PHYSISORPTION OF SOLIDS-A THERMODYNAMIC APPROACH BASED ON GIBBS DIVIDING SURFACE

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ABSTRACT

Adsorption can be defined as the tendency of a system component to concentrate at the interface, where the interfacial composition is different from the corresponding compositions within the phases. The design of the industrial adsorption equipment depends on the knowledge of both the amount of adsorbate that the adsorbent solid can retain and the speed of the process. The classic thermodynamic formalism developed for the description of adsorption phenomena is based on the concept of equilibrium and the model of the Gibbs dividing surface (GDS). Although the Gibbs model has important advantages, particularly a simple formalism that considers the adsorbed layer as a phase, it also exhibits some peculiarities, such as: the use of relative amounts of excess whose meaning can be difficult to understand, essentially when trying to relate these quantities with the amounts adsorbed at the interface and the location of the Gibbs plane, with zero volume, on the surface of the solid.

Introduction

Adsorption is the enrichment (positive adsorption or simply adsorption) or depletion (negative adsorption) of one or more components in an interface or interfacial layer. In this process the species to be adsorbed is the adsorptive, which in the adsorbed state is called adsorbate. When one of the phases involved in adsorption is solid, it is called an adsorbent [1-2]

Adsorption is physical when the nature of the molecular interactions between the adsorbent and the adsorbate is short-range, which is why processes that promote the enrichment of a component in an interface due to long-range forces, such as gravitational forces (phenomena) of sedimentation), they are not considered adsorption [3]

One of the greatest difficulties when considering models to quantitatively describe adsorption phenomena is the lack of knowledge of how species concentrations vary between the surface of the solid and the sine of the fluid phase. GW Gibbs in 1877 introduced the concept of excess surface by referring to the amount of each component on the surface or simply the amount adsorbed.2 To formalize this amount Gibbs proposed studying the adsorption process in a reference system divided into two zones by an imaginary surface, the dividing surface of Gibbs or GDS, of zero volume, which is parallel to the surface of the adsorbent. The reference system occupies the same volume as the real system and the concentrations of each of the components in solution are constant depending on the distance from the sine of the fluid phase to the GDS [1, 3-5]. In Figure 1a the concentration profile of a binary mixture in a system with an interfacial layer of non-zero volume is illustrated, and in Figure 1b the corresponding Gibbs reference model with GDS.
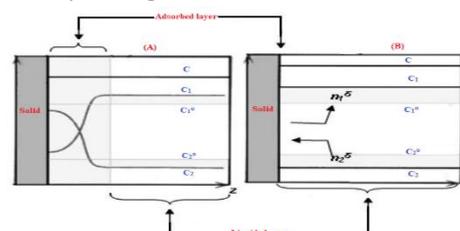

Figure 1. Concentration profiles in a solid / liquid system (competitive adsorption between binary

mixtures or solution). (a) Adsorption in the two component interfacial layer with similar molecular volumes and cross-sectional areas. (b) Gibbs reference model where the GDS coincides with the actual adsorption surface of the solid. C is the total concentration of the fluid phase, C_1^0 and C_2^0 are the initial concentrations of each component, C_1 and C_2 are the equilibrium concentrations. Shaded areas correspond to changes in system concentration. In this model, the amount of excess surface area (n^σ) represents the adsorbed amount of the component under study in the reference system

For the reference system Gibbs defined the surface thermodynamic potentials, P^σ, as those corresponding to the GDS surface phase, as follows

$$P^\sigma = P - P^f - P^s \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where P is for the total adsorption system, P^s for the adsorbent and P^f for the fluid phase.

