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# The surface energy of palygorskite

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## Abstract

An average value for the surface energy ($\bar{\gamma}_S$) of palygorskite was determined from experimental data of spreading pressure, the surface tension of water and its contact angle using a formula based on the combination of the Young equation with a general equation of pair interaction. The value found is 226.6 mJ m$^{-2}$. Some factors that affect the determination of surface energy via solid–liquid interaction are exposed. The backgrounds of previous formulas for the calculation of the surface energy of palygorskite are also critically examined.
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## 1. Introduction

The determination of the surface energy of solids via solid/liquid interfacial interactions depends on the fact that these interactions are described by the Young equation

$$\gamma_S - \gamma_{SL} = \gamma_L \cos\theta + \Pi, \tag{1}$$

were $\gamma_S$, $\gamma_L$ and $\gamma_{SL}$ are the surface tension of the solid, the liquid and the solid/liquid interfacial tension, $\theta$ is the contact angle and $\Pi$ is the spreading or film pressure.

Published data of the surface energy (tension) of palygorskite samples [1] of 29.2 and 29.5 mJ m$^{-2}$ do not obey Eq. (1) given that the value of $\gamma_L \cos\theta$ of 30.77 mJ m$^{-2}$ is higher than the value of $\gamma_S$. Furthermore with $\Pi = 102.9$ mJ m$^{-2}$ as determined experimentally (see below), not only the Young equation is violated but also the thermodynamic Gibbs equation:

$$\Pi = \gamma_S - \gamma_{SV}.$$

where $\gamma_{SV}$ is the solid/vapor interfacial tension and would have an absurd negative value if $\gamma_S = 29.5$ mJ m$^{-2}$.

What is mentioned above is only one example of thousands of incorrect values of surface energy and related properties of solids obtained as a result of the use of incorrect formulas.

Although warnings [[2], and references therein] were raised: "… the surface energies based on the indirect methods, such as the Fowkes equation, the Lifshitz–van der Waals acid–base approach, the van Oss–Chaudhury–Good equation and the Neumann equation of state, are incorrect."; these formulas incomprehensibly perpetuate and still appear in recent publications [3–7].

It is the purpose of the present communication to report a value of the surface energy of palygorskite as determined using an alternative method based on the combination of the Young equation with a general equation of pair interaction. We also, in an Appendix, expound two of the questionable relations that are used to develop the formulas by which the incorrect values of the surface energy of palygorskite and other solids are calculated.

## 2. Properties of palygorskite

Palygorskite (also known as attapulgite) is an Al and Mg rich silicate having the structural composition [8].

$$(Mg, Al, Fe)_5^{VI}(Si, Al)_8^{IV} O_{20}(OH)_2(OH_2)_4 R^{2+} \cdot 4H_2O,$$
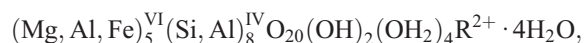
where $R^{2+}$ is a divalent cation (Ca). Commonly the particles are fibrous of rod like morphology with channels of $3.7 \times 10.6$ Å that run parallel to the length of the fiber. Fiber length varies from 100 Å to 5 μm, its width is about 100–300 Å and its thickness is from 50 to 100 Å.

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Outer surfaces of the fiber consist of oxygen octahedral coordinated to Al or Mg. Isomorphous substitution of Al for Si in the tetrahedral positions gives rise to a cation exchange capacity of about $0.2 \text{ m}^2 \text{ g}^{-1}$. The surface area is in the range of $150–200 \text{ m}^2 \text{ g}^{-1}$. The surface composition and the surface charge density suggest a hydrophilic type of surface [9,10].

The interest in palygorskite lies in its special sorptive, colloidal–rheological and catalytic properties which are the basis for many technological applications. Sorptive uses include bleaching and decolourization of vegetable and mineral oils, juices, removal of odours, toxins and pollutants. Rheological applications are in paint, adhesives, cosmetics, fertilizer preparation and drilling mud. In catalysis it is used as a support for many metals such as Zn, Cu, Co, Pt, etc. [11].

