CHAPTER 2

THE van OSS–CHAUDHURY–GOOD THERMODYNAMIC APPROACH (ACID-BASE THEORY) FOR THE ESTIMATION OF SURFACE FREE ENERGY OF SOLIDS

2.1- Introduction

It was stated by Paul Tillich in 1929 that *"The boundary is the best place for acquiring knowledge"* [1]. His quotation comes neither from mineralogy nor from surface chemistry but from theology, and is a reminder that boundaries are the places where changes take place and it is there that processes of change can often be properly understood. In the case of minerals, the boundary is the surface of the mineral; a surface that in nature is also an interface [2], most commonly between the mineral and air, or the mineral and an aqueous fluid (or a melt).

The surface chemistry and surface free energy of materials are important to the performance of many products and process. For example, the surface free energies of talc and its components between two interacting surfaces are critically important in a wide variety of industrial applications for this mineral. The market potentials of the various talc products depend on the surface properties of the mineral, which in turn vary with the ore type, processing technologies, particle size and surface treatment [3]. Therefore, it has been recognized that characterizing talc based on its surface thermodynamic properties e.g., Lifshitz-van der Waals and acid-base determination, hydrophobicity-hydrophilicity balance, electrokinetic properties, are vitally important for defining suitable applications and developing new markets. Adhesives, printing, de-inking, coatings and pitch control in paper mills, reinforcement and nucleation of polymers, cosmetics and pharmaceuticals are only a few examples of market segments where the surface chemistry of talc play a fundamental role [4-7].

The characterization of the surface properties and especially the surface free energy components of the solids are, therefore, recognized as the key to understand the mechanism of surface-based phenomena [8]. Despite the importance of surface chemistry to the ultimate performance of the product, not as much recognition as is deserved has been given to the characterization of surface chemistry and the effects of its variation on product performance [9]. Difficulties with both theoretical descriptions of interfaces and the measurement of surface chemical characteristics make the incorporation of material surface chemical specifications for the manufacturer of many products challenging.

Underlying many of these specialized aspects of surface chemistry are some fundamental thermodynamic concepts. The objective of Chapter 2 is to review the theoretical principles related to the thermodynamic surface properties of solids with emphasis on the acid-base theory using the recently developed model of van Oss, Chaudhury and Good.

2.2- Lifshitz-van der Waals or apolar interactions (LW)

In 1873, the Dutch physicist J. D. van der Waals, when studying the deviation of a real gas behavior from the ideal gas law, proposed the idea that there existed non-covalent and non-electrostatic interactions (apolar interactions) between neutral atoms and molecules [10, 11]. van der Waals forces play a central role in all phenomena involving intermolecular forces, for while they are not as strong as Coulombic (ionic) or hydrogen-bonding interactions, they are ubiquitous and are always attractive between like particles.

Collectively known as the van der Waals force, these electrodynamic intermolecular forces originated from three distinct interactions [12]:

1- **Keesom** showed that a permanent molecular dipole creates an electric filed which has the effect of orienting other permanent dipoles so that they are attracted to the first one. These interactions are referred to as randomly orientated dipole ↔ dipole or orientation interactions, e.g. $HCl_{(g)}$ ↔ $HCl_{(g)}$.

2- **Debye** observed that the electric field of a permanent dipole induces a dipole in a polarizable atom or molecule, and the induced dipole is oriented such that it is attracted. These are called randomly orientated-dipole ↔ induced-dipole or induction interactions, e.g. $HCl_{(g)}$ ↔ $N_{2(g)}$.

3- An instantaneous dipole, arising from the momentary asymmetry of the electron cloud in a atom or molecule, itself induces other dipoles in surrounding atoms and molecules. Once again, the induced dipoles are attracted to the inducing one. This is know as fluctuating dipole ↔ induced-dipole or dispersion interactions, and was described by **London**, e.g. $N_{2(g)}$ ↔ $N_{2(g)}$.

While these three kinds of interactions have distinct origins, they have in common the fact that their interaction energies decay rapidly with the sixth power of the interatomic or molecular distance [12], viz.:

$$w(r)_{Keesom} = \frac{-u_1^2 u_2^2}{3(4\pi\varepsilon_o)^2 kTr^6} \tag{2.1}$$

$$w(r)_{Debye} = \frac{-\alpha u^2}{(4\pi\varepsilon_o)^2 r^6} \tag{2.2}$$

$$w(r)_{London} = -\frac{3}{4}\frac{h\nu\alpha^2}{(4\pi\varepsilon_o)^2 r^6} \tag{2.3}$$

where $w(r)$ is the interaction free energy (in J), u is the dipole moment, ε_o is the dielectric permittivity of free space, κ is the Boltzmann's constant, T is the absolute temperature, α

is the polarizability[1], v is the electronic absorption (ionization frequency), h is Planck's constant and r is the distance between the atoms or molecules. Equations (2.1), (2.2) and (2.3) refer to interactions in vacuum[2].

