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ON PHASE TRANSITION IN CLASSICAL FLUID MIXTURES WITH SURFACE ADSORPTION

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Abstract—We propose continuous systems with an interface as a model in order to describe phase transition and surface adsorption phenomena in classical mixtures. This model allows us to relate the derivative of equilibrium surface tension with respect to the concentration of a constituent in the volume to the adsorption on S.

1. INTRODUCTION

Many mixture theories have been developed in order to supply a rational basis to classical thermochemistry (see [1–5]). However none of them has ever been extended to multiphase systems, which are typical of thermochemistry, to describe phase changes and related phenomena of adsorption on the interface.† To this aim we consider a system of two binary classical three-dimensional mixtures separated by a two-dimensional one made up with the same constituents. In this way we obtain a theory which not only includes classical results about phase equilibrium and surface adsorption but also permits the description of these phenomena in the more general situation of non-homogeneous fields and non-planar interfaces.

In particular the Gibbs' phase rule and the Gibbs' relative adsorption equation are proved with meaningful conceptual simplifications.

More precisely local balance laws of mass, linear and angular momentum, energy and entropy in the volume and on the interface S are derived (Section 2) using a general balance law proposed in [7].

In Section 3 the well-known restrictions on constitutive equations for three-dimensional mixtures are recalled. Moreover they are extended to the constitutive equations of the binary mixture constituting S.

A reduced dissipation inequality on S leads (Section 4) to meaningful equilibrium conditions whose analysis yields the Gibbs' rule as a consequence.

Another consequence of those equilibrium conditions is represented by an equation which relates the derivative of surface tension with respect to the concentration of a constituent in the volume to the adsorption on S (Section 5). A comparison of this equation with the classical one concludes this last section.

2. THERMOMECHANICAL BALANCE EQUATIONS

Let C be a continuous system with two bulk phases C_L and C_V which are binary, non-reacting, fluid mixtures. The interface S separating C_L and C_V is the surface of the discontinuities of three-dimensional fields and moreover is a mathematical model of the real interfacial layer between C_L and C_V.

This means that S is a bidimensional continuum carrying thermomechanical quantities and interacting with both C_L and C_V. In particular it is a binary mixture whose components are the same as those constituting bulk phases.

† One of the authors faced with this problem in [6] but the model there considered does not take into account the adsorption and assumes more restrictive balance laws than those proposed here.

Our aim is to develop a thermodynamical theory of surface adsorption in binary mixtures which implies, when involved fields are homogeneous and the interface is plane, well-known laws dealt with by classical thermodynamical chemistry.

In order to do this we begin with adopting the theory of classical mixtures, since this theory, developed in [2] and [3] when dealing with three-dimensional continua, is the simplest generalization of thermodynamics of homogeneous processes. In other words we will postulate for the system (C_L, C_V, S) balance laws for linear and angular momentum, energy and entropy regarding the mixture as a whole, while the presence of two different components of the mixture will be described assuming the mass balance laws separately valid for each of them. This approach to mixture theory has some limitations, as it has been underlined for three-dimensional mixtures in [3], but we show it is general enough to allow the deduction of the main results in capillarity theory.

More precisely, we accept the following general integral balance law for the whole volume $C \equiv C_L \cup C_V$:

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\int_C f\,\mathrm{d}v + \int_S f_\sigma\,\mathrm{d}\sigma\right) = \int_{\partial C} \mathbf{\Phi}\cdot\mathbf{N}\,\mathrm{d}\sigma + \int_{\partial S} \mathbf{\Phi}_\sigma\cdot\mathbf{v}\,\mathrm{d}l + \int_C R\,\mathrm{d}v + \int_S R_\sigma\,\mathrm{d}\sigma, \tag{2.1}$$

where f, R, Φ are regular functions in C–S having first kind discontinuities together with their derivatives on S; f_σ, R_σ, $\mathbf{\Phi}_\sigma$ regular functions on S, $\mathbf{N}$ the unit exterior normal to ∂C and $\mathbf{v}$ the unit exterior normal to ∂S which is tangent to S.

It can be proved (see [7]) that (2.1) is equivalent to the following local equations:

$$\frac{\partial f}{\partial t} + \operatorname{div}(f\dot{\mathbf{x}} - \mathbf{\Phi}) - R = r \quad \text{in } \overset{0}{C}_L \cup \overset{0}{C}_V$$

$$f'_\sigma + f_\sigma\sigma^\alpha_\alpha - 2H(c_n - v_n)f_\sigma - \operatorname{div}\mathbf{\Phi}_\sigma + [\![f(\dot{\mathbf{x}} - \mathbf{c}) - \mathbf{\Phi}]\!]\cdot\mathbf{n} + R_\sigma = r_\sigma \quad \text{on } S, \tag{2.2}$$

where $\mathbf{v}$ is the velocity of the centre of mass of the particle laying on S whose normal component is v_n; H and c_n are the mean curvature and the geometrical normal speed at any point of S, whose unit normal is $\mathbf{n}$; r and r_σ are so called localization residuals; $[\![\ ]\!]$ represents the jump of bracketed function on S and finally:

$$f'_\sigma \equiv \frac{\delta_n}{\delta t} f_\sigma + \nabla_S f_\sigma\cdot\mathbf{v}_\tau; \qquad \sigma^\alpha_\alpha \equiv v^\alpha_{|\alpha} - 2Hv_n. \tag{2.3}$$

where $\delta_n/\delta t$ is the Thomas derivative operator and $\mathbf{v}_\tau$ the projection of $\mathbf{v}$ on S. From now on we will neglect non-local interactions and therefore we will assume that $r = r_\sigma = 0$.