## 3. Experimental

### 3.1. Materials

The mineral was obtained from Tech Spray Inc. (USA). A suspension of $20 \text{ g L}^{-1}$ was prepared and dispersed by sonification and the fraction $>2 \text{ μm}$ was separated. The remaining fine material ($<2 \text{ μm}$) was saturated with $Ca^{2+}$ by repeated washing with $CaCl_2$ 0.5 M and centrifugation. The excess soluble salt was eliminated by repeated dilutions and centrifugations and the material was finally dried and pulverized.

Kaolinite from Davison Chemicals Co., Georgia (USA), was saturated with sodium by successive washing with 0.5 M NaCl, and then washed with water to eliminate the excess of salt. The clay was dried at 60 °C, powdered, and then passed through a 200 μm sieve. This kaolinite has a cationic exchange capacity (CEC) of $5.38 \text{ cmol}_c \text{ kg}^{-1}$ for the fraction $<2 \text{ μm}$ when saturated with sodium, and a specific surface of $27 \text{ m}^2 \text{ g}^{-1}$ as determined by water vapor adsorption.

### 3.2. Water adsorption isotherm

Samples of 5.0 g of air dried (0.5% humidity) palygorskite were placed in Pyrex glass weighing bottles (diameter = 50 mm, height = 30 mm) and were placed in vacuum desiccators with
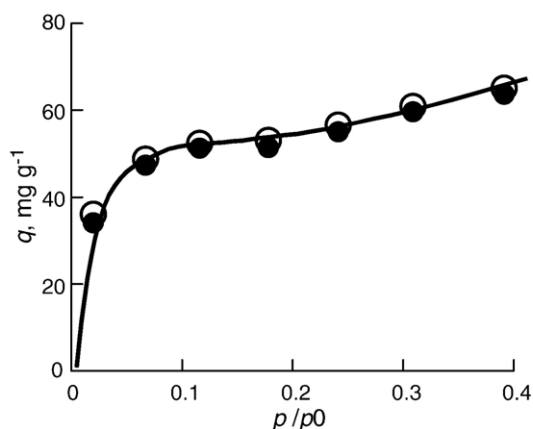


Fig. 1. Water vapor adsorption ($q$, mg $g^{-1}$) on palygorskite as a function of $p/p_0$ of the aqueous solution of $H_2SO_4$ ($p_0 = 23.756$ Torr).

aqueous concentrations of $H_2SO_4$ of different $p/p_0$ values (0.058–0.37) and were maintained at 28 °C. When equilibrium adsorption was reached (constant weight) the quantities of water adsorbed per g of palygorskite were determined by weighing. The experiments were carried out in duplicates. The vapour adsorption isotherm is shown in Fig. 1.

### 3.3. The contact angle

The contact angle of water on palygorskite $\theta_P$ was determined by the capillary rise experimental method [12]. Two alternatives were followed. In the first kaolin was used as a reference of known water contact angle $\theta_K$ (17.4°) [13], hence $\theta_P$ could be expressed by:

$$\cos\theta_P = (r_P h_P / r_K h_K)\cos\theta_K, \tag{2}$$

where $h_K$ and $h_P$ are the maximum heights in cm reached by water and the $r$'s are the effective radii of the pores in the columns which are assumed to be equal for the two minerals.

In the second alternative alcohol was used as a reference with $\theta_A = 0°$ [14], hence $\theta_P$ could be expressed by

$$\cos\theta_P = h_W \rho_W \gamma_A / h_A \rho_A \gamma_W, \tag{3}$$

where the $\rho_A$ and $\gamma_A$ represent the density (0.81 g cm$^{-3}$) and the surface tension of alcohol (22.76 mJ m$^{-2}$), $\rho_W$ and $\gamma_W$ are those of water and $h_A$ and $h_W$ are the maximum heights reached by alcohol and water. Here the effective radius of the pores in the columns is assumed independent of the liquid.