Of the three interactions, Keesom and Debye interactions require that molecules have permanent dipole moments and are therefore not present in all materials. The already small Keesom interaction is virtually completely screened out, especially in aqueous media which contain electrolytes [12]. The London interactions are based on electron clouds of one molecule distorting the adjacent molecule cloud. The distortion of the electron cloud produces an instantaneous polarity and attraction. Therefore, the London interaction requires only that electrons be present and thus will exist in all materials. Since all atoms and molecules are polarizable, the London dispersion forces are the dominant and the most important forces in many systems [12]. The dispersion forces play a role in a host of important phenomena such as adhesion, surface tension, wetting, physical adsorption, the flocculation of particles, the properties of gases, liquids and thin films, the strength of solids and others [8].

2.3- Dispersion forces between two macroscopic materials - The Hamaker's Approach

For two identical atoms or molecules *(i)* separated by a short distance in vacuum, the dispersion interaction can be expressed as [10]:

$$A_{ii} = \pi^2 q_i^2 \beta_{ii} \tag{2.4}$$

where A_{ii} is commonly termed the Hamaker constant, q_i^2 is the number of atoms per unit volume and $\beta_{ii} = 3/4\, h v \alpha^2/(4\pi\varepsilon_o)^2$. From Eq. (2.3), it follows that:

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[1] All atoms and molecules are polarizable. Polarization refers to the dipole moment induced in molecules by the electric fields emanating from nearby molecules [10].

[2] The vacuum dielectric constant, ε, equals 1.

$$w(r)_{London} = \frac{-\beta_{ii}}{r^6} \tag{2.5}$$

where r is the distance between the atoms *i*. According to the Berthelot's principle [13], the **dispersion** interaction constant between dissimilar molecules of different materials can be estimated as the geometric mean of the interaction constants of individual materials. Thus, the extended interaction to two different atoms *i* and *j* becomes:

$$\beta_{ij} = \sqrt{\beta_{ii}\beta_{jj}} \tag{2.6}$$

It follows then that the Hamaker constant for two different atoms is given *by:*

$$A_{ij} = \sqrt{A_{ii}A_{jj}} \tag{2.7}$$

which is known as geometric combining rule, and is widely used for calculating **dispersion energies** of interactions between dissimilar materials.

Hamaker [14] first calculated the dispersion (van der Waals-London) interaction energy for larger bodies by a pair-wise summation of the properties of the individual molecules (assuming these properties to be additive, and non-retarded). Using this macroscopic approximation, the total dispersion energy for two semi-infinite flat parallel bodies (of material *i*), separated by a distance r, in air or in vacuum, becomes (for r greater than a few atomic diameters):

$$w(r)_{London} = \frac{-A_{ii}}{12\pi r^2} \tag{2.8}$$

where A_{ii} is the Hamaker constant for material *i.*

Hamaker's pair-wise summation procedure can also be used to calculate the combined Hamaker constant of two macroscopic identical or different particles interacting in a third medium. For two atoms of the same material, 1, in medium 3 (e.g., two individual clay particles in an aqueous suspension) the combining rule (cf. Eq. (2.7)) gives [10]:

$$A_{131} = (\sqrt{A_{11}} - \sqrt{A_{33}})^2 \tag{2.9}$$

or

$$A_{131} = A_{11} + A_{33} - 2A_{13} \tag{2.10}$$

in which A_{11} and A_{33} refer to the Hamaker constants of the solid and the medium, respectively, in vacuum.

Here, the convention is that the first and the third character in the triplet subscript identify the two particles which are interacting through a liquid medium, identified by the second character. For two different objects (1 and 2), in medium 3, the Hamaker combining rule can be given by:

$$A_{132} = A_{12} + A_{33} - A_{13} - A_{23} \tag{2.11}$$

Equation (2.11) can also be written as:

$$A_{132} = (\sqrt{A_{11}} - \sqrt{A_{33}}).(\sqrt{A_{22}} - \sqrt{A_{33}}) \tag{2.12}$$

Eq. (2.9) suggests that the Hamaker constant, A_{131}, is always positive (or zero). Therefore, two identical molecules or particles in medium 3 (i.e., liquid) always attract each other, although it can become zero, when A_{11}=A_{33}. For two different materials, the Hamaker constant, A_{132} Eq.(2.12), can be negative, i.e., when:

$$\mathrm{A}_{11} > \mathrm{A}_{33} > \mathrm{A}_{22} \tag{2.13}$$

and when:

$$\mathrm{A}_{11} < \mathrm{A}_{33} < \mathrm{A}_{22} \tag{2.14}$$

under which conditions the dispersion interaction energy becomes repulsive, i.e., $w(r)_{London} > 0$ [15-17]. It should be emphasized that there is nothing contradictory in repulsive van der Waals forces. The London dispersion interactions between two molecules or particles (identical or different) in vacuum are always attractive. And the London interactions between two identical molecules or particles immersed in a liquid is always attractive, although it can become zero, when $A_{11} = A_{33}$ (see Eq. (2.9)). But when two different materials 1 and 2 interact, immersed in liquid 3, and when $A_{11} \neq A_{22}$ and the conditions in eqs. (2.13) or (2.14) prevail, a net repulsion occurs.

