From the data of γ_S and γ_{SW} achieved from the three aforementioned approaches to the interfacial free energy, the work of adhesion of water to cassiterite surface ($W_A(1)$) was also calculated from the equation:

$$W_A = \gamma_S + \gamma_W - \gamma_{SW}, \qquad [18]$$

where the W subscript refers to water.

The resulting values are listed in Tables 3 and 5–7. The work of adhesion of water to the cassiterite surface ($W_A(2)$) was also evaluated from

$$W_A = \gamma_L(\cos\theta_L + 1). \qquad [19]$$

The $W_A(2)$ values from Eq. [19] are also included in Table 7.

Of course, it is understandable that when $W_A(1)$ is calculated from Eq. [18] on the basis of the γ_S and γ_{SW} values derived from the measurements of the contact angles of systems of liquids including water, it must be the same as $W_A(2)$ when determined from Eq. [19]. However, in the case of the $W_A(1)$ values obtained on the basis of the equation of state for cassiterite IIb and IIc there is a small difference with those of $W_A(2)$ because the γ_S values were approximately determined (Table 7).

From Table 3 it appears that there is a good agreement for cassiterite Ia and Ib between all the values of $W_A(1)$. But for cassiterite IIa, IIb, and IIc the $W_A(1)$ obtained from the γ_S and γ_{SW} values evaluated from systems of organic liquids are considerably lower than those determined from water-organic systems.

For the $W_A(1)$ presented in Table 5 there is a good accordance for cassiterite IIb and IIc but larger differences for cassiterite Ia and Ib are noticed.

On the basis of the data in Table 6 it is difficult to make any comparison because there are no $W_A(1)$ values for those systems including only organic liquids for cassiterite IIa, IIb, and IIc. For the case of cassiterite Ia and Ib large differences are observed.

Using the γ_S and γ_{SW} data obtained from the equation of state for the $W_A(1)$ determination the largest differences are observed among them (Table 7).

DISCUSSION

Correlation between Geometric Mean, van Oss and Co-Workers, and Neumann and Co-Workers Approaches

TABLE 7

Values of the Surface Free Energy of Cassiterite, Interfacial Free Energy of Cassiterite–Water and Work of Adhesion of Water to Cassiterite Surface Calculated from Eqs. [17], [12], [18], and [19], Respectively, in mJ/m^2

Plate of cassiterite	Liquid	γ_S	γ_{SW}	W_A (1)	W_A (2)
Ia	W	45.77	23.27	95.30	95.30
	G	45.17	23.47	94.50	
	F	45.17	23.47	94.50	
	D	40.25	25.46	87.59	
	B	40.29	25.44	87.65	
Ib	W	29.97	31.23	71.54	71.53
	G	34.85	28.27	79.38	
	F	35.15	28.10	79.85	
	D	39.81	25.67	86.94	
	B	39.53	25.80	86.53	
IIa	W	72.80	0.00	145.60	145.60
	G	62.31	−39.73	174.84	
	D	41.11	25.07	88.84	
IIb	W	67.50[a]	−1.94	142.24	138.23
	G	58.16	34.27	96.69	
	F	56.78	27.92	101.66	
	D	44.68	23.63	93.85	
IIc	W	54.50[a]	23.97	103.33	111.38
	G	49.58	22.50	99.88	
	F	48.87	22.57	99.10	
	D	41.53	24.88	89.45	

[a] Approximated value.

The determination of the solid surface free energy from contact angle measurements, in many cases, independently of the method used, can be very difficult because the presence of a liquid film can influence the surface free energy of a given solid. Many authors (1–15) have assumed for the calculation of γ_S from the Young's equation that $\Pi e_L = 0$ suggesting that when $\gamma_L \geqslant \gamma_S$, the presence on the solid surface of a liquid film does not change its surface free energy. However, the studies carried out by Adamson and co-workers (34, 35) indicate that the negligence of the Πe_L value for the calculation of γ_S can be insecure even for such solids as polymers. There are some proofs that the presence of a film of liquid on the solid surface can not only decreases but also increases its surface free energy (17, 38).