Before continuing with the development of Gibbs thermodynamic formalism for adsorption phenomena, it is necessary to define the following quantities:

$$\Gamma = \frac{n^\sigma}{A} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Surface excess concentration, Γ, defined as the amount of excess surface area per unit area,

$$a_{sp} = \frac{A}{m^s} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

where A is for the surface area and n^σ is the amount of component adsorbed in the GDS.

$$a_{sp}^\sigma = \frac{n^\sigma}{m^s} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Specific surface area, a_{sp}, defined as the surface area, A, per unit mass of the adsorbent, m^s, Amount of specific surface excess, which expresses the amount of excess of each component on the surface per unit mass of adsorbent

In equilibrium the amount of specific surface excess is a function of the pressure, p, or equilibrium concentration, C, of each component in the fluid phase and the temperature of the adsorption system.

$$a_{sp}^\sigma = f(p)_T \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

Equation 5 is called the adsorption isotherm of the component and is the fundamental equation for the thermodynamic description of the equilibrium states of the adsorption phenomenon, based on the behavior of each component in the fluid phase.

ADSORTION AS A PHASE TRANSITION PHENOMENON

Unlike the Gibbs or GDS plane, in a real system like the one illustrated in Figure 1a, there is a concentration gradient across the adsorption layer, which is why it is not considered as a phase. The convenience of the Gibbs reference system is evident when understanding adsorption as an exchange of matter between two phases, the fluid and the GDS, thus allowing to see this process as the transition experienced by the system components from a phase of three dimensions to a two-dimensional surface phase, or simply as the loss of degrees of freedom for the component that is adsorbed.

In the development of the thermodynamic formalism of the GDS it is assumed that the volume of the adsorbent is constant and that the surface is homogeneous and inert, that is to say that the adsorption potential is the same throughout the surface and that it does not modify its surface area, internal energy and entropy during physical adsorption or physisorption, so that

$$\left(\frac{\partial G^s}{\partial n^\sigma}\right)_{T,A} = 0 \qquad\qquad \text{(Eq..6)}$$

According to Equation 6 the thermodynamic equilibrium for the adsorption system is defined as follows,

$$\left(\frac{\partial G}{\partial n^\sigma}\right)_{T,p,A,n} = \left(\frac{\partial G^\sigma}{\partial n^\sigma}\right)_{T,A} + \left(\frac{\partial G^f}{\partial n^\sigma}\right)_{T,p} + \left(\frac{\partial G^s}{\partial n^\sigma}\right)_{T,A} = 0$$
(Eq..7)

Depending on temperature, pressure, surface area of the adsorbent and amount of component

As Figure 1b illustrates, the GDS is located on the surface of the adsorbent, so that the component balance during adsorption for the closed system can be written as follows

$$d_n = dn^\sigma + dn' = 0 \qquad\qquad \text{(Eq..8)}$$

According to the above, the following relationships are met in the balance

$$\left(\frac{\partial G^\sigma}{\partial n^\sigma}\right)_{T,A} = \left(\frac{\partial G^f}{\partial n^\sigma}\right)_{T,p} = \left(\frac{\partial G^f}{\partial n^f}\right)_{T,p} \qquad \text{(Eq..9)}$$

Once again, the suitability of Gibbs formalism for the adsorption phenomenon is appreciated, since with what has been proposed so far, it is possible that in the equilibrium of the transition of the component,

from a phase in three dimensions to one in two dimensions, the equality in the chemical potentials of the components between the adsorbed and the fluid phase is observed, $\mu^\sigma = \mu^f$.

Gibbs adsorption isotherm

Gibbs' thermodynamic energy potential for GDS, when the fluid phase is a binary mixture of n1 moles of solvent and n_2 moles of solute, is expressed as a function of the corresponding state variables: temperature, pressure, components and surface area of the adsorbent

$$G^\sigma = G^\sigma(T, p, n_1, n_2, A) \qquad \text{(Eq.. 10)}$$

The total Gibbs energy differential for the GDS is expressed by the following equation

$$dG^\sigma = -S^\sigma dT + V^\sigma dp + \sum_{i=1}^{2} \mu_i^\sigma \, dn_i^\sigma + \gamma^\sigma dA \qquad \text{(Eq..11)}$$