The powders were placed in glass tubes of 1 cm of internal diameter and 50 cm in length. The columns were fitted with a piece of cloth at their lower end and were dropped 10 times to a fixed height. They were immersed in 1 cm depth of liquid and the liquid rise height was measured as a function of time until maximum height was reached.

As a test for the applicability of Eq. (2) the capillary rise of water in a column of a quartz powder was also measured as a function of time (see Fig. 2). Since the contact angle of quartz and kaolin are known, 20 and 17.4 mJ m$^{-2}$ according to [13] respectively, these data were used to test the validity of Eq. (2). The contact angle of quartz calculated using the capillary rise maximum obtained experimentally was 19.3 mJ m$^{-2}$ which is considered as a satisfactory result for the validation of the use of Eq. (2) for similar minerals.

All experiments were carried out in duplicate. The capillary rise data are given in Figs. 2 and 3.

### 3.4. Calculations

To obtain the spreading pressure $\Pi$, the amount adsorbed $q$ (mmol g$^{-1}$) was plotted against $\ln p$ and $\Pi$ was obtained by graphical integration according to the Gibbs equation

$$\Pi = RT \int_{\ln p=0}^{\ln p_\Gamma} \Gamma \mathrm{d}(\ln p),$$

where $R$ is the gas constant, $T$ the absolute temperature, $\Gamma$ is the amount adsorbed per m$^2$, and $p_\Gamma$ is the pressure corresponding to
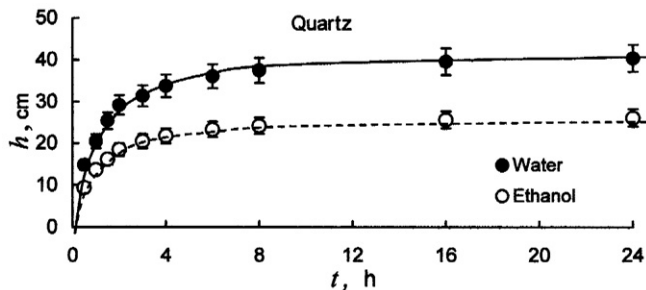
Fig. 2. Capillary rise heights of water (●) and alcohol (○) as a function of time for glass tubes packed with quartz. The error bars are 95% confidence interval from averaging, and the line is the corresponding fits.

the monolayer adsorption ($\ln p_\Gamma = 8.7538$). The area of the graph was found equivalent to 9.375 mmol g$^{-1}$. The adsorption maximum of vapour was 54.5 mg H$_2$O g$^{-1}$ obtained at $p/p_0 = 0.2$. This amount gives a surface area ($A$) of $A = 4.182$ m$^2$ mg$^{-1}$ × 54.5 mg g$^{-1}$ = 227.9 m$^2$ g$^{-1}$. Hence

$$\Pi = [8.314 \times 10^3 \text{ mJ mol}^{-1} \text{ °K}^{-1} \times 301 \text{ °K}$$
$$\times 9.375 \times 10^{-3} \text{ mol g}^{-1}]/227.9 \text{ m}^2 \text{ g}^{-1} \quad (4)$$
$$= 102.9 \text{ mJ m}^{-2}.$$

## 4. Background

The determination of the surface energy of a solid via liquid/solid interfacial interactions depends on the fact that these interactions are described by the Young equation which reads for a positive value of $\cos \theta$

$$\gamma_S - \gamma_{SL} = \gamma_L \cos \theta + \Pi, \quad (1)$$

The combination of Eq. (1) with the pair interaction equation

$$\gamma_S - \gamma_L - k\gamma_{SL} = 0, \quad (5)$$

produce the formula

$$K = \frac{\gamma_S + \gamma_L}{\gamma_S - \Pi - \gamma_L \cos \theta}, \quad (6)$$

where $k$ is an interaction parameter, $\gamma_S$, $\gamma_L$ and $\gamma_{SL}$ are the surface tension of solid, the liquid and the solid/liquid interfacial tension, $\theta$ is the contact angle and $\Pi$ is the spreading or film pressure:

$$\Pi = \gamma_S - \gamma_{SV}, \quad (7)$$

where $\gamma_{SV}$ is the solid/vapour interfacial tension.