In the regular points of the volume fields (i.e. in $C_L \cup C_V$), we are led to the following well-known local equations:

$$\frac{\partial \rho_i}{\partial t} + \operatorname{div}\rho_i\dot{\mathbf{x}} = 0 (i = 1, 2); \qquad \rho\ddot{\mathbf{x}} = \operatorname{div}\mathbf{T} + \rho\mathbf{b}; \qquad \mathbf{T} = \mathbf{T}^T$$

$$\rho\dot{\varepsilon} = \mathbf{T} : \operatorname{grad}\dot{\mathbf{x}} - \operatorname{div}(\mathbf{h} + \mathbf{l}) + \rho R; \tag{2.4}$$

where ρ ρ_i are volume mass densities of the mixture and of the constituent i; $\dot{\mathbf{x}}$, $\dot{\mathbf{x}}_i$ are the velocity fields in tridimensional continuum C of the centre of mass of the whole mixture and of the constituent i respectively; $\mathbf{v}$, $\mathbf{v}_i$ are the velocity fields of the centre of mass of the particle of the mixture and of the constituent i instantaneously lying on the surface; $\mathbf{T}$ is the Cauchy stress tensor in C, $\rho\mathbf{b}$ is the given volume force density, ε is the specific internal energy in C_L and C_V, $\mathbf{h}$ is volume heat flux, R is the specific energy supply in C_L, C_V and finally volume diffusive extraflux of energy is denoted by $\mathbf{l}$. Of course, the usual relations: $\rho = \rho_1 + \rho_2$, $\rho\dot{\mathbf{x}} = \rho_1\dot{\mathbf{x}}_1 + \rho_2\dot{\mathbf{x}}_2$ between mass densities and velocities of the whole mixture and its constituents are accepted.

Similarly we assume that the equality $\rho_\sigma\mathbf{v} = \sum \rho_{\sigma i}\mathbf{v}_i$ holds. If we use the notation:

$$\sigma^\alpha_{i\alpha} \equiv v^\alpha_{i|\alpha} - 2Hv_{\text{in}}$$

it is easy to verify the relation:

$$\rho_\sigma \sigma_\alpha^\alpha = \sum \rho_{\sigma i}\sigma_{i\alpha}^\alpha + \sum (\mathbf{v}_i - \mathbf{v}) \cdot \nabla \rho_{\sigma i}.$$

The application of $(2.2)_2$ leads to the following local equations on S:

$$\begin{gathered}
\rho'_\sigma + \rho_\sigma \sigma_\alpha^\alpha - 2H(c_n - v_n)\rho_\sigma + [\![\rho(\dot{\mathbf{x}} - \mathbf{c})]\!] \cdot \mathbf{n} = 0 \\
\rho'_{\sigma i} + \rho_{\sigma i}\sigma_{i\alpha}^\alpha + (\mathbf{v}_i - \mathbf{v}) \cdot \nabla_S \rho_{\sigma 1} - 2H(c_n - v_{in})\rho_{\sigma i} + [\![\rho_i(\mathbf{x}_i - \mathbf{c})]\!] \cdot \mathbf{n} = 0 \\
\rho_\sigma \mathbf{v}' - \nabla_S \mathbf{T}_\sigma - [\![\mathbf{T}]\!] \cdot \mathbf{n} + [\![(\dot{\mathbf{x}} - \mathbf{v})\rho(\dot{\mathbf{x}} - \mathbf{c})]\!] \cdot \mathbf{n} = 0
\end{gathered}$$

$$\rho_\sigma \varepsilon'_\sigma - \mathbf{T}_\sigma : \nabla_S \mathbf{v} + \mathrm{div}_S \mathbf{h}_\sigma + \mathrm{div}_S \mathbf{l}_\sigma + \left[\!\!\left[\rho\left\{\frac{1}{2}(\dot{\mathbf{x}} - \mathbf{v})^2 + (\varepsilon - \varepsilon_\sigma)\right\}(\dot{\mathbf{x}} - \mathbf{c}) - (\dot{\mathbf{x}} - \mathbf{v}) \cdot \mathbf{T} + \mathbf{h} + \mathbf{l} \right]\!\!\right] \cdot \mathbf{n} + \rho_\sigma R_\sigma = 0. \quad (2.5)$$

in which we denoted by χ_σ the surface field corresponding to the volume field χ. Moreover we assume $T^{\alpha 3} = 0$ and $T^{\alpha\beta} = T^{\beta\alpha}$. Using $(2.4)_1$ $(2.5)_1$ for the quantities $c_i \equiv \rho_i/\rho$; $c_{\sigma i} \equiv \rho_{\sigma i}/\rho_\sigma$ we have:

$$\begin{gathered}
\rho \dot{c}_i + \mathrm{div}(\rho_i(\dot{\mathbf{x}}_i - \dot{\mathbf{x}})) = 0 \quad \text{in } \overset{0}{C}_L \cup \overset{0}{C}_V \\
\rho_\sigma c'_{\sigma i} + \mathrm{div}_S(\rho_{\sigma i}(\mathbf{v}_i - \mathbf{v})_\tau) - c_{i\sigma}[\![\rho(\dot{\mathbf{x}} - \mathbf{c}) + \rho_i(\dot{\mathbf{x}}_i - \mathbf{c})]\!] \cdot \mathbf{n} = 0 \quad \text{on } S.
\end{gathered} \quad (2.6)$$