The presence of a water film on the cassiterite surface can change the true picture of its surface free energy because in all the calculations of this energy or its components we have assumed that $\Pi e_L = 0$. Such a situation is possible for the cassiterite samples treated before measurements of contact angle by HNO_3 60% (cassiterite IIa, IIb, and probably IIc), and for which we observe different values for γ_S^n (Table 3) depending if it was calculated from data of contact angle obtained from organic-water or two organic pairs of liquids. The same conclusion can be drawn out on the basis of the γ_S values determined using the Neumann and co-workers (16–18) approach to the interface solid–liquid free energy (Table 7).

In the case of the van Oss and co-workers (10–15) approach it is impossible to say anything about the surface free energy components of cassiterite IIa, IIb, and IIc because there is only one system of three liquids for cassiterite IIb and IIc and no system for cassiterite IIa without water whose contact angle were used for the γ_S^{LW}, γ_S^+, and γ_S^- calculation (Tables 5 and 6).

The influence of a water film on the obtained results of the surface free energy of the cassiterite samples can be displayed in Figs. 2a–2d. Figure 2a shows the equilibrium state of the system cassiterite–liquid drop–air in which the water film is not present. It is probable that this case describes the equilibrium state of systems as cassiterite Ib, and for which no differences among the γ_S^n values are observed. In Fig. 2b, the water film is present on cassiterite surface under and around the liquid drop but its pressure is the same in both sides. This picture is quite possible for systems as cassiterite Ia and IIc for which only slightly differences among the γ_S^d and γ_S^n values obtained from contact angles for different systems of liquids are observed. However, Figs. 2c or 2d can describe the equilibrium state of cassiterite IIa and IIb. The Fig. 2c represents a system in which the film of water is present on the surface under and around the liquid drop but the change of the surface free energy of cassiterite is different in both positions. Finally, Fig. 2d is a plot of a system in which water film is only present around the liquid drop.

It is possible that the liquids used for the contact angle measurements interact with water film in different ways. The polar molecules of glycerol and formamide can penetrate into water film but in the case of diiodomethane and bromoform their apolar molecules probably do not penetrate into the film. A quite different problem exists for water because for solids for which the work of adhesion of water to its surface is lower than the work of water cohesion it is possible the case described by Fig. 2d happens; i.e., the water film "practically" exists on cassiterite surface only around the water drop. We described such a situation in an earlier paper (39).

The above discussion does not explain quantitatively the influence of a water film on the contact angle value for a given liquid, however, indicates that the presence of a water film can make that the equilibrium state of the system cas-