Eq. (8) can also be written as

$$k = \frac{1 + x}{1 - mx}, \quad (8)$$

where $x = \gamma_L / \gamma_S$ and $m = (\gamma_L \cos \theta + \Pi)/\gamma_L$.

Eqs. (6) and (8) contain two unknowns $\gamma_S$ and $k$ and an extra exact relation is necessary for a complete solution to be obtained. Since this is yet to be found, we turn our attention to

the range where $\gamma_S$ lies. This, however, can be obtained using the Young equation subject to two conditions:

(1) $\gamma_L < \gamma_{SL} < \gamma_S$ [15,16],

(2) $\gamma_{SL} \leq \sqrt{\gamma_S \gamma_L}$ [17,18].

Hence the lower limit of the range for $\gamma_S$ is given by the Young equation for $\gamma_{SL} = \gamma_L$, and the upper limit is given for $\gamma_{SL} = \sqrt{\gamma_S \gamma_L}$. Thus $\gamma_S - \gamma_L = \gamma_L \cos \theta + \Pi$, and $\gamma_S - \sqrt{\gamma_L}\sqrt{\gamma_S} - (\gamma_L \cos\theta + \Pi) = 0$, respectively.

Knowing the range where $\gamma_S$ lies makes it possible the calculation of some average value ($\bar\gamma_S$) for this range.

The mean value $\bar x$ ($\bar x = \gamma_L / \bar\gamma_S$), can be calculated from the formula (9) obtained using a probability function [19]

$$\bar x = \frac{\int_{x_2}^{x_1} x \frac{dk}{dx} dx}{k(x_1) - k(x_2)}, \quad (9)$$

where $x_1$ and $x_2$ are the limit values of $x$ in the range where the surface energy lies.

Integration of Eq. (9) gives

$$\bar x = \frac{\left[ \frac{(1+m)}{m^2}\left( \ln(1-mx) + \frac{1}{(1-mx)} \right) \right]_{x_2}^{x_1}}{k_1 - k_2}. \quad (10)$$

## 5. Results and discussion

The contact angle of water on palygorskite calculated from Eq. (3) using the maximum heights of 26.5 cm for ethanol and 13.5 cm for water was 79° (78.8°).

The value obtained using Eq. (2) with kaolin as a reference was 69°. The difference between our two values is rather large and in terms of Eq. (2) it is possibly due to that the two minerals have surfaces with important differences in chemical properties. It appears, therefore, that Eq. (2) is useful when the two minerals have similar properties as is shown above (Section 2) for quartz and kaolin. This conclusion is substantiated by the data shown in Figs. 2 and 3, where for quartz and kaolin the alcohol curves are below those for water, while for palygorskite (Fig. 3) the alcohol curve is above that obtained for water.

A contact angle of 69° will be adopted in this work rather than of 79° for reasons, mentioned below, related to the use of organic liquids as references to obtain contact angles.

The value of the contact angle of 69° contradict with the conclusion that the surface of palygorskite is hydrophilic as obtained from results of adsorption of organic dyes molecules. In that study [9] neutral dyes molecules failed to bind to the surface of palygorskite. A surface charge density of 0.08 C m$^{-2}$ [10] also supports the idea of a hydrophilic type surface. However, the hydrophilicity of clays is not a simple subject to deal with, for example montmorillonite, talc and quartz have Si–O surfaces, nevertheless talc is hydrophobic ($\theta = 60°$) while montmorillonite and quartz are hydrophilic.

