We propose in this paper a whole family of models for isothermal diphasic equilibrium, which generalize the classical Langmuir isotherm. The main tool to obtain these models is a fine modelling of each phase, which states various constraints on the equilibrium. By writing down the Gibbs conditions of thermodynamical equilibrium for both phases, we are lead to a constrained minimization problem, which is solved through the Lagrange multipliers. If one of the phases is an ideal solution, we can solve explicitly the equations, and obtain an analytic model. In the most general case, we have implicit formulae, and the models are computed numerically. The models of multicomponent isotherm we obtain are in this paper designed for chromatography, but can be adapted mutatis mutandis to other cases.

1. Introduction

In this paper, we give a systematic description of a family of multicomponent diphasic equilibria at constant temperature, which contains as its simplest case the classical Langmuir\(^1\) isotherm. Such models, which we shall call isotherms for short, encounter very often in Chemical Engineering; one can also mention polynomial
models, and, for instance, Sips\textsuperscript{21} and Freundlich\textsuperscript{3} isotherms, which are designed for adsorption equilibria. We mention here as a general reference for isotherms used in chromatography a book by Guiochon & al.\textsuperscript{4}, which contains also a large bibliography on the subject. The common feature to the models we are about to describe is that they are built up from statistical thermodynamics modelling. Even though they may look quite different one from another, they share some structural properties, in particular the thermodynamical consistency which is defined below.

The idea of the model originated from gas-solid adsorption in chromatography, and was given by J.M. Moreau and P. Valentin in 1983, but unfortunately was not published at this time (see Ref.\textsuperscript{8}). The formal derivation of the isotherm, and a generalization to gas-liquid absorption were given in Ref.\textsuperscript{7}, as well as several models of chromatographic propagation. Both models were limited by the fact that one of the phases was assumed to be an ideal solution. This was justified for the mobile phase in the context of gaseous chromatography, but was of course forbidding the modelling of liquid chromatography. In Ref.\textsuperscript{9}, we gave a generalization for this isotherm using a lattice-gas model for both phases, which allows the application to non ideal solutions. The aim of this paper is to summarize these results and give a few examples of one-component isotherms.

The ansatz of the method is the following: take for both phases any model from statistical thermodynamics: ideal solution, or non-ideal lattice-gas model, in view of taking into account possible interactions between components. We can obtain explicitly the corresponding thermodynamical potentials (energy, enthalpy, ...). Then assume that the system constituted by the two phases is at a state of stable isothermal equilibrium. This leads to minimize the total energy of the system, under several constraints which arise naturally in the modelling of the phases. These constraints are dealt with using Lagrange multipliers, and we obtain a system of equations for the equilibrium state, which plays the same part as the classical Gibbs equalities for unconstrained diphasic equilibrium.

These equations can be formally solved, and give the requested isotherm. If both phases are modelled by a lattice-gas, the equilibrium equations cannot be solved explicitly, but the numerical resolution is quite straightforward. If we assume one of the phases to be an ideal solution, these equations are explicitly solved with respect to quantities in the ideal solution, so we get an analytic expression for the isotherm.

An important feature of that family of isotherms is the following intrinsic property of thermodynamical consistency. Suppose the isotherm between phase 1 and phase 2 is given by $N^2 = h(N^1)$, where $N^j$ is the vector of quantities in phase $j$. From the equations of equilibrium (Gibbs equalities), one can show that necessarily the jacobian matrix $J = h'(N^1)$ is diagonalisable, its eigenvalues being positive (see Ref.\textsuperscript{10,7}). This property is not obvious when given a physical model of diphasic equilibrium, and the lack of it may lead to physical incoherences. It appears also in the simulation of chromatographic columns by systems of Partial Differential Equations (see Ref.\textsuperscript{18,7}). Indeed the diagonalization ensures a property called hyperbolicity
of the system, which means we deal with nonlinear propagation of “concentration waves” along the column.

Let us mention here a paper by Moreau & al.\textsuperscript{12}, which states the specific form of the isotherm in the case of a binary mixture with at most ternary interactions between adsorbed molecules. The authors show that the equation they obtain gives a good description of the adsorption isotherm of several compounds on graphitized carbon.

Working along similar lines on the adsorption on zeolithes, Ruthven\textsuperscript{20} and Rota\textsuperscript{17}, have obtained analogous formulæ. However their model is restricted to adsorption, and does not give direct access to the interaction energies and degeneracy numbers. We emphasize that the models we give here are examples of a general framework which can be used to compute more general equilibria.