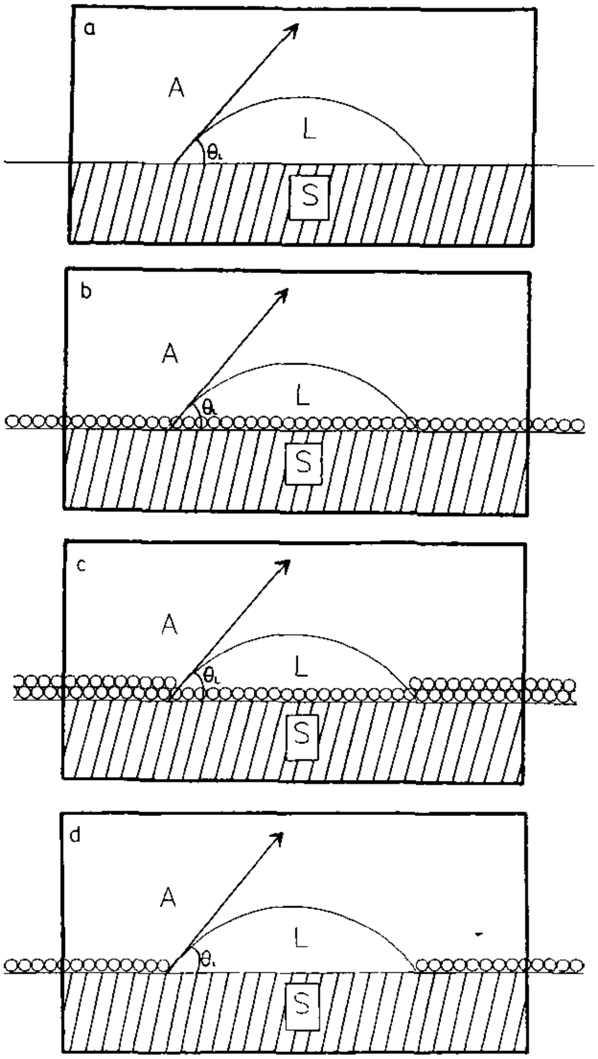

FIG. 2. Schemata of the equilibrium state of the system solid–liquid drop–air: (a) The liquid film is not present on the solid surface. (b) The liquid film is present on the solid surface around and under the liquid drop but its pressure is the same. (c) The liquid film is present on the solid surface around and under the liquid drop but its pressure is not the same. (d) The liquid film is present on the solid surface around the liquid drop.

siterite–liquid drop–air for each studied liquid can be expressed by different conditions. Therefore probably the disagreement among the γ_S^n or γ_S^{LW}, γ_S^+, and γ_S^- values calculated using different systems of liquids for the same cassiterite sample are observed. However, the divergence can also results from the values of γ_L^d and γ_L^n or γ_L^{LW}, γ_L^+ and γ_L^-. According to our discussion in the Theory section, for the calculation of γ_S^d and γ_S^n values the γ_L^d and γ_L^n values for glycerol and formamide were taken the same as γ_L^{LW} and γ_L^{AB} ones. These γ_L^{LW}, γ_L^+ and γ_L^- values were determined by van Oss *et al.* (15) from the measurements of the contact angle of glycerol and formamide on different solid surfaces including those for which water film can be present, which differ from those obtained from interfacial liquid–liquid tensions measurements (40).

The influence of the accuracy of a given component of the liquid surface tension on the calculated γ_S^{LW}, γ_S^+ and γ_S^- values can be seen from the comparison of their values for a given cassiterite sample. Because van Oss and co-workers (26) suggest that the small γ_D^+ value for diiodomethane can be neglected for γ_S^{LW}, γ_S^+, and γ_S^- calculation we have determined these values in both ways using $\gamma_D^+ = 0$ and $\gamma_D^+ = 0.72$ mJ/m^2 (Tables 6 and 5, respectively). The last value was determined earlier (37) from water-diiodomethane interfacial tension (29).

On the basis of the data presented in Tables 5 and 6 we can say that the small value of $\gamma_D^+ = 0.72$ mJ/m^2 plays an important role in γ_S^{LW}, γ_S^+, and γ_S^- calculations. The values of γ_S^{LW} for a given cassiterite obtained from $\gamma_D^+ = 0$ are 20–30% higher than those from $\gamma_D^+ = 0.72$ mJ/m^2 and they change in quite different direction in the series of cassiterite samples studied here. There are also some differences among the γ_S^+ and γ_S^- values determined in both ways. It is interesting to note that despite of such big differences among the γ_S^{LW}, γ_S^+, and γ_S^- values obtained by those two ways there is agreement between the γ_S values (Tables 5 and 6).

There is also agreement between some values of γ_S for the same cassiterite sample obtained from different approaches to solid and solid–liquid interface free energy, it is clearly seen from Table 8 where the average values of γ_S, γ_{SW}, $\gamma_{SW}(1)$, and $W_A(1)$ are shown. In the case of the cassiterite Ia, Ib, and IIc the γ_S values obtained using different approaches are almost the same; however, for cassiterite IIa and IIb the values of γ_S determined on the basis of the geometric mean approach are higher than those from contact angle using the van Oss and co-workers (10–15) and the Neumann and co-workers (16–18) approaches.