After taking into account the following relationships, [1, 3, 6]

$$\left(\frac{\partial G}{\partial T}\right)_{p, n_1, n_2, A} = -S^\sigma \qquad \text{(Eq..12)}$$

$$\left(\frac{\partial G}{\partial p}\right)_{p, n_1, n_2, A} = V^\sigma \qquad \text{(Eq..13)}$$

$$\left(\frac{\partial G}{\partial n}\right)_{T, p, n1, A} = -\mu^\sigma_i \qquad \text{(Eq..14)}$$

$$\left(\frac{\partial G}{\partial A}\right)_{T, p, n_1, n_2,} = -\gamma^\sigma \qquad \text{(Eq..15)}$$

Equation 15 introduces the intensive amount of interfacial tension, corresponding to the solid-fluid interface, which in the Gibbs reference model would be the GDS, to quantify the changes in Gibbs energy of the system by changes in the surface area of the adsorbent.

After applying to Equation 11 Euler's theorem and differentiating it has, [3-4]

$$dG^\sigma = \sum_{i=1}^{2} \mu_i^\sigma \, dn_i^\sigma + \sum_{i=1}^{2} n_i^\sigma \, d\mu_i^\sigma + Ad\gamma^\sigma + \gamma^\sigma dA \qquad (16)$$

Comparing Equations 11 and 16, and taking into account Equation 2, it is concluded that

$$d\gamma^\sigma = -\sum_{i=1}^{2} \Gamma_i \, d\mu_i^\sigma \qquad (17)$$

Equation 17 is an equation of the Gibbs-Duhem type that shows the relationship between the intensive quantities of the two phases, at constant Γ and p, without a significant contribution from the surface. When in the fluid phase the relation n2 / n1 is small, in the Gibbs plane it is fulfilled that $\Gamma_1 \approx 0$, so that Equation 17 is finally as

$$\Gamma_2^{(1)} = -\left(\frac{\partial \gamma^\sigma}{\partial \mu_2^\sigma}\right)_T \qquad (18)$$

The quantity $\Gamma_2^{(1)}$ is called the relative excess concentration of component 2 with respect to 1, and Equation 18 is known as Gibbs adsorption isotherm. To relate to measurable quantities $\Gamma_2^{(1)}$, we recall the conclusion of Equation 9 of equality of the chemical potential of the solute between the fluid phase and the GDS for the steady state, and that the derivative of the chemical potential with respect to the solute is $d\mu^\sigma_2 = d\mu^f_2 = RTdlna^f_2$, where a^f_2 is for the solute activity in the fluid phase. These considerations allow you to write Equation 18 as follows

$$\Gamma_2^{(1)} = -\frac{1}{RT}\left(\frac{\partial \gamma^\sigma}{\partial \ln a_2^f}\right) \qquad (19)$$

Equation 19 obtained by developing thermodynamic formalism for the Gibbs model, relates the amounts of excess that describe adsorption to amounts that can be measured or inferred from experimental data, such as interfacial tension and concentration. The dependence of surface tension on concentration is established experimentally, since there is no state equation that relates them. So from the positive or negative slope of the surface tension curve depending on the concentration, it is established whether there is enrichment or depletion of the solute during the adsorption process.

Equation of state from adsorption isotherms: Henry's limit law

In the solid-liquid interface an expansive pressure takes place, π, caused by the accumulation of solute molecules in it during adsorption. This expansive pressure is naturally counteracted by the tendency of the interface to contract under normal surface tension forces, γ^σ, as the following relationship shows: γ^σ = - π, where is the initial surface tension of the solid.

Equation 19 is modified to include the expansive pressure of the interface, leaving

Dr. MOUSTFA M.H ESHTEWI

$$\Gamma_2^{(1)} = \frac{1}{RT} \left(\frac{\partial \pi}{\partial \ln a_2^r} \right) \tag{20}$$

To illustrate the importance of Equation 20, using Henry's limit law, we will deduce the state equation that defines the adsorbed layer of a gas (or diluted ideal solution).