We shall now proceed as follows. The next section is devoted to the modelling of the phases, by means of statistical thermodynamics: monatomic gas for one of them, lattice-gas for the other. Section 3 states the equilibrium conditions, and in particular the constraints acting on each phase. Section 4 gives the full computation of the isotherms in two cases, gas-solid and gas-liquid equilibria, which differ from each other by constraints. Finally, section 5 gives a few examples of isotherms, and shows that the Langmuir isotherm appears as a special case of our model.

2. Phase modelling

We give in this section the precise modelling of the phases, and we shall consider two models arising from statistical thermodynamics. The most general one is a lattice-gas model which allows us to take into account interactions between components within this phase. The second model stands for an ideal solution, actually it can be interpreted as a particular case of the preceding one. We explicitly state it in order to recover several formulæ given in Ref.\textsuperscript{8,12}.

More specific features of the modelling, namely the fact that a phase is adsorbed on a solid, or a liquid one, will appear as constraints on the variables. For instance, the constant temperature will lead us to make use of thermodynamic potentials where temperature appears as a parameter: Gibbs enthalpy, or Helmholtz free energy.

We shall give here the modelling –i.e. the thermodynamic potentials and the constraints– in three interesting cases regarding chromatography: ideal gaseous solution, solid adsorbed phase, and liquid phase. We refer to Hill\textsuperscript{6} for a thorough statement of the statistical thermodynamics techniques we use here.

Throughout this paper, we shall use the following notations. We consider a mixture of $M$ components, indexed by $1 \leq m \leq M$, to which we add in each phase a particular species denoted by 0. This species will play the part of the vector fluid in mobile phase, or the part of the adsorbent in a stationary phase. We denote by $N_{m0}$, $0 \leq m \leq M$, the quantity of component $m$; by $V$ the volume of the system we consider; $U$ and $S$ are respectively the associated internal energy and entropy. Temperature, pressure and chemical potential of species $m$ are respectively denoted
by $T$, $p$ and $\mu_m$, $0 \leq m \leq M$. We also set $\mathbb{R}_+^n = \{ v \in \mathbb{R}^n; v_i \geq 0, 1 \leq i \leq n \}$, and $\mathbb{R}^- = \{ v \in \mathbb{R}^n; v_i > 0, 1 \leq i \leq n \}$.

2.1. The lattice-gas model

We define complex species in a classical way by a 2 or 3-dimensional lattice-gas model, on which the simple species fasten (cf. Hill). The thermodynamic phase we consider is thus broken up in a lattice containing a number $\sigma_*$ of adsorption sites, and we have $M + 1$ basic species:

- the $M$ chemical components of the mixture we are interested in;
- a species indexed by 0, representing the empty sites. These can be interpreted as the molecules of an adsorbent on which species fasten (see section 4). The first hypothesis for the modelling is:

H 2.1. A given site can receive at most one molecule of a component.

We thus limit ourselves to the case where all the molecules we deal with occupy the same surface. This is not really limitative for chromatography, since we consider components with very similar chemical properties, thus with similar structure. However, one can encounter, for instance in some extraction problems, molecules of various sizes, occupying different surfaces on the lattice. A given molecule can therefore fasten on several sites.

For the modelling of an adsorbing solid surface, we shall consider a 2-dimensional lattice, and a 3-dimensional one in the case of liquid absorption. According to the case, we shall have surfacic or volumic sites, with the following homogeneity property:

H 2.2. The surface, or volume, of a site is a constant which does not depend on the nature or the position of the site.

The extensive variable to be considered here is the total number of sites $\sigma_*$, and this assumption relates it to the phase volume or surface $V$:

$$V = \sum_{m=0}^{M} N_m = \sigma_*.$$  \hspace{1cm} (2.1)

The intensive conjugue variable, analogous to pressure, is called surface pressure.

We partition now our lattice in cells, each containing $q$ sites, $q \geq 1$. The cells form a partition of the lattice, in the sense that every site belongs to one cell and only one. Let us denote by $\mathcal{I}$ a multi-index of $N^M$, $i = (i_1, \ldots, i_M)$, and $|i| = i_1 + \cdots + i_M$. Finally, $A_*$ is the total number of cells: one has $\sigma_* = qA_*$. Such a model will be referred as a degree $q$ model.