TABLE 8
Average Values of γ_S, γ_{SW}, and W_A (1)

Plate of cassiterite		γ_S	γ_{SW}	γ_{SW} (1)	W_A (1)
Ia	g–g	43.93	20.77	20.21	95.96
	O_1 (a)	42.05	22.14	21.64	92.71
	(b)	42.10	19.61		95.3
	O_2 (a)	42.77	21.81		93.81
	(b)	42.59	26.30		89.10
	N	43.33	24.22		91.91
Ib	g–g	39.16	40.72	44.38	71.24
	O_1 (a)	36.40	33.31	34.52	75.88
	(b)	38.12	39.39		71.53
	O_2 (b)	39.18	42.16		69.82
	N	35.86	27.81		80.85
IIa	g–g	68.40	3.51	3.19	137.69
	O_1	61.96	−10.83	−11.18	145.59
	O_2	62.81	−9.99		145.60
	N	58.74	−4.89		136.43
IIb	g–g	61.65	9.09	8.59	125.35
	O_1 (a)	57.01	−8.63	−9.92	138.44
	(b)	57.02	−8.42		138.23
	O_2 (b)	57.84	−7.60		138.23
	N	56.78	20.97		108.61
IIc	g–g	49.31	15.50	14.73	106.61
	O_1 (a)	47.01	8.74	6.76	111.07
	(b)	46.99	8.41		111.39
	O_2 (b)	49.45	10.91		111.37
	N	48.62	23.48		97.94

Note. g–g, geometric mean approach (1–4). O_1, van Oss and co-workers (10–15) approach; $\gamma_D^+ = 0.72$ mJ/m^2. O_2, van Oss and co-workers (10–15) approach; $\gamma_D^+ = 0$. N, Neumann and co-workers (16–18) approach.

In the case of the van Oss and co-workers (10–15) approach the two set of average values are presented for a given cassiterite with exception of cassiterite IIa for which only one value is determined using the contact angle for the GDW system. The "a" set of values deals with the average values calculated from all the possible combination of three liquids for a given sample. Moreover the "b" set of values deals with the average values for the WDG, WBG, WDF, WBF, and FGW systems. The results of γ_S^{LW}, γ_S^+, and γ_S^- calculated from these latter systems are encumbered with the lowest error (41).

The agreement among the γ_S values obtained by different methods does not mean that all approaches are useful in the same way for the surface free energy determinations. A measure of the usefulness of a given approach can be done for its capacity to predict for example the solid–liquid interface free energy and the work of liquid adhesion to the solid surface.

Generally, we can say that the γ_{SW} values for cassiterite Ia–water and for cassiterite Ib–water calculated on the basis of the γ_S^d and γ_S^n values are close to those obtained from the γ_S^{LW}, γ_S^+, and γ_S^- values; however, the γ_{SW} values determined from the equation of state [12] are different (Tables 3 and 5–8). For cassiterite IIa–water and cassiterite IIb–water the values of γ_{SW} obtained by different methods show the biggest discrepancy. The γ_{SW} values obtained from Eqs. [8] and [12] for these systems are negative.

The possibility to obtain negative values for the interface free energy between two phases being in contact is the main argument of van Oss and co-workers (10–15) to state that the geometric mean approach is "incorrect."

However, it is very difficult to understand how negative values can be obtained for the interfacial free energy with water for a nonsoluble mineral as cassiterite but perhaps it could be explained if a water film was present on the cassiterite surface. In such case the value of the free energy obtained could refer to the interfacial free energy of cassiterite/water film–water system instead of the cassiterite–water one. It must be emphasized that the negative values of γ_{SW} for cassiterite IIb–water system are obtained from Eq. [8] in all the possible cases but from Neumann equation (Eq. [12]) only when the γ_S value determined from θ_W is employed. However, as this value of γ_W gives only an approximated value of γ_S for cassiterite IIb (see Fig. 1) it is very difficult to discuss about the negative value of γ_{SW} for the cassiterite IIb–water interface calculated from the Neumann and co-workers (16–17) approach.

A negative value of a solid–liquid interface exists when the two phases being in contact are highly mutual soluble. Thus a question can be raised, is it possible to determine the interfacial free energy for two mutual saturated phases being in contact from parameters dealing with the "pure" phases? On the other hand, can the van Oss and co-workers (10–15) approach "work well" in the case of highly mutual soluble phases? The same question can be raised for the geometric mean (1–4) and the Neumann and co-workers (16–18) approaches. However, on the basis of the data presented here it is impossible to solve this problem.