$$\pi = \frac{KRT}{a_{sp}} p \tag{21}$$

To make a first approximation of a real system to the formalism previously developed for the Gibbs reference system, we conveniently assume, from Equation 5, that the adsorption of a gas on a solid is described by an isotherm of the form $a_{sp}^\sigma = f(p)_T = K_p$ (experimentally verifiable for a low pressure or infinitely diluted system), where K is the constant of proportionality (or Henry's constant) and p the pressure, then Equation 20 is as follows (for ideal gas the activity is directly related to the pressure), after integrating from scratch for p and π

This last equation can be expressed in the form

$$\pi = \frac{k_B T}{\rho} \tag{22}$$

where k_B is the Boltzmann constant and ρ is the area per molecule defined as follows,

$$\rho = \frac{m^s a_{sp}}{n^\sigma N_A}$$

where N_A is for the Avogadro number. Equation 22 means that when the equilibrium states of adsorption are described by Henry's limit law, the adsorbed phase behaves like an ideal gas in a two-dimensional phase ($\pi\rho = k_B T$).

Adsorption isotherm from state equations: 7 deviations from ideality

A second approximation of a real system to Gibbs formalism is made considering that there are adsorbate-adsorbate interactions, that is, molecular interactions between adsorbed species. Interactions that imply deviations from the ideal behavior of the two-dimensional adsorbed layer.

Assuming that the state equation that defines the adsorbed layer when there are intermolecular interactions, is as follows

$$\pi \left(\rho - \rho^0 \right) = k_B T \tag{23}$$

where ρ^0 refers to the area occupied by the molecule on the surface in the absence of molecular interactions, and ρ is for the area occupied by each

molecule in the presence of the interactions, which is a function of the amount of excess adsorbed. By incorporating in Equation 20 the definition given in the previous section for the molecular area, and replacing in it the differentiation of Equation 23 with respect to ρ, the following expression is reached

$$-\left(\frac{\rho}{(\rho - \rho^0)^2} \right) d\rho = d \ln p \tag{24}$$

After integrating Equation 24 indefinitely, you get

$$\ln\left(\frac{\theta}{1-\theta} \right) + \frac{\theta}{1-\theta} = \ln p + C \tag{25}$$

Where $\frac{\rho}{\rho_o} = \frac{1}{\theta}$ The variable θ is called the coating fraction, which is equal to the amount adsorbed divided by the maximum amount that must be adsorbed to fully cover the surface of the adsorbent, forming what is called a monolayer, $\theta = n^\sigma / n_m^s$. Strictly in the definition of θ we should, instead of nσ, include a quantity ns that refers to the actual amount adsorbed.

Reorganizing Equation 25, with the purpose of eliminating the logarithm, we arrive at the following expression

$$K' p = \left(\frac{\theta}{1-\theta} \right) e^{\left(\frac{\theta}{1-\theta} \right)} \tag{26}$$

Given that at very low pressures the coating fraction is close to zero, the exponential of Equation 26 quickly converges to zero, so this equation is finally as follows

$$K' p = \frac{\theta}{1-\theta} \tag{27}$$

Equation 27 can be rearranged to give it the shape of the Langmuir isotherm

$$\theta = \frac{pK'}{1 + pK'} \tag{28}$$

At very low pressures, at the ideal gas limit, Equation 28 would be reduced to Henry's law, so its validity is restricted to the vicinity of this limit behavior.

ENERGIES INVOLVED IN ADSORTION

The interpretation of adsorption as a transition process of a component, from a phase in three dimensions to one in two dimensions, allows qualitative analysis of changes in thermodynamic potentials, Gibbs energy, entropy and enthalpy. Due to this transition, the imbalance of attractive forces that exist on a surface is reduced and therefore, the surface free energy of a heterogeneous system

decreases, supporting the spontaneity of the process. Likewise, this transition, due to the loss in the number of degrees of freedom of the adsorbed components, is accompanied by the decrease in entropy. So using the following fundamental equation, $\Delta_{ads}G = \Delta_{ads}H - T\Delta_{ads}S$, it is arrived at that the adsorption $\Delta adsH$ must always be negative.