If η and η_σ denote the volume and surface specific entropy respectively, the second principle of thermodynamics implies:

$$\begin{gathered}
\rho \dot{\eta} \geq -\mathrm{div}(\mathbf{h}/\theta) + \rho R/\theta \quad \text{in } \overset{0}{C}_L \cup \overset{0}{C}_V \\
\rho_\sigma \eta'_\sigma - [\![\rho(\eta - \eta_\sigma)(\dot{\mathbf{x}} - \mathbf{c}) + \mathbf{h}/\theta]\!] \cdot \mathbf{n} \geq 0 \quad \text{on } S.
\end{gathered} \quad (2.7)$$

Finally, the volume and surface dissipation inequalities can be written in terms of specific free energies:

$$\psi \equiv \varepsilon - \theta\eta; \qquad \psi_\sigma \equiv \varepsilon_\sigma - \theta_\sigma \eta_\sigma.$$

Making use of (2.7), $(2.4)_4$, $(2.5)_4$ we obtain

$$\begin{gathered}
\rho(\dot{\psi} + \eta\dot{\theta}) - \mathbf{T} : \nabla\dot{\mathbf{x}} + \mathrm{div}\,\mathbf{l} + \frac{\mathbf{h} \cdot \nabla\theta}{\theta} \leq 0 \quad \text{in } \overset{0}{C}_L \cup \overset{0}{C}_V \\
-\rho_\sigma(\psi'_\sigma + \eta_\sigma \theta') + \mathbf{T}_\sigma : \nabla_S \mathbf{v} - \frac{\mathbf{h}_\sigma \cdot \nabla_S \theta_\sigma}{\theta_\sigma} + \left[\!\!\left[\rho(\dot{\mathbf{x}} - \mathbf{c})(\psi_\sigma - \psi) - \frac{1}{2}\rho(\dot{\mathbf{x}} - \mathbf{v})^2(\dot{\mathbf{x}} - \mathbf{c}) + \mathbf{l} + \mathbf{h} + \mathbf{T} : (\dot{\mathbf{x}} - \mathbf{v}) \right]\!\!\right] \cdot \mathbf{n} + \mathrm{div}_S \mathbf{l}_\sigma \geq 0 \quad \text{on } S,
\end{gathered} \quad (2.8)$$

where we suppose that $[\![\theta]\!] = 0$ on S.

3. THERMOMECHANICAL RESTRICTIONS ON CONSTITUTIVE EQUATIONS

For three-dimensional mixtures the forms of constitutive equations allowed by entropy principles are carefully studied in the literature. For this reason we limit ourselves to quote here the results obtained by Gurtin and Vargas in [3] when applied to the particular case of *binary and non-reacting* mixture.

More precisely denoting by A the generic member of the set

$$\{\psi, \eta, \mathbf{T}, \mathbf{l}, \mathbf{h}\}$$

and assuming constitutive equations of the form:

$$A \equiv A(\rho, c_1, \theta, \nabla\rho, \nabla c_1, \nabla\theta)\dagger; \quad (3.1)$$

† In a binary mixture we have $c_1 + c_2 = 1$, so that the specified set of independent variables actually specifies the state of the bulk phases.

in [3] the following relations are proved:

$$\mathbf{T} = -p\mathbf{I}$$

$$\psi = \psi(\rho, \theta, c_1)$$

$$p = p(\rho, \theta, c_1) = -\rho^2 \frac{\partial \psi}{\partial \rho}$$

$$\eta = -\frac{\partial \psi}{\partial \theta}$$

$$\mathbf{l} = \rho_1 \mu_1 (\dot{\mathbf{x}}_1 - \dot{\mathbf{x}}) \quad \text{where} \quad \mu_1 = \frac{\partial \psi}{\partial c_1}\dagger$$

$$-\rho_1(\dot{\mathbf{x}} - \dot{\mathbf{x}}_1)\nabla \mu_1 + \mathbf{h} \cdot \nabla \theta \leq 0. \tag{3.2}$$

In a completely analogous way we will deal with the corresponding problem for *surface constitutive equations*. Let a generic member of these equations given in the form:

$$A_\sigma \equiv A_\sigma(\rho_\sigma, c_{1_\sigma}, \theta, \nabla_S \rho_\sigma, \nabla_S c_{1_\sigma}, \nabla_S \theta, a)\ddagger. \tag{3.3}$$