Despite the Neumann and co-workers approach (16–18) (Eq. [12]) does not give the same results for the prediction of γ_{SW} and W_A (Table 8) as the geometric mean (1–4) and the van Oss and co-workers (10–15) approaches it can be interesting to explain why the γ_{SW} values are close to the $\gamma_{SW}(1)$ ones calculated from Eqs. [13] and [14], respectively. Therefore for this purpose the dependence between ϕ and γ_{SL} were analyzed. From comparison of Eq. [4] and Eq. [10]

$$\phi = \frac{(\gamma_S^d \gamma_L^d)^{1/2} + (\gamma_S^n \gamma_L^n)^{1/2}}{(\gamma_S \gamma_L)^{1/2}} = f[\gamma_S + \gamma_L - 2(\gamma_S^d \gamma_L^d)^{1/2} - 2(\gamma_S^n \gamma_L^n)^{1/2}] \quad [20]$$

and also from comparison of Eq. [8] and Eq. [10]

$$\phi = \frac{(\gamma_S^{LW} \gamma_L^{LW})^{1/2} + (\gamma_S^+ \gamma_L^-)^{1/2} + (\gamma_S^- \gamma_L^+)^{1/2}}{(\gamma_S \gamma_L)^{1/2}} = f[\gamma_S + \gamma_L - 2(\gamma_S^{LW} \gamma_L^{LW})^{1/2} - 2(\gamma_S^+ \gamma_L^-)^{1/2} - 2(\gamma_S^- \gamma_L^+)^{1/2}] \quad [21]$$

The calculations were made for γ_S^d in the range of 20–40 mJ/m^2 because most of the experimental data found in literature (1, 24) and our own results lay in this interval and γ_S^n from 0 to $\gamma_L - \gamma_S^d$ and for γ_S^{LW} in the range of 20–40 mJ/m^2 and γ_S^{AB} from 0 to $\gamma_L - \gamma_S^{LW}$ and $\gamma_S^{AB} = 2(\gamma_S^+ \gamma_S^-)^{1/2}$ where γ_S^+ was ranged from 10 to 50% of γ_S^{AB}. The above limitation includes practically the γ_S value calculated by Neumann and co-workers (16–18). The values of α and β (see Eq. [11]) calculated from Eqs. [20] and [21], respectively the standard deviation (S) and the regression coefficient (r) for each of the five liquids used by us are presented in Table 9. Also these former parameters were calculated for all data for all liquids together, and the resulting equations are, from Eq. [20]

$$\phi = -0.00846\gamma_{SL} + 1.00745. \quad [22]$$

Being the standard deviation $S = 0.000426$ and the regression coefficient $r = 0.962$.

In the case of computing from Eq. [21] we obtain the relationship:

$$\phi = -0.00811\gamma_{SL} + 1.00925 \quad [23]$$

with an standard deviation of $S = 0.000518$ and a regression coefficient of $r = 0.964$.

TABLE 9

Values of α and β in Eq. [11] Determined from Eqs. [20] and [21], Respectively

	From Eq. [20]				From Eq. [21]			
Liquid	α	β	r	S	α	β	r	S
W	0.00807	1.0142	0.987	0.000227	0.00737	1.0128	0.985	0.000327
G	0.00805	1.0101	0.966	0.000204	0.00725	1.0158	0.956	0.000263
F	0.00808	1.0079	0.933	0.000172	0.00755	1.0159	0.921	0.000243
D	0.01112	1.0158	0.987	0.000148	0.01094	1.0127	0.989	0.000120
B	0.01315	1.0089	0.986	0.000076	0.01319	1.0085	0.985	0.000087

Note. W, water; G, glycerol; F, formamide; D, diiodomethane; B, bromoform; r, regression coefficient; S, standard deviation.

These equations slightly differ from that obtained by Neumann *et al.* (17) on the basis of contact angle measurements made by Zisman and co-workers (31–33, 42):

$$\phi = -0.00784\gamma_{SL} + 1.004. \qquad [24]$$

In the case of three polar liquids (Table 9) the values of α and β obtained from Eqs. [22] and [23] are near the same than those of Eq. [24]. Therefore, if $\Pi e_L = 0$, using geometric mean (1–4) and van Oss and co-workers (10–15) approaches to determine the surface free energy components on the basis of contact angle measurements, for many cases, we should obtain near the same values of the total surface free energy of a given solid. The agreement between Eqs. [22], [23], and [24] also explains the concordant values of γ_{SW} and $\gamma_{SW}(1)$ previously obtained. These statements are confirmed by the results shown in Tables 3 and 5.