In the quantitative study of adsorption energy, one of the following two methods is usually used: isostatic and immersion calorimetry. [1, 9]

Isosteric method

This method is useful for estimating the standard differential enthalpy of adsorption, under the constraint of constant surface coating fraction. Recalling that the following fundamental equation is satisfied for a system in thermodynamic equilibrium, [10]

$$\Delta G_{ad}^0 = -RT \ln K_{eq} = \Delta H_{ad}^0 - T\Delta S_{ad}^0 \qquad (29)$$

where K_{eq}, is for the dynamic equilibrium constant, chemical equilibrium type, as is the case of the equilibrium established by transfer of components between the fluid phases and the GDS during adsorption. In this way the constant K 'of the Langmuir isotherm, Equation 28, is directly related to the equilibrium constant of Equation 29, in the vicinity of Henry's limit law. Incorporating the Langmuir isotherm in Equation 29 we get

$$\Delta G_{ad}^0 = -RT \ln\left| \frac{\theta}{(1-\theta)}\frac{1}{p} \right| = \Delta H_{ad}^0 - T\Delta S_{ad}^0 \qquad (30)$$

Assuming that the standard differential enthalpy and standard entropy of Equation 30 are approximately constant over a narrow temperature range, the differential of Equation 30 with respect to temperature, at a constant coating fraction, is

$$\left[\frac{\partial}{\partial T}(\ln p) \right]_\theta = -\frac{\Delta H_{ad}^0}{RT^2} \qquad (31)$$

Equation 31 is a Clausius-Clapeyron type equation, for which there are well-defined conditions in terms of the magnitude of the pressure (or concentration of a solution), the temperature range and constraints on fluid phase structures and adsorbed, which cannot be altered during application.

To directly relate the standard differential enthalpy of adsorption to a constant coating fraction or isostatic adsorption enthalpy, with the heat involved in the adsorption, the monolayer capacity must be constant depending on the temperature, as can be seen in the following equation 8

$$\Delta H_{ad} = Q + \delta \frac{RT^2}{1-\theta} \qquad (32)$$

Where $\delta = \frac{1}{n_m^S}\left[\frac{\partial n_m^S}{\partial T} \right]$ The considerations made to arrive at Equation 32 can be consulted in reference 8. Figure 2 shows that monolayer capacity is a function of temperature. If it is not taken into account that the capacity of monolayer can vary with temperature, erroneous conclusions can be reached regarding the exothermicity of the process, as shown in Figure 3.
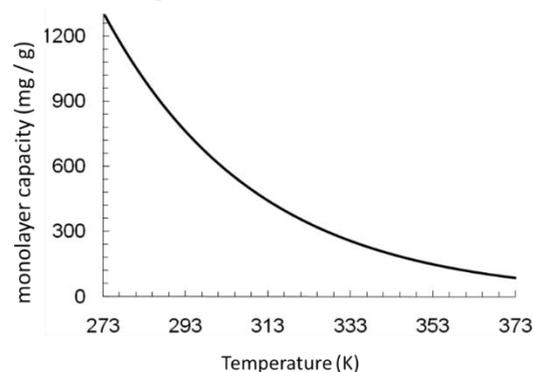

Figure 2. Dependence of monolayer capacity with respect to temperature, for adsorption in a system of a solute in a solvent in contact with a microporous adsorbent, calculated from the following empirical equation deduced from experimental evidence, where $n_m^S(T) = \exp\left[\chi \left(1 - \frac{T}{T^o} \right) \right]$ is the monolayer capacity at a reference temperature T^0 and χ is a dimensionless constant8
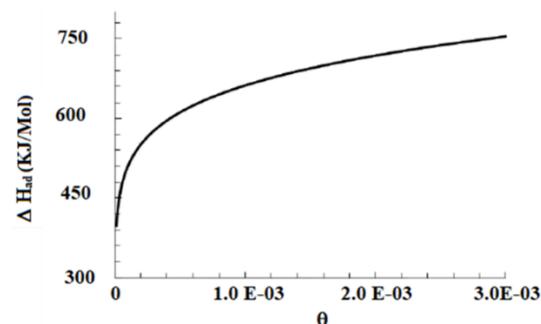

