

RELATIONSHIP BETWEEN HEAT OF IMMERSION AND SURFACE GIBBS ENERGY OF FLUORITE AND CASSITERITE

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(Received January 17, 1994; in revised form November 11, 1994)

Abstract

Calorimetric measurements were made of the heat of immersion in water of cassiterite that was either untreated or treated with 60% HNO₃. The heats of immersion of cassiterite and fluorite were also calculated theoretically from the surface Gibbs energy components, and compared with the heat of immersion measured for cassiterite and that taken from the literature for fluorite. The results of the measurements and calculation revealed that the heat of immersion depends on the degree of hydration of the surface of cassiterite and fluorite. It was also found that it is possible to predict the heats of immersion in water of cassiterite and fluorite from the Lifshitz-van der Waals and acid-base components of the surface Gibbs energy.

Keywords: calorimetry, heat of immersion, surface Gibbs energy

Introduction

One of the most important parameters influencing the phenomena taking place at solid-liquid and solid-gas interfaces is the surface Gibbs energy of the solid involved; hence, a knowledge of this parameter is extremely useful as concerns the prediction of material processes and properties. However, accurate determination of surface and interfacial energies is not an easy task because of various theoretical and experimental difficulties.

The experimental methods for measuring the surface Gibbs energies of solids can be classified into two broad categories: mechanical and thermodynamic. The mechanical method includes techniques such as crack propagation and strain energy release. The thermodynamic method involves procedures such as

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the measurement of contact angles [1–7], zeta potential [8, 9], adsorption [1, 10], heat of adsorption [1] and heat of immersion [1, 11, 12].

Unfortunately, in many cases there are considerable differences between the values of the surface Gibbs energy of a given solid determined by different methods. For example, the surface Gibbs energy of a solid determined by using the method based on contact angle measurements is frequently lower than those obtained from the adsorption isotherm of the vapour of an apolar or polar liquid [13, 14].

The literature affords few tests of the surface Gibbs energy determined from measurements of the heat of immersion. Quite good agreement was found between the values of the surface Gibbs energy of low energetic polymers determined from measurements of the heat of immersion in different liquids and those obtained with the contact angle technique. However, for minerals there are considerable discrepancies between the values of the surface Gibbs energy determined from the heat of immersion and by other methods.

The purpose of this paper, therefore, is to study the relationship between the values of the surface Gibbs energies of fluorite and cassiterite evaluated from measurements of the heat of immersion and from measurements of the contact angle.

Experimental

The cassiterite came from Bolivia (Huanuni Mine) and contained about 0.7% Fe_2O_3 and small traces of other impurities, such as Si, B and Al. The mineralogical specimens of cassiterite were powdered in a ball-mill and sized to a particular fraction. The fraction chosen for measurements of the heat of immersion was 20–40 μm . The specific surface area of the sample was 0.0582 m^2/g , as determined by N_2 adsorption (BET).

The samples of cassiterite were prepared in two different ways prior to measurements. Some were washed several times in doubly distilled and deionized water, cleaned in an ultrasonic bath for 15 minutes and dried at room temperature. Other cassiterite samples were boiled in 60% HNO_3 for a few minutes, then washed several times in doubly distilled and deionized water, cleaned in an ultrasonic bath for 15 minutes and dried at room temperature.

The calorimetric measurements of the heat of immersion of cassiterite in doubly distilled and deionized water were made with an LKB 8700 calorimeter at 293 K, operating as described earlier [15].

Results and discussion

The measured heat of immersion of cassiterite in water indicated that it depends on the mode of preparation of the cassiterite sample. For cassiterite untreated with acid, the heat of immersion in water was found to be zero, within the experimental error, whereas for cassiterite treated with 60% HNO₃ it was 575±72 mJ/m². This lies in the range obtained for fluorite (202–663 mJ/m²) [15–17], and is close to the heats of immersion in water of other oxide minerals [18].

An earlier study [19] demonstrated that 'bare' and 'dry' cassiterite is hydrophobic and its surface Gibbs energy results mainly from Lifshitz–van der Waals intermolecular interactions (Table 1). In response to the action of acids or alkalis, however, strongly hydrated OH groups, with amphoteric properties, are formed on the surface of cassiterite, leading to its surface Gibbs energy arising from both Lifshitz–van der Waals and Lewis acid-base intermolecular interactions [19] (Table 1).

The heat of immersion in water of 'bare' and 'dry' fluorite was measured earlier [15] with the same LKB 8700 calorimeter. Its surface Gibbs energy also results from Lifshitz–van der Waals intermolecular interactions [20], but for the hydrated form of fluorite there is also a contribution from Lewis acid-base interactions.

The degree of hydration of the surface of cassiterite treated with 60% HNO₃ can be assumed to be responsible for the fact that its heat of immersion in water was close to the values obtained for other metal oxides [18]. It should be remembered that all the metal oxides can be easily hydrated and the OH groups determine their surface properties.