Moreover let us assume that the interface S may be described as an "isotropic" membrane. This is equivalent to assume that the surface Cauchy stress tensor is given by:

$$\mathbf{T}_\sigma = \gamma \mathbf{I}_\sigma, \tag{3.4}$$

where γ is the surface tension and $\mathbf{I}_\sigma$ is the identity operator on S. We underline that this hypothesis is coherent with the results obtained for classical three-dimensional mixtures in [3]. In order to obtain the residual entropy inequality and some of the searched restrictions on constitutive equations, let us substitute (3.3) and (3.4) in $(2.8)_2$. When we make use of $(3.2)_{1,5}$ we obtain:

$$\begin{aligned}
&-\rho_\sigma\bigg(\frac{\partial \psi_\sigma}{\partial c_{1_\sigma}} c'_{1_\sigma} + \frac{\partial \psi_\sigma}{\partial \rho_\sigma}\rho'_\sigma + \frac{\partial \psi_\sigma}{\partial \theta}\theta' + \frac{\partial \psi_\sigma}{\partial a} a' + \frac{\partial \psi_\sigma}{\partial(\nabla_S c_{1_\sigma})}\nabla_S c'_{1_\sigma} \\
&+ \frac{\partial \psi_\sigma}{\partial \nabla_S \theta}\nabla_S \theta' + \frac{\partial \psi_\sigma}{\partial(\nabla_S \rho_\sigma)}\nabla_S \rho'_\sigma + \eta_\sigma \theta'\bigg) - \gamma \sigma^\alpha_\alpha - \mathbf{h}_\sigma \cdot \nabla_S \theta/\theta \\
&+ \left[\!\!\left[\rho\left\{(\psi_\sigma - \psi) - \frac{1}{2}(\dot{\mathbf{x}} - \mathbf{v})^2\right\}(\dot{\mathbf{x}} - \mathbf{c})\right]\!\!\right] \cdot \mathbf{n} + \mathrm{div}_S \mathbf{l}_\sigma \\
&+ [\![(\dot{\mathbf{x}} - \mathbf{v})p + \mu_1 \rho_1 (\dot{\mathbf{x}}_1 - \dot{\mathbf{x}})]\!] \cdot \mathbf{n} \geq 0.
\end{aligned}$$

If, for simplicity, we introduce the quantities:

$$\mu_{\sigma^1} \equiv \frac{\partial \psi_\sigma}{\partial c_{1_\sigma}} \qquad \boldsymbol{\lambda}_\sigma = \mathbf{l}_\sigma + \rho_{\sigma^1}\mu_{\sigma^1}(\mathbf{v}_1 - \mathbf{v})_\tau.$$

and use $(2.5)_{1,2}$ together with the relation:

$$a' = 2a(\sigma^\alpha_\alpha + 2H(v_n - c_n))$$

in the previous inequality, we obtain:

$$\begin{aligned}
&-\rho_\sigma\left(\frac{\partial \psi_\sigma}{\partial \theta} + \eta_\sigma\right)\theta' + [\![\rho_1(\dot{\mathbf{x}}_1 - \mathbf{c})(\mu_{\sigma^1} - \mu_1)]\!] \cdot \mathbf{n} \\
&+ \rho_{\sigma^1}(\mathbf{v}_1 - \mathbf{v})_\tau \cdot \nabla_S \mu_{\sigma^1} - \rho_\sigma\left(\frac{\partial \psi_\sigma}{\partial \nabla_S c_{1_\sigma}}\nabla_S c'_{1_\sigma} + \frac{\partial \psi_\sigma}{\partial \nabla_S \rho_\sigma}\nabla_S \rho'_\sigma + \frac{\partial \psi_\sigma}{\partial \nabla_S \theta}\nabla_S \theta'\right)
\end{aligned}$$

† In literature μ_1 is called reduced chemical potential (see [3]).

‡ If $a_{\alpha\beta}$ denotes the surface metric tensor we put $a \equiv \det a_{\alpha\beta}$. In [8] its introduction as an independent variable is fully justified.

$$+\sigma^{\alpha}_{\alpha}\left(\rho_\sigma^2\frac{\partial\psi_\sigma}{\partial\rho_\sigma}-2a\rho_\sigma\frac{\partial\psi_\sigma}{\partial a}+\gamma\right)-(v_n-c_n)\left\{2H\rho_\sigma^2\frac{\partial\psi_\sigma}{\partial\rho_\sigma}-2a\rho_\sigma\frac{\partial\psi_\sigma}{\partial a}-[\![p]\!]\right\}$$
$$-\left[\!\!\left[\rho(\dot{\mathbf{x}}-\mathbf{c})\left\{\psi_\sigma-\psi-p/\rho+\rho_\sigma\frac{\partial\psi_\sigma}{\partial\rho_\sigma}-c_{1_\sigma}\mu_{1_\sigma}+c_1\mu_1-\frac{1}{2}(\dot{\mathbf{x}}-\mathbf{v})^2\right\}\right]\!\!\right]\cdot\mathbf{n}$$
$$-\frac{\mathbf{h}_\sigma\cdot\nabla_S\theta}{\theta}+\frac{\partial\boldsymbol{\lambda}_\sigma}{\partial\rho_\sigma}\cdot\nabla_S\rho_\sigma+\frac{\partial\boldsymbol{\lambda}_\sigma}{\partial c_{1_\sigma}}\cdot\nabla_S c_{1_\sigma}+\frac{\partial\boldsymbol{\lambda}_\sigma}{\partial\theta}\cdot\nabla_S\theta+\frac{\partial\boldsymbol{\lambda}_\sigma}{\partial\nabla_S\rho_\sigma}:\nabla_S(\nabla_S\rho_\sigma)$$
$$+\frac{\partial\boldsymbol{\lambda}_\sigma}{\partial\nabla_S c_{1_\sigma}}:\nabla_S(\nabla_S c_{1_\sigma})+\frac{\partial\boldsymbol{\lambda}_\sigma}{\partial\nabla_S\theta}:\nabla_S(\nabla_S\theta)+\frac{\partial\boldsymbol{\lambda}_a}{\partial a}\nabla_S a\geq 0.$$