Padday and Uffindell [18] demonstrated the applicability of Hamaker approach to the n-alkanes by calculating the theoretical values of surface tensions (γ_{ii}) of various n-alkanes using the following equation:

$$W_{ii} = 2\gamma_{ii} = \frac{A_{ii}}{12\pi r_{ii}^2} \tag{2.15}$$

where W_{ii} is the work of cohesion resulting from London dispersion forces, r_{ii} is the separation distance between two atoms in the bulk. The calculated results have shown a good agreement with experimentally measured values of surface tension, which suggest that the intermolecular forces of n-alkane are mainly of dispersion type. It is clear that the calculated value of surface tension depends critically on the assumed value of r_{ii}, which is discussed in the Section 2.5.

However, as pointed out by Horn [19], the Hamaker approach turns out to be not entirely accurate because of many-body effects, i.e. the fact that the field which one atomic dipole creates at a neighbor is also influenced by other atoms in the vicinity, so that the total force is not obtained by simply adding up the effects of each pair of atoms. Yildirim [8] added that Hamaker approach cannot be applicable to some colloidal systems since, like the classical DLVO theory, it ignores the existence of hydrophobic interactions between particles of hydrophobic materials.

2.4- Dispersion forces between two macroscopic materials - The Lifshitz Approach

In contrast to Hamaker's approach, which started with single interatomic interactions, to arrive at the total interaction energy for macroscopic bodies by a process of pair-wise summation, Lifshitz has constructed a more accurate approach through a purely macroscopic framework. The problems associated with the use of summation process have been completely eliminated in this macroscopic treatment of dispersion forces. Lifshitz treated the interacting bodies as continuous media. The dispersion forces in this approach have been derived in terms of the macroscopic properties of interacting bodies, such as their dielectric constants or refractive indexes.

Lifshitz calculated interaction energy using quantum mechanical and electromagnetic approach. The derivation of Lifshitz model is beyond the scope of this work and the full theory is complicated, as can be discovered by reading the complete and thorough presentation of it given by Mahanty and Niham [20]. For more descriptive and accessible references it is advisable to consult Hough and White [21] and Israelachvili [22].

Applying the Lifshitz theory the Hamaker constant is given by [12]:

$$A_{132} = \frac{3}{4}kT\left(\frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3}\right)\left(\frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3}\right) + \frac{3h\nu}{8\sqrt{2}} \frac{\left(n_1^2 - n_3^2\right)\left(n_2^2 - n_3^2\right)}{\left(n_1^2 + n_3^2\right)^{1/2}\left(n_2^2 + n_3^2\right)^{1/2}\left\{\left(n_1^2 + n_3^2\right)^{1/2} + \left(n_2^2 + n_3^2\right)^{1/2}\right\}} \tag{2.16}$$

and

$$A_{131} = \frac{3}{4}kT\left(\frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3}\right)^2 + \frac{3h\nu_e}{16\sqrt{2}} \frac{\left(n_1^2 - n_3^2\right)^2}{\left(n_1^2 + n_3^2\right)^{3/2}} \tag{2.17}$$

where ε_1 , ε_2 and ε_3 are the dielectric constants of the three media and n_1 , n_2 and n_3 are the refractive indexes of the same. In each of Eqs. (2.16) and (2.17), the first term on the right hand side gives the *zero-frequency energy* of the van der Waals energy (which includes the Keesom and Debye interaction energies), while the latter term represents the dispersion energy which includes London energy contribution. v_e is the absorption frequency in the UV region ($\approx 3\text{x}10^{15}$ s^{-1}) [12]. The Lifshitz theory is capable of making more accurate predictions of the Hamaker constant (A) and consequently of the van der Waals forces if complete and accurate optical data are available for the materials of interest [19].

Israelachvilli [23] calculated the Hamaker constants of different liquids from the data of their refractive indices. He then calculated the surface tensions of these liquids using the following equation:

$$\gamma_i = \frac{A_{ii}}{24\pi r^2} \tag{2.18}$$

where γ_i stands for the apolar component of the surface tension, γ^{LW} , of substance *i*. Eq. (2.18) is equivalent to Eq. (2.15) and they differ only in the approach used to calculate A_{ii}. Israelachvilli, using r=0.2054 nm, found a very good agreement between the calculated surface tension of saturated hydrocarbons and the corresponding experimental values whereas the opposite was true for water. He concluded that the Lifshitz and additivity theories may not be used to calculate the surface free energies of highly polar liquids where short range forces other than dispersion forces (e.g. hydrogen bonds) are also involved.