It also confirms conclusions which have been written earlier (19, 20) that on the basis of the approaches to the surface free energy taking into account its division into components we can obtain some constant values being function of a given kind of intermolecular interactions but they do not quite result from these interactions which "work well" in some systems (19, 20). Of course, it also can be stated that practically for the liquids used it should be probable to find a slightly different "constant" value in the so-called state equation and then for water there is not solution against γ_S in the range of contact angle values from 17.5 to 65.2 and therefore we can stated that not only the accuracy (18) of the contact angle measurements are the origin of errors in the determination of the γ_S values using the equation of state (16–18).

The Influence of Water on Cassiterite Surface Free Energy

Among the approaches discussed above, the geometric mean (1–4) and the van Oss and co-workers approach (10–15) seem to have a similar usefulness for the determination of the cassiterite surface free energy components; however, we will discuss this energy and its components only on the basis of, for example, the van Oss and co-workers (10–15) approach, but of course, only for the γ_S^{LW}, γ_S^+, γ_S^- values obtained from $\gamma_D^+ = 0.72$ mJ/m^2.

The surface free energy for dry cassiterite (sample named cassiterite Ib) results mainly from Lifshitz–van der Waals interactions, which, as mentioned above, arise from dispersion, dipole–dipole, and induced dipole–dipole interactions. Van Oss and co-workers (14) suggest that contributions from dipole–dipole and induced dipole–dipole interactions are small. Therefore, only dispersion forces seem to play an important role in the surface properties of this sample. The very low values of the γ_S^+ and γ_S^- components of surface free energy for cassiterite Ib indicate the presence of weak acid–base interactions, probably coming from the presence on the surface of adsorbed water molecules or impurities. Unfortunately the influence of impurities on the surface properties of dry cassiterite can not be quantitatively estimated on the basis of an elemental microanalysis.

However, we can state that only 1% of impurities are present in the cassiterite used for measurements and they probably possess only a slight influence on the surface free energy of cassiterite. Of course it depends on the structure of cassiterite together with impurities.

Water molecules adsorbed on cassiterite influence particularly the acid–base component of the surface free energy. As it can be seen from Table 5, for cassiterite Ia which was dried at room temperature and kept in a chamber filled with saturated water vapor before measurements, the values of γ_S^+ and γ_S^- increase in reference to cassiterite Ib and simultaneously γ_S^{LW} decreases. The surface properties of tin and other metal oxides that could be present in the structure of cassiterite are strongly changed by acids and alkalis. Under influence of HNO_3, hydroxo-complex of tin can be created:

$$SnO_2 + nH_2O + H^+ \Rightarrow [Sn(OH)_3(OH_2)_{n-1}]^+.$$

Washing and cleaning in water in an ultrasonic bath, leads to

$$[Sn(OH)_3(OH_2)_{n-1}]^+ + OH^- \Rightarrow Sn(OH)_4(OH_2)_{n-1}.$$

This kind of compound is probably present on the surface of cassiterite IIa. As a consequence, the basic component of the surface free energy for this sample rises up to 50.4 mJ · m^{-2} against the value of 0.7 mJ · m^{-2} found for dry cassiterite (cassiterite Ib) and the γ_S^{LW} component decreases about 7 mJ · m^{-1} in reference to cassiterite Ib. Also it is worthwhile to emphasize that the basic component of surface free energy of cassiterite IIa is at least ten times higher than the acid one. These facts are in accordance with results found from other authors who showed that cassiterite after boiling in the HNO_3 acid is quite hydrophilic (43).