Since the inequality is linear in the following quantities which can be arbitrarily chosen:

$$B\equiv\{\theta',\ \sigma^{\alpha}_{\alpha},\ (\nabla_S c_{i\sigma})',\ (\nabla_S\rho_\sigma)',\ (\nabla_S\theta)',\ \nabla_S(\nabla_S\rho_\sigma),\ \nabla_S(\nabla_S c_{1_\sigma}),\ \nabla_S(\nabla_S\theta),\ \nabla_S a\}$$

we obtain the set of relations†:

$$\eta_\sigma=-\frac{\partial\psi_\sigma}{\partial\rho_\sigma},\qquad \gamma=-\rho_\sigma^2\frac{\partial\psi_\sigma}{\partial\rho_\sigma}+2a\rho_\sigma\frac{\partial\psi_\sigma}{\partial a},$$
$$\psi_\sigma=\psi_\sigma(\rho_\sigma,c_{1_\sigma},\theta,a),\qquad \boldsymbol{\lambda}_\sigma=\mathbf{0}\quad\text{or equivalently } \mathbf{l}_\sigma=-(\mathbf{v}_1-\mathbf{v})_\tau\rho_{\sigma^1}\mu_{\mu^1},\tag{3.5}$$

which are similar to their three-dimensional counterparts (3.2), and moreover the residual inequality:

$$\rho_{\sigma^1}(\mathbf{v}_1-\mathbf{v})_\tau\cdot\nabla_S\mu_{\sigma^1}+[\![\rho_1(\dot{\mathbf{x}}_1-\mathbf{c})(\mu_{\sigma^1}-\mu_1)]\!]\cdot\mathbf{n}-\{2H\gamma-[\![p]\!]\}(v_n-c_n)-\frac{\mathbf{h}_\sigma\cdot\nabla_s\theta}{\theta}$$
$$+\left[\!\!\left[(\dot{\mathbf{x}}-\mathbf{c})\left(\mu-\mu_\sigma-c_1\mu_1+c_{1_\sigma}\mu_{\sigma^1}-\frac{1}{2}(\dot{\mathbf{x}}-\mathbf{v})^2\right)\right]\!\!\right]\cdot\mathbf{n}\geq 0,\tag{3.6}$$

where we introduced the specific chemical potentials:

$$\mu\equiv\frac{\partial\rho\psi}{\partial\rho};\qquad \mu_\sigma\equiv\frac{\partial\rho_\sigma\psi_\sigma}{\partial\rho_\sigma}.$$

4. RELATIONS CHARACTERIZING EQUILIBRIUM STATES

In this section we will use the residual entropy inequalities $(3.2)_6$ and (3.6) to derive remarkable conditions at equilibrium. These last ones, together with (2.4) (2.5), in the static situation, supply a set of equations we will at least prove to characterize phase equilibrium when the forces derive from a potential $U(\mathbf{x})$ and the interface S is plane, i.e. $H=0$. Let us regard first member of inequality (3.6) as a function σ of the following variables:

$$X_\alpha\equiv\{(\dot{\mathbf{x}}-\mathbf{c})^+,(\dot{\mathbf{x}}-\mathbf{c})^-,\nabla_S\theta,(\dot{\mathbf{x}}_1-\mathbf{c})^+,(\dot{\mathbf{x}}_1-\mathbf{c})^-,(\mathbf{v}_1-\mathbf{v}),(v_n-c_n)\}.$$

A state for which all X_α vanish will be called an *equilibrium state* (see [1]). In this case σ reaches a minimum since we have

$$\sigma(X_\alpha)\geq 0\quad\text{and}\quad\sigma(\mathbf{0})=0.$$

Moreover we have assumed that on S $\theta^+=\theta^-=\theta$ so that the other variables on which σ depends are

$$Y_\alpha\equiv\{H,\theta,\rho^\pm,c_1^\pm,\rho_\sigma,c_{1_\sigma}\}.$$

Therefore the equilibrium values for Y_α are given by the equations:

$$\left.\frac{\partial\sigma}{\partial X_\alpha}\right|_{X_\alpha=0,Y_\alpha}=0;\tag{4.1}$$

† In order to derive $(3.5)_4$ we have used lemma (10.2) in [3], as the quantity $\boldsymbol{\lambda}_\sigma$ (because of clear physical reasons) is an isotropic vector function.

which actually reads

$$
\begin{gathered}
[\![p]\!] = 2H\gamma \\
\nabla_S \mu_{1_\sigma} \,|_{X_\sigma=0} = 0 \Rightarrow \mu_{1_\sigma} \,|_0 = \text{const.} \\
\mu_1^- \,|_0 = \mu_1^+ \,|_0 = \mu_{1_\sigma} \,|_0; \qquad \mathbf{h}_\sigma \,|_0 = \mathbf{0} \\
(\mu - c_1\mu_1)^- \,|_0 = (\mu - c_1\mu_1)^+ \,|_0 = (\mu_\sigma - c_{1_\sigma}\mu_{1_\sigma})|_0.
\end{gathered} \tag{4.2}
$$

These equations show that in this more general equilibrium situation the convenient thermodynamical potentials are a suitable combination of the total and reduced chemical potentials as it is usually assumed in classical thermochemistry.