2.5- Interfacial Lifshitz-van der Waals interactions

The surface tension γ_i, i.e., the surface free energy per unit area, of a liquid, in vacuum, is equal to one half the free energy of cohesion (ΔG_{ii}), and opposite in sign [24].

$$\gamma_i = -\frac{1}{2}\Delta G_{ii} \tag{2.19}$$

For solids, Eq. (2.19) is equally true, but solids differ from liquids in that ΔG_{ii} is not their free energy of cohesion, but just the free energy available for interacting with liquids [25]. Fowkes [26-28] proposed that the surface free energy of materials could be considered to be a sum of components resulting from each class of intermolecular interaction, i.e.:

$$\gamma_i = \sum_j \gamma_i^j \tag{2.20}$$

where the γ^j terms represent the specific contributors, e.g., hydrogen bonding, dipolar, dispersion, metallic, etc.

Using the Lifshitz approach for van der Waals interactions in condensed media, Chaudhury [29] experimentally demonstrated in 1984 that the dispersion (London), induction (Debye) and dipole (Keesom) contributions to the Lifshitz-van der Waals (or apolar) component of the surface tension, γ^{LW}, are additive:

$$\gamma^{LW} = \gamma^L + \gamma^D + \gamma^K \tag{2.21}$$

Thus, it follows that on a macroscopic level the three types of van der Waals interactions (Keesom, Debye and London) can be treated together as the total of apolar, or Lifshitz-van der Waals (LW) interactions [10, 30].

The interfacial tension γ_{12} between two different materials 1 and 2 is one of the most important concepts in colloid and surface science, as it leads directly to a quantitative expression for the free energy of interparticle or intermolecular interaction in condensed phase systems [27, 31, 32]. Interfacial tensions between two reasonably immiscible liquids can readily be measured [33], but interfacial tensions between solids and liquids and between solids and solids cannot be determined directly [31]. It thus becomes important to arrive at these interfacial tensions, γ_{12}, via the surface tensions γ_1 and γ_2 of the interacting materials 1 and 2.

Good and Grifalco [31, 32, 34] and Fowkes [27, 28] demonstrated experimentally that if only dispersion interaction forces are available between two condensed phase materials, e.g., a solid and a liquid, the interfacial tension between them (γ_{12}^{LW}) is given by the following equation:

$$\gamma_{12}^{LW} = \left(\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_2^{LW}}\right)^2 \tag{2.22}$$

or:

$$\gamma_{12}^{LW} = \gamma_1^{LW} + \gamma_2^{LW} - 2\sqrt{\gamma_1^{LW}\gamma_2^{LW}} \tag{2.23}$$

which is referred to as Good-Grifalco-Fowkes combining rule [35]. Equation (2.22) has been shown experimentally to be accurate to within 2% [36].

Recalling Eq. (2.19), the apolar component of the free energy of cohesion of material 1 is:

$$\Delta G_{11}^{LW} = -2\gamma_1^{LW} \tag{2.24}$$

and the free energy of interaction between materials 1 and 2 *in vacuum* is related to the surface tensions of these materials by the Dupré equation [30]:

$$\Delta G_{12}^{LW} = \gamma_{12}^{LW} - \gamma_1^{LW} - \gamma_2^{LW} \tag{2.25}$$

Substituing Eq. (2.23) into Eq. (2.25) one obtains,

$$\Delta G_{12}^{LW} = -2\sqrt{\gamma_1^{LW}\gamma_2^{LW}} \tag{2.26}$$

which is a very important relation. This equation states that the atoms at an interface are pulled by those in the neighboring phase. Since the Lifshitz-van der Waals forces are universal and always available at the surface, Eq. (2.26) also suggests that the energy of interaction is negative, i.e., the interaction energy between two purely polar condensed phases is always attractive.

Similarly, the interaction energy between molecules or particles of material 1 immersed in a liquid 2 is:

$$\Delta G_{121}^{LW} = -2\gamma_{12}^{LW} \tag{2.27}$$

and two different objects (1 and 2) immersed in a liquid (3) are related to the interfacial tensions by:

$$\Delta G_{132}^{LW} = \gamma_{12}^{LW} - \gamma_{13}^{LW} - \gamma_{23}^{LW} \tag{2.28}$$

Using Eqs. (2.22) and (2.25) to expand the interfacial surface tensions in Eq. (2.28) gives:

$$\Delta G_{132}^{LW} = -2\gamma_3^{LW} - 2\sqrt{\gamma_1^{LW}\gamma_2^{LW}} + 2\sqrt{\gamma_1^{LW}\gamma_3^{LW}} + 2\sqrt{\gamma_2^{LW}\gamma_3^{LW}} \tag{2.29}$$

Since from Eq. (2.26) :

$$\Delta G_{12}^{LW} = -2\sqrt{\gamma_1^{LW}\gamma_2^{LW}}$$

it follows from Eq. (2.29) that:

$$\Delta G_{132}^{LW} = \Delta G_{33}^{LW} + \Delta G_{12}^{LW} - \Delta G_{13}^{LW} - \Delta G_{23}^{LW} \tag{2.30}$$

which is the confirmation of the Hamaker combining rule (Eq. (2.7)) obtained via a purely surface thermodynamic treatment [37], provided that: (a) the the geometric mean combining rule (Eq. (2.22)) holds for LW interactions (which is the case) and (b) r (interatomic equilibrium distance, Eq. (2.18)) has the same value for all types of ΔG interactions [38]. The constancy of r for LW interactions of all materials was confirmed by van Oss *et al.* The best empirical value of r, at 20°C, was determined to be 0.157±0.009 nm [35]. Isrealachvili used 0.165 nm in his calculations [12].