Figure 3. Isosteric enthalpy as a function of the coating fraction (θ), for the adsorption process of a solute in contact with a microporous adsorbent, using the Clausius-Clapeyron equation (31). The positive value of the isostetic enthalpy of adsorption would indicate an endothermic process

When the experimental data do not fit properly to the description of a Langmuir-type isotherm, it is possible that when using this in the calculation of the isostatic enthalpy, erroneous conclusions are also reached. There is a wide variety of proposals for adsorption isotherms, among which we highlight Toth's isotherm, Equation 33, considering the dependence of monolayer capacity with temperature, and an empirical constant that is also a function of temperature,

$$n^s = n^s_m \frac{Kp}{\left[1 + (Kp)^t \right]^{1/t}} \qquad (33)$$

where n^s is the adsorbed amount, p the equilibrium pressure, K' a constant characteristic of the adsorption n^s_m and t a parameter related to the heterogeneity of the system. The parameters t and n^s_m empirically depend on the temperature as follows

$$t(T) = t_0 + \alpha \left(1 - \frac{T_0}{T} \right) \qquad (34)$$

And

$$n^s_m(T) = n^s_{m0} e^{\chi \left(1 - \frac{T}{T_0} \right)} \qquad (35)$$

where t_0 is the value of t at a reference temperature T_0, α and χ are dimensionless constants n^s_m and the monolayer capacity at a reference temperature T_0.

By replacing the Totth isotherm in Equation 31, it is obtained that the differential isostatic adsorption enthalpy is expressed as follows, 8

$$\Delta H_{ad} = Q + \frac{1}{t} \alpha R T_0 \left[\ln \left(\frac{\theta}{(1-\theta^t)^{1/t}} \right) - \frac{\ln \theta}{1-\theta^t} \right] \qquad (36)$$

Equation 36 directly relates the isostatic adsorption enthalpy to the heat involved in the process when the coating fraction tends to zero. Figure 4 shows that the isostatic adsorption enthalpy is exothermic as a function of the coating fraction.
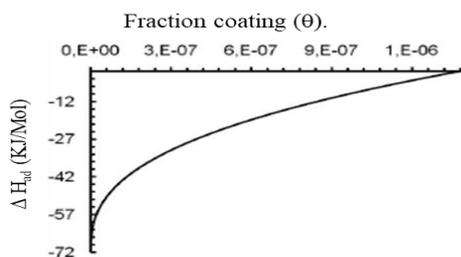

Figure 4. Exothermic isothermal enthalpy as a function of the coating fraction (θ), for the

adsorption process of a solute in contact with a microporous adsorbent, according to Equation 36

Immersion calorimetry

This method seeks to directly determine the adsorption enthalpy, without reference to either a standard state and or to an adsorption isotherm. In a first approach to this method the solid under vacuum is immersed in a pure liquid, at a certain temperature and pressure.[11] The enthalpy measured by this method is called immersion enthalpy, and can be associated with changes in the surface area of the solid or to the variation in interfacial tension. However, it is important to clarify that in these methods, normally the surface area of the solid is assumed constant during the immersion process. The enthalpy of immersion per unit area is usually described by equation, [1, 11]

$$-\Delta_{imm}H = (\gamma_s^o - \gamma_{SL}) - T \left(\frac{\partial(\gamma_s^o - \gamma_{SL})}{\partial T} \right)_p \quad (Eq..38)$$

where γ_s^o it is for the surface tension of the solid in vacuum and γ_{SL} for the solid-liquid interface. Equation 37 is obtained by analyzing the enthalpy change in the solid, when it goes from being dry (empty) to being wet. The situation is a bit more complex when a given amount of liquid is vaporized from this phase and adsorbed on the surface of the solid. The variation in the enthalpy of this system is defined as the wetting enthalpy per unit area, [11]

$$-\Delta_w H = (\gamma_s^o - \gamma_{SL}) - T \left(\frac{\partial(\gamma_s^o - \gamma_{SL})}{\partial T} \right)_p \quad (Eq..38)$$

where γ_s^o is the solid-vapor interfacial tension, for some partial pressure values of the liquid p_L. When a liquid is placed on the surface of a solid, previously in contact with the vapor phase, it may tend to "expand" on the surface of the solid if the expansive stress, σ^{SLV}, defined as $\sigma^{SLV} = \gamma^{SV} - \gamma^{LV} - \gamma^{SL}$, It is positive (this tension can also be noted as the work of liquid expansion on the solid per unit area) [2,7]