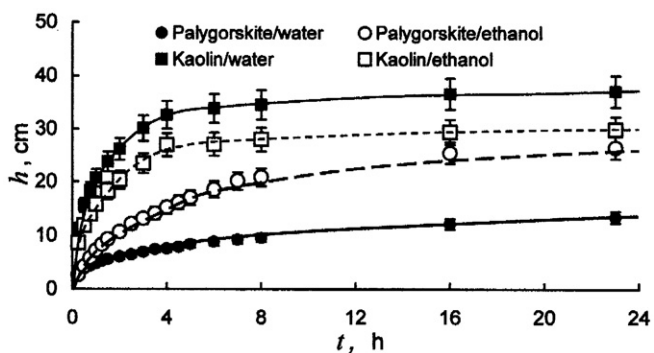Fig. 3. Capillary rise heights of water and alcohol as a function of time for glass tubes packed with palygorskite ($\bullet$, $\circ$) and/or kaolin ($\blacksquare$, $\square$). The error bars are 95% confidence interval from averaging, and the line is the corresponding fits.

Another aspect of the problem is related to the method by which the contact angle is obtained. It is a common experimental observation [12,20] that capillary rise and penetration methods (Washburn) using organic liquids as reference liquids produce large contact angle values for water on powder solids which contrast with the low values obtained by direct methods (Wilhelmy) using flats and rods of the solids. The reason for such behavior is due to that the solid/organic liquid surface interactions may not be described by the Young equation. To give an example from published values [20] for the quartz/cyclohexane system: $\theta$ for cyclohexane on quartz=0, the calculated water contact angle on quartz using cyclohexane as a wetting liquid, $\theta_w=37°$, $\gamma_S$ for quartz= 282.6 mJ m$^{-2}$ (see below). The solid/liquid interfacial tension (quartz/cyclohexane) $\gamma_{SL}=85$ mJ m$^{-2}$ calculated from $\gamma_{SL}=\sqrt{\gamma_S\gamma_L}$, where $\gamma_L=25$ mJ m$^{-2}$. This data give the Young equation as

$$282.6-\Pi = 84.05 + 25,$$

hence $\Pi=173.5$ mJ m$^{-2}$, which is an impossible value for the spreading pressure of cyclohexane on a quartz surface. Thus cyclohexane/quartz interactions are not described by the Young equation. Hence cyclohexane cannot be used as a reference wetting liquid for the calculation of the contact angle of water on quartz using capillary penetration equations [12,20]. In other words capillary rise or penetration methods may be valid only when the solid/liquid interactions obey the Young equation. With octane we get a similar relation with quartz [12]: $282.6-\Pi=78.48+21.8$, indicating a wide spread problem.

For $\Pi=102.94$ mJ m$^{-2}$, $\gamma_L=72.8$ mJ m$^{-2}$, $m=1.7723$ and $\theta=69°$ the range of $\gamma_S$ is 201.83–268.96 mJ m$^{-2}$ corresponding to $k$ values between 2.4425 and 3.7721. Eq. (10) gives $\bar{x}=0.3212$, hence the mean surface energy of palygorskite $\bar{\gamma}_S=226.6$ mJ m$^{-2}$, and $\bar{k}=3.0676$.

The $\bar{\gamma}_S$ value of 226.6 mJ m$^{-2}$ is of an order of magnitude similar to those obtained for other Al-silicate minerals, using the same method of calculation given above. Thus $\bar{\gamma}_S=231.4$ for kaolin, for talc=217.3 and for montmorillonite=223.3 mJ m$^{-2}$ [16,19,21]. The value for montmorillonite should probably lie

a little higher since the value of $\Pi$ used in the calculations (60 mJ m$^{-2}$) is somewhat low.