2.6- Polar or Lewis acid-base interactions

For some time it was thought that the Keesom dipole-dipole interactions should be treated separately from the Debye and London interactions. Because of the dipolar nature of the Keesom phenomenon, the term "polar" was applied to these interactions, in contrast to the "apolar" Debye and London interactions. This distinction between all three apolar electrodynamic forces impeded progress in the search for the true polar surface interactions. After Chaudhury [29] showed that the three, apolar, electrodynamic forces are simply additive, and should be treated as a single entity, the LW interactions, it became possible to examine the nature of the polar (Lewis) properties of surfaces as an entirely separate phenomenon from their electrodynamic (LW) apolar properties.

In the last twenty years significant advances have been made in the thermodynamic treatment and interpretation of interfacial tension between two interacting surfaces, i.e., solid and liquid. It is now clear that in aqueous media, and especially for solid surfaces which are rich in oxygen such as silicate minerals, the principal polar interaction is hydrogen bonding, involving donors and acceptors [10]. As this type of interaction can be treated as occurring between a Brønsted acid (the hydrogen donor) and a Brønsted base (the hydrogen acceptor), polar interactions must account for the dual nature of such interactions [10, 39]. Moreover, polar surface interactions are not restricted to hydrogen bonding, so that the polar concept has been extended to include all electron donating and electron accepting phenomena, as encompassed in the more general acid-base paradigm of Lewis [35, 40-44]. To emphasize the (Lewis) **acid-base** character of the polar interactions, the designation **AB** has been used.

As the polar and apolar components of the surface tension are additive [35, 42, 45, 46]:

$$\Delta G = \Delta G^{LW} + \Delta G^{AB} \tag{2.31}$$

where ΔG^{LW} is the free energy change due to Lifshitz-van der Waals interaction, and ΔG^{AB} is the same due to acid-base interactions.

And rewriting Eq. (2.19) as

$$\Delta G_{ii} = -2\gamma_i \tag{2.32}$$

it follows that:

$$\gamma_{\mathrm{i}}^{\mathrm{Total}} = \gamma_{\mathrm{i}}^{\mathrm{LW}} + \gamma_{\mathrm{i}}^{\mathrm{AB}} \tag{2.33}$$

where γ_i^{LW} and γ_i^{AB} refer to the apolar (Lifshitz-van der Waals) and polar (acid-base) components of surface tension of material *i*, respectively.

The work conducted by Fowkes [45] is a good example for demonstrating the presence and importance of acid-base interactions between two interacting surfaces. This author determined the values of acid-base (W_{SL}^{AB}) and Lifshitz-van der Waals (W_{SL}^{LW}) components of work of adhesion for various acidic and basic liquids on polymer surfaces as a function of acidity or basicity of polymer. He showed that the contribution of acid-base (or polar) component to the work of adhesion (W_{SL}) is strictly dependent on the acidity or basicity of the solid (polymer) of interest.

For example, when studying polyethylene (a basic polymer) which is co-polymerized with various contents of acrylic acid (an acidic monomer), he found that the acid-base contribution to the work of adhesion increased with increasing acid content of the polymer in the case of using basic liquids such as dimethylsulfoxide, dimetylformamide and 0.1 M aqueous solution of sodium hydroxide, in the adhesion (contact angle) measurements. However, a strongly acidic liquid (35% phenol in tricresylphosphate) had nothing but dispersion force interactions with the acidic polymer; no dipole contribution to adhesion was observed.

The author obtained similar results with acidic liquids on copolymers of ethylene with varying contents of vinyl acetate, which is a basic monomer. In this case, he showed that W_{SL}^{AB} for acidic liquids (35, 48 and 72% phenol in tricresylphosphate, respectively) increased with increasing vinyl acetate content of the polymer, and, W_{SL}^{AB} for pyridine, a basic liquid, was zero; again no dipole contribution was observed. Recently, there have been numerous publications in the field of acid-base interactions either to prove [47-52] or disprove [53-55] the existence of these types of interactions between two interacting surfaces.