It is commonly known that the heat of immersion is connected with the surface Gibbs energy of a solid and a liquid and the interfacial solid–liquid Gibbs energy through the work of immersion [18]:

$$\Delta h_i = - \left(W_1 - T \frac{\partial W_1}{\partial T} \right) \quad (1)$$

where Δh_i is the heat of immersion per unit surface area of the solid and W_1 is the work of immersion, which can be related to the surface Gibbs energy of the solid, γ_s , and to the solid–liquid interfacial Gibbs energy, γ_{sL} , by the equation [18]

$$W_1 = \gamma_s - \gamma_{sL} \quad (2)$$

Recently, van Oss *et al.* divided the surface Gibbs energy of a solid and a liquid into two components, γ^{LW} and γ^{AB} , where γ^{LW} results from Lifshitz–

van der Waals and γ^{AB} from Lewis acid-base intermolecular interactions [7, 21, 22]. The component γ^{AB} can be expressed as a function of the geometric mean of electron-acceptor (γ^+) and electron-donor (γ^-) parts. Thus, the surface Gibbs energy can be written [7, 21, 22] as

$$\gamma = \gamma^{LW} + 2 (\gamma^+ \gamma^-)^{1/2} \quad (3)$$

According to the van Oss *et al.* approach, the following equation can be used in the case of the solid-liquid interfacial Gibbs energy [7, 21, 22]:

$$\gamma_{SL} = \gamma_s + \gamma_L - 2(\gamma_s^{LW} \gamma_L^{LW})^{1/2} - 2(\gamma_s^+ \gamma_L^-)^{1/2} - 2(\gamma_s^- \gamma_L^+)^{1/2} \quad (4)$$

However, Girifalco *et al.* propose a different equation to relate the solid-liquid interfacial Gibbs energy to the surface Gibbs energy of the solid and liquid [23, 24]:

$$\gamma_{SL} = \gamma_s + \gamma_L - 2\phi (\gamma_s \gamma_L)^{1/2} \quad (5)$$

where ϕ is a parameter resulting from different kinds of interfacial interactions.

Introducing Eq. (5) into Eq. (2), we obtain:

$$W_I = -\gamma_L + 2\phi (\gamma_s \gamma_L)^{1/2} \quad (6)$$

Combining Eqs (1) and (6) gives

$$\Delta h_i = \gamma_L - 2\phi (\gamma_s \gamma_L)^{1/2} + T \frac{\partial [2\phi (\gamma_s \gamma_L)^{1/2} - \gamma_L]}{\partial T} \quad (7)$$

Fowkes has shown [1] that the surface Gibbs energies of many solids change only slightly with temperature. Thus, for cassiterite or fluorite it is possible to assume $\partial (\gamma_s)^{1/2} / \partial T \approx 0$. Since ϕ should not depend on temperature either [23, 24], Eq. (7) can be written as

$$\Delta h_s = \gamma_L - 2\phi (\gamma_s \gamma_L)^{1/2} - T \frac{\partial \gamma_L}{\partial T} + 2\phi T (\gamma_s)^{1/2} \frac{\partial (\gamma_L)^{1/2}}{\partial T} \quad (8)$$

Then, in a knowledge of the surface Gibbs energy of the solid and liquid, the parameter ϕ and the dependence of the surface tension of the liquid on temperature, it is possible to calculate Δh_i from Eq. (8).

The parameter ϕ can be evaluated from Eqs (4) and (5):

$$\varphi = \frac{(\gamma_s^{LW} \gamma_L^{LW})^{1/2} + (\gamma_s^+ \gamma_L^-)^{1/2} + (\gamma_s^- \gamma_L^+)^{1/2}}{(\gamma_s \gamma_L)^{1/2}} \quad (9)$$

Following the introduction of the components γ^{LW} , γ^+ , and γ^- for cassiterite, fluorite and water (Table 1) into Eq. (9), the φ values for the systems fluorite-water and cassiterite-water were calculated and are also listed in Table 1.

Table 1 Values of the surface Gibbs energy components (in mJ/m^2) of fluorite and cassiterite nontreated (I) and treated with acid (II), taken from literature [19, 20], and water, and φ parameter calculated from Eq. (9)

Substance		γ_s^{LW}	γ_s^+	γ_s^-	γ_s^{SB}	γ_s	φ
Fluorite	I	35.79	0.031	0.03	0.06	35.85	0.5813
	II	27.28	5.58	52.21	34.14	61.42	1.0887
Cassiterite	I	37.39	0.37	0.67	1.00	38.39	0.6763
	II	30.12	5.03	50.38	31.84	61.96	1.0238
Water		21.8	25.5	25.5	51.0	72.8	

Then, with the assumptions $\partial\gamma_w/\partial T = -0.137 \text{ mJ/m}^2 \text{ K}$ and $\partial(\gamma_w)^{1/2}/\partial T = -8.05 \times 10^{-3} \text{ mJ/m}^2 \text{ K}$ [18], the heat of immersion Δh_i was calculated from Eq. (8) and is presented in Table 2. It appears from this Table that the Δh_i values for 'bare' and 'dry' fluorite and cassiterite are considerably lower than for the samples hydrated by being treated with acid. The heats of immersion calculated for the hydrated surfaces of cassiterite and fluorite are nearly the same.