It can be interesting to note the similar behavior of cassiterite IIa and other mineral surfaces, as the quartz surface, which has a high affinity for water after being treated in some particular way (44, 45). In this sense, the value of γ_S^{LW} for cassiterite IIa (30.1 mJ/m^2) is quite similar to the γ_S^d value calculated by Fowkes for a quartz surface covered by a monolayer of physisorbed water (30 mJ/m^2). Also Bernett and Zisman (42) found for the system quartz–diiodomethane–air at high relative humidity (95%) a contact angle equal to 37°, quite similar to the contact angle diiodomethane–cassiterite IIa (39°, Table 1). This suggests that when there are OH groups and water molecules on the surface of a given solid, the surface free energy probably does not depend on the kind of mineral but only on the amount of OH groups and water molecules present on the surface.

Drying the cassiterite plate at 110°C (cassiterite IIb) water molecules are desorbed from its surface according to

$$\mathrm{Sn(OH)_4(OH_2)_{n-1} \Rightarrow SnO(OH)_2 + }n\mathrm{H_2O},$$

and then it is observed an increase of the Lifshitz–van der Waals component of the cassiterite free energy and a decrease of the acid and base components. However, the ratio base to acid components is higher than for cassiterite IIa. Raising the temperature brings about an increment of the contact angle for water, glycerol, and formamide but a reduction for diiodomethane (Table 1). The studies of wettability of quartz made by Bernett and Zisman (42) also reported that at low relative humidity the contact angle for diiodomethane on quartz surface is lower than at high humidity.

For the cassiterite sample dried at 200°C (cassiterite IIc) is observed a strong decrease in the γ_S^- component of its surface free energy, from 42.6 to 16.6 $\mathrm{mJ \cdot m^{-2}}$ (see Table 5), but the components γ_S^{LW} and γ_S^+ hardly change. Also, it is observed that plates dried at 200°C for a time longer than one hour show an increase in the contact angle for water from 58° to 77°. This behavior can be related with the fact that $\mathrm{SnO(OH)_2}$, which is present in the cassiterite surface, loses water stepwise between 110°C and 600°C, conducting to a surface with a behavior similar to dry cassiterite (cassiterite Ib). Unfortunately, it is impossible to heat the cassiterite plates at temperatures above 200°C because the plates break up.

On the basis of measurements and calculations done, it can be stated that the wettability of the cassiterite surface strongly depends on the acid–base interactions resulting from the presence of OH groups and coordinate and physically adsorbed water on it. Therefore, natural cassiterite is proved to be one of the most difficult minerals to float.

From the point of view of the flotation process it is important to know the possibilities of the particles of a given solid to aggregate in water. Therefore we will consider the free energy of aggregation of cassiterite particles in water on the basis of its surface free energy components.

Using the Lifshitz–van der Waals and the acid–base components of cassiterite and the surface free energy of water, it is possible to calculate the interaction energy between particles of cassiterite in water.

According to van Oss and co-workers (12, 27), the free energy (ΔG_{SWS}) of interaction between two identical particles of a solid (S) immersed in water (W), can be calculated from

$$\Delta G_{SWS} = -2[(\gamma_S^{LW})^{1/2} - (\gamma_W^{LW})^{1/2}]^2 - 4[(\gamma_S^+\gamma_S^-)^{1/2} + (\gamma_W^+\gamma_W^-)^{1/2} - (\gamma_S^+\gamma_W^-)^{1/2} - (\gamma_S^-\gamma_W^+)^{1/2}]. \quad [25]$$

Thus, introducing into Eq. [25] the previously determined values of the Lifshitz–van der Waals, electron-acceptor and electron-donor components for cassiterite (Table 5) and for water (Table 4), the free energy of interaction in the system cassiterite/water/cassiterite was calculated. For convenience, only values of γ_S^{LW}, γ_S^+, and γ_S^- evaluated from contact angles for water, glycerol, and diiodomethane were used. The ΔG_{SWS} values in the series of cassiterite Ia, Ib, IIa, IIb, and IIc are: −40.07, −79.35, 21.65, 16.75, and −16.74 $\mathrm{mJ/m^2}$. On the basis of these values we can state that cassiterites Ia, Ib, and IIc should aggregate in water. This conclusion was confirmed by experiments. The cassiterite samples not treated by acid and dried at room temperature and at 100°C were aggregated but those treated by $\mathrm{HNO_3}$ 60% and dried at room temperature did not aggregate.

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