van Oss and co-workers [42] suggested, based on Fowkes's acid-base interaction approach [45], that electron-acceptor (Lewis acid) and electron-donor (Lewis base) interactions are essentially asymmetrical in the sense that of a given polar substance *i* the electron-acceptor and the electron-donor parameters are usually quite different and play different roles in the interfacial interactions. Therefore, they must be described by two distinct parameters. This is very different from the LW interactions where, for example, recalling Eq. (2.26):

$$\Delta G_{12}^{LW} = -2\sqrt{\gamma_1^{LW}\gamma_2^{LW}}$$

Such a simple combining rule is not applicable to AB interactions. For the AB interactions, the free energy of interaction between two materials, *i* and *j* is defined as [42]:

$$\Delta G_{ij}^{AB} \equiv -2\sqrt{\gamma_i^{\ominus}\gamma_j^{\oplus}} - 2\sqrt{\gamma_j^{\ominus}\gamma_i^{\oplus}} \tag{2.34}$$

where the electron donor parameter is designated as $\gamma^{\ominus}$ (basic component) and the electron acceptor parameter is designated as $\gamma^{\oplus}$ (acidic component). There are two terms in Eq. (2.34) because there exist two kinds of interactions each of which must be accounted for, i.e., an electron donor of *i* interacting with an electron acceptor of *j* (the first term) and an electron donor of *j* interacting with an electron acceptor of *i* (the second term). To attempt, as is sometimes done, to treat the polar interactions with a single term leads to profoundly erroneous results [56]. The negative sign is made imperative by the thermodynamic convention that a negative sign for ΔG signifies an attraction, given that ΔG_{ij}^{AB} is always attractive, or zero, whilst the two right-hand terms under the square root signs are positive, or zero [10]. It should also be noted that Eq. (2.34) is not to be confused with a simple geometric combining rule interaction (as in Eq.(2.26)), but rather that it express a double asymmetrical interaction and thus are nonadditive [42, 46]. Kollman also expressed this interaction in a similar fashion [57].

Further, either term in Eq. (2.34) may be zero because, e.g. surface *i* may exhibit electron donating properties ($\gamma_i^{\ominus} > 0$) but no electron accepting properties ($\gamma_i^{\oplus} = 0$). Such a material is termed monopolar [35, 42, 46]. For this situation:

$$\gamma_i^{AB} = 0 \tag{2.35}$$

and

$$\gamma_i = \gamma_i^{LW} \tag{2.36}$$

which is precisely what one would expect for a purely apolar surface. Thus, the condition in Eq. (2.35) should not be taken as an indication of the apolar nature of material. Indeed monopolar substances can strongly interact with bipolar materials, and with monopolar materials of the opposite polarity, notwithstanding the seemingly apolar nature of their surface tension.

The polar (AB) free energy of cohesion of material *i* is then defined as [10]:

$$\Delta G_{ii}^{AB} \equiv -4\sqrt{\gamma_i^{\oplus}\gamma_i^{\ominus}} \tag{2.37}$$

Since $\Delta G_{ii} = -2\gamma_i$, the polar component of the surface tension of material *i* then is defined as:

$$\gamma_i^{AB} \equiv 2\sqrt{\gamma_i^{\ominus}\gamma_i^{\oplus}} \tag{2.38}$$

The factor of 2 in Eqs. (2.34) and (2.38) is needed by the concern to maintain values of a comparable order of magnitude for $\gamma_i^{\ominus}$, $\gamma_i^{\oplus}$ and γ_i^{AB} [42].

From Dupré equation (see Eq. (2.25)), which is applicable for any type of interaction, one may define:

$$\Delta G_{12}^{AB} = \gamma_{12}^{AB} - \gamma_1^{AB} - \gamma_2^{AB} \tag{2.39}$$

one can express the interfacial tension, γ_{12}^{AB} ,between substances 1 and 2 as follows:

$$\gamma_{12}^{AB} = \Delta G_{12}^{AB} + \gamma_1^{AB} + \gamma_2^{AB} \tag{2.40}$$

and, substituting the value for ΔG_{ij}^{AB} from Eq. (2.34) and the values for γ_1^{AB} and γ_2^{AB} from Eq. (2.38), gives:

$$\gamma_{12}^{AB} = 2(\sqrt{\gamma_1^{\ominus}\gamma_1^{\oplus}} + \sqrt{\gamma_2^{\ominus}\gamma_2^{\oplus}} - \sqrt{\gamma_1^{\ominus}\gamma_2^{\oplus}} - \sqrt{\gamma_2^{\ominus}\gamma_1^{\oplus}}) \tag{2.41}$$

which can also be written as:

$$\gamma_{12}^{AB} = 2(\sqrt{\gamma_1^{\oplus}} - \sqrt{\gamma_2^{\oplus}}).(\sqrt{\gamma_1^{\ominus}} - \sqrt{\gamma_2^{\ominus}}) \tag{2.42}$$

which is equivalent to Eq. (2.22) for Lifshitz-van der Waals (LW) interactions.