Published values for the surface energies of Al-silicates as calculated by equations different from those presented in the present work, are not only too low but also contradict valid thermodynamic equations. For instance, the values reported for talc are 30.7, 36.6 and 44.8 mJ m$^{-2}$ [22–24]. These values are less than the value reported [22] of the experimental spreading pressure of 84.16 mJ m$^{-2}$, and the first value is less than $\gamma_L \cos\theta$ (=36.4 mJ m$^{-2}$) [19], thus contradicting the Gibbs equation:

$$\Pi = \gamma_S - \gamma_{SV}, \tag{7}$$

and the Young Eq. (1).

For montmorillonite the values of 186 [25] and 178.9 mJ m$^{-2}$ [13] were reported using Fowkes type formulas. These values would indicate a surface less hydrophilic than talc which is known to be untrue, since the contact angle of water on montmorillonite is much less than that for talc [13,19].

For the surface energy of kaolin a value of 171 mJ m$^{-2}$ was reported [26] using Fowkes type formulas. This value is lower than the minimum value of 181 mJ m$^{-2}$ calculated from the Young equation using their data [16].

Another example of an adverse result produced as an outcome of the use of the so called Lifshitz–VDW–acid/base approach is concerned with zeolite [27] where in addition to the very low value of $\gamma_{SV}$ reported for a silicate surface (34.49 mJ m$^{-2}$) the zeolite surface treated with silane had a higher value of 39.3 mJ m$^{-2}$.

Similarly, the surface energy of quartz is given equal to 151 using the criticized [2,28,29] Fowkes type formulas while Eq. (9) gives it equal to 282.6 mJ m$^{-2}$ using the authors data, $\Pi=107$ mJ m$^{-2}$ and $\theta=0°$ [30]. It is worth mentioning that the surface energies of clays and related minerals calculated by the Lifshitz–VDW–acid/base approach are even much lower than those calculated by the Fowkes type formulas viz. 29–52 mJ m$^{-2}$ [31].

Not only for silicates but also for organic surfaces the literature is full with data that contradict the Young and other valid relations [3–7,32]. Only few examples will be given here. For example for polytetrafluoroethylene/water [32] $\gamma_L=12.8$ mJ m$^{-2}$, $\gamma_S=19$ mJ m$^{-2}$, $\theta=113°$ which gives $\gamma_{SL}=\sqrt{\gamma_S\gamma_L}=37$ mJ m$^{-2}$, thus violating the Young equation; since

$$\gamma_S < \gamma_{SL} + \gamma_L \cos\theta.$$

For Teflon/n-hexane [7], the interfacial tension has a negative value which is an impossible result.

## 6. Conclusion

An average value for the surface energy of palygorskite is obtained by determining the range where the value lies and calculating the mean value within this range using a probability function. The value found is 226.6 mJ m$^{-2}$. This value is of an

order of magnitude similar to those obtained for other aluminum silicates.

## Acknowledgements

## Appendix A

Relations used to develop the incorrect formulas for the calculation of surface energy of solids

### A.1. A basic relation

The basic relation used to obtain the formulas of Good [33], van Oss [34,35], Neumann [36] is

$$\Delta G_{ij} = \gamma_{ij} - \gamma_j - \gamma_i, \tag{A.1}$$

$\Delta G_{ij}$ is defined as the free energy of adhesion for two immiscible substances [36] or as the free energy change for the interaction between two condensed phases $(i, j)$ in vacuum [34].

The right hand side (RHS) of Eq. (A.1) is identical to that of the equation of the work of adhesion $W_A$

$$W_A = \gamma_A + \gamma_B - \gamma_{AB}, \tag{A.2}$$

$W_A$ is defined as the work to separate an interface AB (liquid/liquid for example) into two (liquid/vapor) interfaces A and B [37].

Since $W$ is a Helmholtz free energy $(\Delta F)$ while $\Delta G$ is a Gibbs free energy, it is clear that they cannot be represented by the same relation i.e. the RHS of Eqs. (A.1) and (A.2) is the same (the relation between $\Delta F$ and $\Delta G$ is [[15], p. 26]: $\Delta F = \Delta G - \Delta(PV)$).