Similarly from $(3.2)_6$ we deduce:

$$
\nabla \mu_1 \,|_0 = 0 \Rightarrow \begin{cases} \text{in } \overset{0}{C}_L & \mu_1 \,|_0 = \bar{\mu}_{1_L} \\ \text{in } \overset{0}{C}_V & \mu_1 \,|_0 = \bar{\mu}_{1_V} \end{cases} \tag{4.3}
$$

$$
\mathbf{h} \,|_0 = \mathbf{0} \quad \text{in } C_L \cup C_V
$$

where $\bar{\mu}_{1_V}$ and $\bar{\mu}_{1_L}$ are constants.

Recalling (2.4), (2.5) and (4.3) we obtain the following set of equilibrium conditions†:

$$
\begin{gathered}
\nabla p_L = \rho_L \nabla U(\mathbf{x}) \\
\mu_{1L}(\mathbf{x}) = \bar{\mu}_{1L} \quad \text{in } \overset{0}{C}_L \\
\theta_L(\mathbf{x}) = \theta_0 \\
\nabla p_V = \rho_V \nabla U(\mathbf{x}) \\
\mu_{1V}(\mathbf{x}) = \bar{\mu}_{1V} \quad \text{in } \overset{0}{C}_V \\
\theta_V(\mathbf{x}) = \theta_0
\end{gathered}
$$

$$
p^+ - p^- = 2\gamma H; \qquad \nabla_S \gamma = 0 \Rightarrow \gamma = \text{const.} \tag{4.4}
$$

$$
\mu_1^+ = \mu_1^- \qquad \text{on } S \qquad g^+ - c_1^+\mu_1^+ = g^- - c_1^-\mu_1^- \tag{4.5}
$$

$$
\mu_{1_\sigma} = \mu_1^+; \quad \mu_\sigma - c_{1_\sigma}\mu_{1_\sigma} = g^+ - c_1^+\mu_1^+. \tag{4.6}
$$

In $(4.5)_3$ and $(4.6)_2$ we used the equality $\mu = g$ which holds for closed systems. In all these equations the unknowns are the basic volume fields ρ_L, ρ_V, c_{1L}, c_{1V} and surface fields ρ_σ, c_{1_σ} as the temperature field θ has been assumed uniformly equal to θ_0 in $C_L \cup C_V$.

Now it is possible to simplify the solution of this system if other variables are adopted, especially in the case of *plane interface*.

First of all owing to this last hypothesis, the surface quantities disappear in (4.4), (4.5). In second place, if the relations :

$$
\begin{gathered}
p = p(\rho, c_1) \\
\mu_1 = \mu_1(\rho, c_1)
\end{gathered} \tag{4.7}
$$

$$
\begin{gathered}
\gamma = \gamma(\rho_\sigma, c_{1_\sigma}) \\
\mu_{1_\sigma} = \mu_{1_\sigma}(\rho_\sigma, c_{1_\sigma})
\end{gathered} \tag{4.8}
$$

are separately invertible, we can adopt as set of basic fields: p_L, p_V, μ_{1L}, μ_{1V}, γ, μ_{1_σ} instead of ρ_L, ρ_V, c_{1L}, c_{1V}, ρ_σ, c_{1_σ}.

Of course the hypothesis of invertibility of the aforesaid system is equivalent to a requirement of physical admissibility on the constitutive equations. In order to solve system (4.4), (4.5) we begin observing that the chemical potential μ_1 is uniform in *all the volume* $C_v \cup C_L$ and that from now on we will denote its constant value by $\bar{\mu}_1$.

Moreover equation $(4.5)_1$ (when $H = 0$) permits to regard $(4.5)_3$ as an implicit relation between p^+ and $\bar{\mu}_1$:

$$
f(p^+, \bar{\mu}_1) = 0. \tag{4.9}
$$

If it is solvable with respect to p^+ we attain to a function:

$$
p^+ = \phi(\bar{\mu}_1). \tag{4.10}
$$

† We oriented the normal toward the phase C_V so that f^+ is the evaluation of f_V on the interface.

On the other hand since μ_1 is a constant, equation $(4.4)_1$ can be written in the usual form:

$$\nabla(P_L(p_L(\mathbf{x}), \bar{\mu}_1) - U(\mathbf{x})) = 0,$$

where

$$P_L(p_L, \bar{\mu}_1) = \int \frac{\mathrm{d}p_L}{\rho_L(p_L, \bar{\mu}_1)}.$$

Consequently, when we take into account (4.10) and fix the arbitrary constant U in a suitable way, we have:

$$P_L(p_L(\mathbf{x}), \bar{\mu}_1) - U(\mathbf{x}) = P_L(\phi(\bar{\mu}_1), \bar{\mu}_1).$$

Similarly from $(4.4)_3$ and the condition $p^+ = p^-$ when we define the function P_V in a similar way as done for P_L we deduce that:

$$P_V(p_V(\mathbf{x}), \bar{\mu}_1) - U(\mathbf{x}) = P_V(\phi(\bar{\mu}_1), \bar{\mu}_1).$$

Moreover, μ_{1_σ} and γ are determined by (4.6) since the terms on the right sides are known.†
To conclude we can state that

when the body forces are conservative, the interface is flat, the temperature field is uniform, (4.7) (4.8) *are invertible and* (4.9) *defines implicitly* (4.10), *one and only one equilibrium solution is determined when the quantity $\bar{\mu}_1$ is given (i.e. the value of reduced chemical potential in a point and consequently in the whole volume, or equivalently (see* (4.10)) *the external uniform pressure p_e).*

Obviously the corresponding distributions of ρ and c_1 are generally non-uniform. Quoted result is an extension to a more general situation of the well-known Gibbs' phase rule for plane interfaces according to which the variance of a binary system with two phases is two (i.e. the temperature and the chemical potential or the external pressure).