Examination of the expression for the AB component of the interfacial tension (Eq. (2.42)) shows that γ_{12}^{AB} is not restricted to positive values or zero, as is the case for γ_{12}^{LW}. Rather, γ_{12}^{AB} will be negative when either [10]:

$$\gamma_1^{\oplus} > \gamma_2^{\oplus} \quad and \quad \gamma_1^{\ominus} < \gamma_2^{\ominus} \tag{2.43}$$

or

$$\gamma_1^{\oplus} < \gamma_2^{\oplus} \quad and \quad \gamma_1^{\ominus} > \gamma_2^{\ominus} \tag{2.44}$$

Fowkes' surface tension components approach [27] can be applied to interfacial tensions as follows:

$$\gamma_{12} = \gamma_{12}^{LW} + \gamma_{12}^{AB} \tag{2.45}$$

Therefore, since the AB and LW components of the interfacial tension are additive, the total expression for the interfacial tension between two condensed phases is:

$$\gamma_{12} = (\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_2^{LW}})^2 + 2(\sqrt{\gamma_1^{\ominus}\gamma_1^{\oplus}} + \sqrt{\gamma_2^{\ominus}\gamma_2^{\oplus}} - \sqrt{\gamma_1^{\ominus}\gamma_2^{\oplus}} - \sqrt{\gamma_1^{\oplus}\gamma_2^{\ominus}}) \tag{2.46}$$

which can be rewritten as:

$$\gamma_{12} = \gamma_1^{Total} + \gamma_2^{Total} - 2\sqrt{\gamma_1^{LW}\gamma_2^{LW}} - 2\sqrt{\gamma_1^{\oplus}\gamma_2^{\ominus}} - 2\sqrt{\gamma_1^{\ominus}\gamma_2^{\oplus}} \qquad (2.47)$$

As will be shown in Chapter 3, the values of the surface tension components and parameters of an unknown solid are determined by measuring contact angles of different liquids on the solid, and solving Young's equation.

2.7- Attractive and repulsive polar forces

Using the Dupré equation for three condensed media (of which at least one, i.e., #3, must be a liquid) gives:

$$\Delta G_{132} = \gamma_{12} - \gamma_{13} - \gamma_{23} \qquad (2.48)$$

Expanding this in terms of the AB and LW components yields:

$$\begin{aligned}\Delta G_{132} = 2[&\sqrt{\gamma_1^{LW}\gamma_3^{LW}} + \sqrt{\gamma_2^{LW}\gamma_3^{LW}} - \sqrt{\gamma_1^{LW}\gamma_2^{LW}} - \gamma_3^{LW} + \sqrt{\gamma_3^{\oplus}}(\sqrt{\gamma_1^{\ominus}} + \sqrt{\gamma_2^{\ominus}} - \sqrt{\gamma_3^{\ominus}}) \\ &+ \sqrt{\gamma_3^{\ominus}}(\sqrt{\gamma_1^{\oplus}} + \sqrt{\gamma_2^{\oplus}} - \sqrt{\gamma_3^{\oplus}}) - \sqrt{\gamma_1^{\oplus}\gamma_2^{\ominus}} - \sqrt{\gamma_1^{\ominus}\gamma_2^{\oplus}}\,]\end{aligned} \qquad (2.49)$$

Similarly, the interaction energy between two identical materials, 1, immersed in liquid 3 gives:

$$\begin{aligned}\Delta G_{131} &= -2\gamma_{13} \\ &= -2(\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_3^{LW}})^2 - 4(\sqrt{\gamma_1^{\oplus}\gamma_1^{\ominus}} + \sqrt{\gamma_3^{\oplus}\gamma_3^{\ominus}} - \sqrt{\gamma_1^{\oplus}\gamma_3^{\ominus}} - \sqrt{\gamma_3^{\oplus}\gamma_1^{\ominus}})\end{aligned} \qquad (2.50)$$

and, lastly, the interaction between two different substances, 1 and 2, in vacuum is:

$$\Delta G_{12} = -2(\sqrt{\gamma_1^{LW}\gamma_2^{LW}} + \sqrt{\gamma_1^{\oplus}\gamma_2^{\ominus}} + \sqrt{\gamma_2^{\oplus}\gamma_1^{\ominus}}) \qquad (2.51)$$

It is clear form Eq. (2.51) that the sign of the interaction energy between any two materials *in vacuum* is always negative, i.e., there is an attraction between them, and cannot be zero because γ^{LW} for all materials is finite and positive. When in aqueous systems low energy substances interact with each other, γ_{13} is positive and ΔG_{131} negative, giving rise to an attraction. The opposite is true for high surface energy substances. Similar analysis can be done for ΔG_{132} interactions. It is important to point out that both the sign and magnitude of ΔG_{132} are important. The sign would determine whether the interaction, e.g. adsorption, between substances 1 and 2 is thermodynamically possible or not. For example, a negative ΔG_{132} would indicate a feasible adsorption reaction whereas a positive ΔG_{132} would indicate that no adsorption would be possible. On the other hand, the magnitude of a negative ΔG_{132} is indicative of the strength of the adsorption interaction – the larger the magnitude, the stronger the interaction [58].