Table 2 Values of the heat of immersion, Δh_i , calculated from Eq. (8), and Δh_{it} of fluorite and cassiterite nontreated (I) and treated with acid (II) in mJ/m^2

Substance		Δh_i	Δh_{it}
Fluorite	I	-37.13	301.87
	II	72.89	411.89
Cassiterite	I	-21.67	317.33
	II	72.87	411.87

For samples of cassiterite and fluorite whose surfaces were 'bare' and 'dry', the calculated Δh_i values are negative. The value calculated for cassiterite (-21.67 mJ/m^2) differs only slightly from the measured one (0 mJ/m^2).

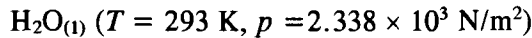
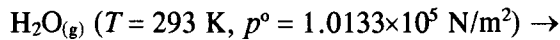
For the hydrated surfaces of cassiterite and fluorite, the heats of immersion calculated from Eq. (9) are significantly lower than the measured ones [15-17], but for these samples an adsorbed film of water is present on their surfaces and

the heat of liquefaction should therefore be taken into consideration [11]. Thus, the heat of immersion can be approximately expressed as

$$\Delta h_i = - \left(W_i - T \frac{\partial W_i}{\partial T} \right) - \Gamma h_L \quad (10)$$

where Γ is the surface concentration of adsorbed species per unit area and h_L is the heat of liquefaction.

Girifalco and Good [23] have stated that the Gibbs energy of liquefaction of an adsorbed water film can be calculated from a consideration of the following process:



Hence, the specific Gibbs energy of liquefaction, is

$$\Delta G_L = \frac{n R T}{S_{\text{H}_2\text{O}} N_A} \ln \frac{p_o}{p} = \frac{8.3143 \times 10^7 \times 293}{7.06 \times 10^{-16} \times 6.023 \times 10^{23}} \times \ln \frac{2.338 \times 10^3 \text{ N/m}^2}{1.0133 \times 10^5 \text{ N/m}^2} = -216 \text{ mJ/m}^2 = -2.97 \gamma_w \quad (11)$$

where $S_{\text{H}_2\text{O}}$ is the surface area of a water molecule and N_A is the Avogadro number.

The same result can be obtained from the enthalpy of liquefaction and the entropy changes:

$$\Delta G_L = \frac{\Delta H_L - T (S_l - S_g)}{S_{\text{H}_2\text{O}} N_A} \quad (12)$$

From the above calculations, it results that $\Delta G_L \approx 3 \gamma_w$. Thus, we can assume that $\Gamma \cdot h_i \approx 3 E_s$, where E_s is the energy of liquefaction per unit area of a water film on the cassiterite or fluorite surface, which at 20°C is equal to 113 mJ/m² [18]. On adding this contribution ($3 E_s = 339 \text{ mJ/m}^2$) to the Δh_i values calculated from Eq. [8] we obtain the total value of the heat of immersion (Δh_{it}). This is presented in Table 2.

From this Table, it appears that the Δh_{it} values for hydrated fluorite and cassiterite are similar and close to the values measured for fluorite (202–663 mJ/m²) [15–17], and somewhat lower than the value measured for cassiterite ($575 \pm 72 \text{ mJ/m}^2$). These values are also comparable to the heats of immer-

sion of other hydrated minerals, and particularly metal oxides [18]. The fact that the heats of immersion of many hydrated oxides or salts are nearly the same may demonstrate that the heat of immersion measured by calorimetry is the sum of two effects: the immersion wetting and the liquefaction of a water film.

The results of the present studies should be confirmed by other investigations, but they do indicate that there is a correlation between the surface Gibbs energy of a solid determined from contact angle measurements and the calorimetrically measured heat of immersion per unit area.

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One of the authors (B.J.) very much appreciates the support obtained from the Spanish MEC for his sabbatical stay at the Department of Physical (Extremadura University, Spain).

Financial support for this work by DGICYT under project No. PB89-0519 is gratefully acknowledged.

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Zusammenfassung — Mittels kalorimetrischen Methoden wurde die Immersionswärme in Wasser von unbehandeltem und mit 60% HNO_3 behandeltem Zinnstein gemessen. Die Immersionswärme von Zinnstein und Flußspat wurden auch theoretisch anhand der Gibbs'schen Oberflächenenergiekomponenten berechnet und mit der für Zinnstein gemessenen und für Flußspat der Literatur entnommenen Immersionswärme verglichen. Der Vergleich von Messung und Berechnung erwies, daß die Immersionswärme vom Grad der Hydratation der Oberfläche von Zinnstein und Flußspat abhängt. Man fand weiterhin, daß für Zinnstein und Flußspat die Immersionswärme in Wasser anhand der Lifshitz van der Waals und Säure-Basenkomponenten der Gibbs'schen Oberflächenenergie vorhergesagt werden kann.