Young's relationship describes the equilibrium position when a drop is placed on a flat, horizontal solid surface. If the general case of a drop of a liquid on a solid is considered, in equilibrium with its vapor phase, Young's ratio for this system is expressed as, (Figure 5)

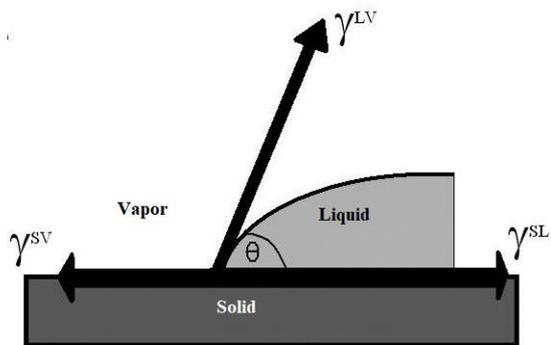$$\gamma^{LV} \cos\theta = \gamma^{SV} - \gamma^{SL} \qquad (Eq..39)$$

Figure 5. General scheme of the different components of Young's equation, when a drop is placed on a flat and horizontal solid surface

By replacing Young's Equation 39 in Equation 38 and also, assuming a perfect wetting of the liquid to the surface (zero contact angle), the enthalpy of immersion wetting per unit area is reduced to[1,11],

$$-\Delta_w H = \gamma_{L,V} - T\left(\frac{\partial(\gamma_{L,V})}{\partial T}\right)_p = H_L \text{ (Eq..40)}$$

where H_L is the superficial enthalpy of the liquid. This last equation can be written as $-\Delta_w H^* = a^s_p H_L$, where a^s_p is the specific surface area of the solid. This relationship has been widely discussed by Gregg and Sing, since it is an alternative to the BET (Brunauer-Emmett-Teller) method for determining surface areas of solids.

By subtracting Equation 38 from 37, we establish how the enthalpy of adsorption is related to that of wetting and immersion [11]

$$\Delta_{ads}H = \Delta_{imm}H - \Delta_w H \qquad \text{(Eq..41)}$$

CONCLUSIONS

The most outstanding contribution of G. W Gibbs for the thermodynamic description of adsorption is the consideration that this phenomenon takes place in an imaginary plane that allows the adsorption zone to be seen as a phase. From this model the phenomenon of adsorption can be understood as a process of transfer of component between phases, which is well defined in the balance by the equality of the chemical potential of the components between the phases involved. Although it is a simplified or idealized model, it allows rigorously developing the thermodynamic formalism that describes adsorption. Thus, starting from a generalized state equation, such as Equation 10, we deduce the Gibbs adsorption isotherm, or from a state equation 22, we deduce the Langmuir isotherm. Likewise, the formalism allows that from considering a certain adsorption isotherm, such as Henry's limit law, a state equation such as 22 can be deduced. Another aspect of Gibbs's thermodynamic formalism for adsorption, it is the demonstration of the restrictions that must be imposed on the system, such as low pressures or very dilute solutions, so that the equation of state and the adsorption isotherm properly describe a real system.

In contrast to the direct determination of the enthalpy of adsorption by immersion calorimetry, in the quantification of this by the isostatic method the following aspects are clear: that this really refers to a standard differential enthalpy of adsorption and that to correlate it with the Actual enthalpy of adsorption, its estimation must be made in a narrow temperature range, and that adjusting the data to an inappropriate isotherm can lead to erroneous conclusions regarding the magnitude and exothermicity of the adsorption.

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Dr. MOUSTFA M.H ESHTEWI