Absolute values of electron donor or acceptor parameters, $\gamma^{\ominus}$ and $\gamma^{\oplus}$, of the polar component are known at present for any compound and the determined values for various substances are based on the reference values established for water. Because for water γ_W^{AB}= 51mJ/m^2 [28] and in the absence of any known $\gamma_W^{\oplus}/\gamma_W^{\ominus}$ ratio, the assumption of unity for that ratio for water, at 20°C was considered as the most practical one [59], i.e., $\gamma_W^{\oplus}=\gamma_W^{\ominus}=25.5\ \text{mJ/m}^2$. It was mathematically demonstrated that this assumption has no influence on the outcome of the determination of the polar surface tension components, interfacial tensions and free energies of interaction of polar liquids and/or solids (i.e. $\gamma_i^{AB}, \gamma_{12}^{AB}, \Delta G_{131}^{AB}, \Delta G_{132}^{AB}\ \ and\ \ \Delta G_{12}^{AB}$ values) [42, 59]. It should be stressed that γ_i^{AB} is a surface tension component of condensed material, *i*, similar to γ_i^{LW}, such that $\gamma_i=\gamma_i^{LW}+\gamma_i^{AB}$. One must not confound surface tension **<u>components</u>** with the polar (AB) surface tension **<u>parameters</u>**, $\gamma_i^{\oplus}$ and $\gamma_i^{\ominus}$. These are factors of γ_i^{AB}, such that $\gamma_i^{AB}=2\sqrt{\gamma_i^{\oplus}\gamma_i^{\ominus}}$. The values of the surface tension components (e.g. γ_i^{AB}) are not influenced by assumptions about the value of the $\gamma_W^{\oplus} / \gamma_W^{\ominus}$ ratio, but the values of surface tension parameters $\gamma_i^{\oplus}$ and $\gamma_i^{\ominus}$ are indeed influenced by such assumption.

2.8- The practical importance of the acid-base theory

The practical applications of the acid-base theory for solids are innumerous. With respect to the field of industrial minerals, it is a powerful predictive tool that allows one to estimate the interaction between the minerals and the other materials they often interact with in real industrial applications. A remarkable example was given by Yildirim, Yoon *et al.* [58] who showed that amongst many minerals (calcium carbonate, kaolin, bentonite) talc was the one that had the strongest attraction for pitch[3] in pulp and paper applications. The interaction in this case was quantitatively predicted by the ΔG_{132} parameter.

It is well known that many properties of polymers are markedly changed by the incorporation of a filler as a second phase [60]. In addition to component properties, the mechanical properties of these materials are significantly influenced by interfacial interactions, which depend on the size of the interface and the strength of the interaction [61]. Thus, in order to optimize the balance of properties in filled plastics, much attention is being given to the control and modification of filler-matrix interaction [62]. Polymers interact with their surroundings mainly by two kinds of attractive forces, London dispersion forces and acid-base interactions [63-65]. Again, the acid-base theory allows one to estimate the degree of interaction matrix/filler throughout the ΔG_{132} parameter.

Another main use of the theory is that it allows, in conjunction with other theories, the prediction of the stability of mineral suspensions [66-68] which is very important in many applications such as paper coating, pitch control, paints, waste water treatment, i.e., all markets in which the mineral is supplied in a

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[3] Resinous sticky contaminants from wood.

slurry form. In a simplistic view, for low charged materials, the sign and the magnitude of the interfacial free energy of interaction of a given mineral (1) in water (w), ΔG_{1w1}, dictates the behavior of the suspension. The more positive the value of ΔG_{1w1}, the more stable the suspension is and vice-versa [30, 69].

The acid-base theory has been also used to assess the surface free energy components and parameters of various minerals of practical importance [30, 70] and to determine the effects of the comminution [71] and surface treatment on the surface chemistry of minerals [7, 72]. It has been applied to determine the acid-base behavior of polymers [73, 74] and to elucidate the mechanisms of adsorption from solution [75, 76] and specific separation processes [77, 78]. Nonpolar and acid-base interactions were also determined to be amongst the fundamental forces governing any adhesional process [36, 41, 79, 80]. The importance of the theory extends to explain some phenomena occurring in other fields such as biology [33, 81] and pharmaceuticals [82].

Finally, it is important to emphasize that other approaches other than the one from van Oss and co-workers for the surface thermodynamic characterization of solids do exist. The subject has been recently reviewed by Etzler [9]. Some other models are being developed [83], but at the present the practical importance of the van Oss-Chaudhury-Good theory is by far the greatest.

In Chapter 3, that follows, the most used techniques for contact angle determination with solids are reviewed and tested. The results are then used to calculate the surface free energy components of talc using the van Oss-Chaudhury-Good thermodynamic approach for solids.

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