5. THE INFLUENCE OF MASS ADSORPTION ON SURFACE TENSION

In the previous section we proved that there are infinitely many equilibrium states with plane interface and uniform temperature. One of them is determined when we fix either the value of the reduced chemical potential or that of the external pressure.

On the other hand (4.9) implies p^+ to be constant on S together with ρ^-, c_1^- (and ρ^+, c_1^+) owing to (4.7). In other words, an equilibrium state is characterized when the value of one of the variables

$$p_e,\ \mu_1^+ = \mu_1^-,\ p^+ = p^-,\ \rho^\pm,\ c_1^\pm,$$

is fixed.

In particular, the surface tension γ, which at equilibrium is constant on S, can be regarded together with the other equilibrium fields as functions of the variable c_1^-.

Now it is experimentally verified (see [9, 10]) that $\gamma(c_1^-)$ is either an increasing or a decreasing function.

The first circumstance occurs when $c_{1_\sigma}(c_1^-) < c_1^-$ (negative adsorption), while the other one when $c_{1_\sigma}(c_1^-) > c_1^-$ (positive adsorption).

In order to obtain theoretically this result in [11] Gibbs assumed it was possible to substitute the actual system constituted by bulk phases separated by a narrow interfacial layer with a fictious one in which the quoted layer is substituted by a plane suitably chosen inside it and where bulk phases are assumed to homogeneously fill the remaining part of the same layer. This plane is assumed placed in such a way that Gibbs' relative surface excess (see for instance [10] or [11]) of one of the constituents of the mixture vanishes.

† It remains to take into account $(4.2)_5$, $(4.3)_3$ which refer to heat conduction. We will suppose, according with $(3.35)_1$ in [2] the constitutive equations relative to $\mathbf{h}$ and $\mathbf{h}_\sigma$ be such that heat conduction vanishes when $\operatorname{grad} \mu_1 = \operatorname{grad} \theta = \mathbf{0}$, $\operatorname{grad} \mu_{1_\sigma} = \operatorname{grad} \theta_\sigma = \mathbf{0}$. In this way quoted equations are satisfied at every equilibrium state.

Under these assumptions Gibbs derived the relative adsorption equation (see [12], p. 25):

$$\mathrm{d}\gamma = -\Gamma_{12}\,\mathrm{d}\hat{\mu}_1\,\dagger \tag{5.1}$$

where Γ_{12} and $\hat{\mu}_1$ in our notations are given by:

$$\Gamma_{12} = \rho_\sigma\left(\frac{c_{1_\sigma} - c_1}{c_2}\right)$$
$$\hat{\mu}_1 = g + c_2\mu_1. \tag{5.2}$$

Other models of the surface layer have been proposed in [12] and [13]. The greater complexity of these models makes it possible to avoid the introduction of "*ad hoc*" surfaces in deriving (5.1). Our aim is to deduce within the framework of our theory a relation between γ and c_1^- at equilibrium corresponding to (5.1). To this end, from now on we will neglect the explicit dependence of ψ_σ on a so that from $(4.6)_2$ we obtain:

$$\gamma/\rho_\sigma = \psi_\sigma - \psi^- - p^-/\rho^- + c_1\mu_1 - c_{1_\sigma}\mu_{1_\sigma}.$$

Henceforth we omit the mark $(\;)^-$ bearing in mind that all quantities are evaluated on the interface and refer to the liquid phase.

Moreover, recalling the remarks at the beginning of this section we will regard all the equilibrium quantities as functions of c_{1L}.

Using $(4.6)_1$ the previous relation becomes:

$$\gamma = \rho_\sigma\{\psi_\sigma - \psi - p/\rho + \mu_1(c_1 - c_{1_\sigma})\}. \tag{5.3}$$

As every quantity in both members of (5.3) are to be regarded as functions of c_{1L}, we can calculate the total derivative of the first and second members:

$$\begin{aligned}
\frac{\mathrm{d}\gamma}{\mathrm{d}c_1} &= \frac{\mathrm{d}\rho_\sigma}{\mathrm{d}c_1}\{\psi_\sigma - g + (c_1 - c_{1_\sigma})\mu_1\}\\
&\quad + \rho_\sigma\left\{\frac{\partial\psi_\sigma}{\partial\rho_\sigma}\frac{\mathrm{d}\rho_\sigma}{\mathrm{d}c_1} + \frac{\partial\psi_\sigma}{\partial c_{1_\sigma}}\frac{\mathrm{d}c_{1_\sigma}}{\mathrm{d}c_1} - \frac{\partial g}{\partial c_1} - \frac{\partial g}{\partial\rho}\frac{\mathrm{d}\rho}{\mathrm{d}c_1} + (c_1 - c_{1_\sigma})\left(\frac{\partial\mu_1}{\partial\rho}\frac{\mathrm{d}\rho}{\mathrm{d}c_1} + \frac{\partial\mu_1}{\partial c_1}\right) + \mu_1\left(1 - \frac{\partial c_{1_\sigma}}{\partial c_1}\right)\right\}\\
&= \frac{\mathrm{d}\rho_\sigma}{\mathrm{d}c_1}\{\mu_\sigma - \mu_{1_\sigma}c_{1_\sigma} - g + \mu_1 c_1 + \gamma/\rho_\sigma\}\\
&\quad + \rho_\sigma\left\{-\gamma/\rho_\sigma^2\frac{\mathrm{d}\rho_\sigma}{\mathrm{d}c_1} + \mu_1\frac{\mathrm{d}c_{1_\sigma}}{\mathrm{d}c_1} - \left(\frac{\partial\psi}{\partial c_1} + 1/\rho\frac{\partial p}{\partial c_1}\right) - \left(\frac{\partial\psi}{\partial\rho} - p/\rho^2 + 1/\rho\frac{\partial p}{\partial\rho}\right)\right.\\
&\quad \left.\times\frac{\mathrm{d}\rho}{\mathrm{d}c_1} + (c_1 - c_{1_\sigma})\frac{\mathrm{d}\mu_1}{\mathrm{d}c_1} + \mu_1\left(1 - \frac{\mathrm{d}c_{1_\sigma}}{\mathrm{d}c_1}\right)\right\}.
\end{aligned}$$

Owing to $(3.5)_2$ and $(4.2)_4$ together with the definitions of chemical and chemical reduced potential, we finally obtain:

$$\frac{\mathrm{d}\gamma}{\mathrm{d}c_1} = -\rho_\sigma(c_{1_\sigma} - c_1)\frac{\mathrm{d}\mu_1}{\mathrm{d}c_1} - \frac{\rho_\sigma}{\rho}\frac{\mathrm{d}p}{\mathrm{d}c_1}. \tag{5.4}$$

In order to compare (5.4) and (5.1) we observe that $(5.2)_2$ implies:

$$\begin{aligned}
\frac{\mathrm{d}\hat{\mu}_1}{\mathrm{d}c_1} &= \frac{\partial g}{\partial\rho}\frac{\mathrm{d}\rho}{\mathrm{d}c_1} + \frac{\partial g}{\partial c_1} - \mu_1 + c_2\frac{\mathrm{d}\mu_1}{\mathrm{d}c_1}\\
&= \left(\frac{\partial\psi}{\partial\rho} - \frac{p}{\rho^2} + \frac{1}{\rho}\frac{\partial p}{\partial\rho}\right)\frac{\mathrm{d}\rho}{\mathrm{d}c_1} + \left(\frac{\partial\psi}{\partial c_1} + \frac{1}{\rho}\frac{\partial p}{\partial c_1}\right)\\
&\quad - \mu_{1L} + c_2\frac{\mathrm{d}\mu_1}{\mathrm{d}c_1} = \frac{1}{\rho}\frac{\mathrm{d}p}{\mathrm{d}c_1} + c_{2L}\frac{\mathrm{d}\mu_1}{\mathrm{d}c_1}.
\end{aligned}$$

† $\hat{\mu}_1 \equiv \dfrac{\partial\rho\psi}{\partial\rho_1}$ is the ordinary chemical potential.

This relation, together with that one linking the concentrations, allows us to put (5.4) in the form:

$$\frac{d\gamma}{dc_1} = -\rho_\sigma \frac{(c_{1_\sigma} - c_1)}{c_2} \frac{d\hat{\mu}_1}{dc_1} - \frac{\rho_\sigma c_{2_\sigma}}{\rho c_2} \frac{dp}{dc_1}. \tag{5.5}$$

We will conclude with some observations:

(a) Since c_1^- is the evaluation of the concentration field c_{1L} on the surface, then equations (5.5) and (5.1) coincide when this field is uniform in the volume† and:

$$\frac{c_{2_\sigma}}{\rho} \frac{dp}{d\hat{\mu}_1} \ll |c_{1_\sigma} - c_1|.$$

This last condition is verified at least for ideally diluted liquid mixtures, see [10], p. 333.

(b) Since‡:

$$\frac{d\hat{\mu}_{1L}}{dc_{1L}} > 0$$

and because of the considerations referred to in (a), both equations (5.1) and (5.5) prove that the function $\gamma\,(c_1)$ actually has the experimentally observed behaviour.

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NOTATIONS

Bold Roman indicates a vectorial quantity denoted for instance by $\mathbf{v}$.

A dot on a letter indicates the material derivative. For instance $\dot{\theta}$ means the material derivative of the temperature field.

If $v^\alpha \mathbf{e}_\alpha$ is a surface vector field (the vectors $\mathbf{e}_\alpha$ being an arbitrary set of independent tangent vectors) with the simbol $v^\alpha_{|\beta}$ we denote its covariant derivative.

∂ is the symbol of partial differentiation.

∇ means nabla.

† As usually assumed in classical thermochemistry.
‡ See for instance [14] equation (96.7), p. 319.

div and div_S respectively denote volume and surface divergence operators.

: Sharing two tensor quantities denotes the operation of saturation between them. For instance $\mathbf{T}:\nabla\dot{\mathbf{x}}$ denotes the scalar quantity:

$$T^i_j \frac{\partial \dot{x}^j}{\partial x_i} \text{ sum over both indexes } i \text{ and } j.$$