As demonstrated by Gibbs [38] and also in books of thermodynamics [15] a pressure volume term should be taken into account in the calculation of $W$. As shown by Gibbs (see also below) the contribution of such term to $W$ is $\frac{2}{3}$ that spent in forming the surface of tension, and of opposite sign, hence the factor $\frac{1}{3}$ in the Gibbs equation:

$$W = \frac{1}{3}(\sigma_{AC}S_{AC} + \sigma_{BC}S_{BC} - \sigma_{AB}S_{AB}), \tag{A.3}$$

where $W$ is the work which must be expended in order to form a lentiform mass (or a drop) of phase C between masses of infinite extent having the phases A and B. The $\sigma$'s are the interfacial tensions and the $S$'s are the areas of the interfaces.

A simple derivation of Eq. (A.3) is as follows. The infinitesimal work $dW$ required to increase the volume $V$ of the interfacial layer (phase C) found between two phases of infinite extent A and B is [15]:

$$dW = -PdV + \gamma dS, \tag{A.4}$$

since

$P = 2\gamma/r$ (the Laplace relation),

$V = \frac{1}{3} r \, dS$ (a geometric relation) and

$dV = \frac{1}{3} r \, dS,$

where $r$ is the radius of curvature and $S$ is the interface area, we get from Eq. (A.4)

$$dW = -\frac{2}{3}\gamma dS + \gamma dS = \frac{1}{3}\gamma dS. \tag{A.5}$$

Further development of Eq. (A.5) for the three interfaces AC, BC and AB gives the Gibbs Eq. (A.3).

### A.2. The work of adhesion

It is in order to show that the work of adhesion defined as the work required to separate an interface AB (liquid/liquid) into two liquid vapor interfaces A and B [37] is not given by Eq. (A.2) but should be given by (if there is no $PV$ work and the three interfaces are of equal areas):

$$W_A = (\gamma_{AB} + \gamma_B) - (\gamma_A + \gamma_B) = \gamma_{AB} - \gamma_A, \tag{A.6}$$

when B is the upper immiscible liquid.

This is because thermodynamics require the calculation of the energy differences between the final and initial states of the system. In the present case the final state is an A and B surfaces but the initial state is an AB interface and a B surface, hence Eq. (A.6). Incidentally $W_A$ is related to the heat of immersion $\Delta H$ by $W_A = \Delta H - \Delta(TS)$; $T$ is the temperature and $S$ is the entropy.

In addition to what is mentioned above, Eqs. (A.2) and (A.3) differ also in:

1. The signs of the terms

For example for a drop of liquid on a solid surface Eq. (A.2) reads

$$W_A = \gamma_{SV} + \gamma_{LV} - \gamma_{SL}, \tag{A.7}$$

while Eq. (A.3) reads

$$W = \frac{1}{3}(\gamma_{LV}S'_{LV} + \gamma_{SL}S'_{SL} - \gamma_{SV}S'_{SV}), \tag{A.8}$$

thus $\gamma_{SV}$ is with a positive sign in Eq. (A.7) and is with a negative sign in Eq. (A.8) while the reverse occurs for $\gamma_{SL}$.

2. Absence of the factor $\frac{1}{3}$ in Eqs. (A.2) and (A.7).

3. Absence of the areas of the 3 interfaces in Eqs. (A.2) and (A.7), i.e. the $S$ values in Eqs. (A.3) and (A.8).

### A.3. The geometric mean (square root approximation)

The geometric mean which is known to overestimate the quantities sought [17,18] is used extensively to obtain the formulas for the calculation of the surface energy of solids. Some equations contain as much as 5 geometric means [29,34,35] and usually the corresponding publications contain an overwhelming number of square roots. Such practice raises serious doubts about the values obtained for surface energies and

other properties of palygorskite, knowing also that these values are obtained after neglecting the surface pressure term in the Young equation which is of considerable magnitude viz. $\Pi = 102.94$ mJ m$^{-2}$ as determined experimentally for this mineral.

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