Definition 2.1 We call type $i$ cell a cell containing $i_m$ molecules of component $m$, $1 \leq m \leq M$.

A type $i$ cell thus contains $(q - |i|)$ empty sites. The set of valid indexes $i$ is therefore $\mathcal{I} = \{ i = (i_1, \ldots, i_M); 0 \leq i_m \leq q, |i| \leq q \}$. We define also the set $\mathcal{I}_*$ of the indexes associated to the sites which are actually occupied: $\mathcal{I}_* = \mathcal{I} \setminus \{(0, \ldots, 0)\}$. 
It is easily seen that
\[ K \equiv \text{card} \mathcal{I} = \frac{(q + 1) \ldots (q + M)}{M!}. \]

This definition leads to the notion of “complex chemical species of type \( i \)”, or “cellular species \( i \)”. These species have no real physical significance: they are nothing but a modelling of the possible “mixtures” of our \( M \) basic components, occurring in the stationary phase. Our purpose is to give a thermodynamical meaning to the “complex model” we describe now.

We consider a lattice, of which the sites are precisely the cells we have defined above. On these sites we distribute in an indistinguishable way our cellular species, and apply the same techniques as for the ideal lattice-gas model. This latter model obviously corresponds to the case \( q = 1 \), that is cells containing just one site. It leads to the Langmuir adsorption isotherm (see section 5). For \( q > 1 \), we get more complex formulæ, taking account of interactions between molecules, in a way we shall now explicit.

Here are first the bounds between cellular species and basic components: let \( a_i \) be the number of type \( i \) cells, and \( A \) the Avogadro constant. For every \( 1 \leq m \leq M \), the mole number of component \( m \) is given by
\[ N_m = \frac{1}{A} \sum_{i \in \mathcal{I}} i_m a_i. \tag{2.2} \]

Concerning the number of empty sites, one has
\[ N_0 = \frac{1}{A} (qA - \sum_{i \in \mathcal{I}} |i| a_i). \tag{2.3} \]

We obtain the thermodynamics of the complex system by using Boltzmann’s approximation:

**H 2.3.** The cellular species follow a Boltzmann statistics with a single energy level.

We also state an homogeneity assumption, which gives the degeneracy number of energy levels:

**H 2.4.** Energy levels are independant of the relative positions of species within the phase.

This means that a type \( i \) cell is characterized from the energetic point of view by the proportion of each component, and not by the position of these components in the cell. We note by \( E_i \) the energy level of a type \( i \) cell. The degeneracy number \( n_i \) of energy level \( E_i \) is the number of possible permutations between positions of species in the cell:
\[ n_i = \frac{q!}{i_1! \ldots i_M!(q - |i|)!}. \]

The energy \( E_i \) we introduce here represents on the one hand interactions with the adsorbent, on the other hand adsorbate-adsorbate interactions between species.
We assume the energy $E_i$ to be given in the following way:

$$E_i = \varepsilon_i + \sum_{m=1}^{M} i_m E_m, \quad \varepsilon_1 = 0 \text{ if } |i| = 1. \quad (2.4)$$

In this formula, $E_m$ is the interaction energy between one molecule of component $m$ and the adsorbent, and will often be called energy of order 1. The term $\varepsilon_i$ is the adsorbate-adsorbate interaction energy between species. We say $\varepsilon_i$ is an interaction energy of order $p \leq M$ if $p$ integers in $i_1, \ldots, i_M$ are non zero. The partition function $\zeta_i$ of species $i$ in the considered phase is given by:

$$\zeta_i = n_i e^{-\beta E_i}. \quad (2.5)$$

The canonical partition function $Z_C$ associated to the system constituted by $a_i$ indistinguishable molecules of cellular species $i$, $i \in \mathbb{I}_*$, distributed on the total number of cells $A_*$, is given by

$$Z_C = \frac{A_*!}{\prod_{i \in \mathbb{I}_*} a_i!} \prod_{i \in \mathbb{I}_*} \zeta_i^{a_i}. \quad (2.6)$$

Indistinguishability means that the relative positions of complex species have no influence on the thermodynamics.

The computation of thermodynamic potentials is made more rigorous by using the grand partition function $Z^G$ (see Hill):

$$Z^G = \sum_{\sum a_i = A_*} \exp[\sum_{i \in \mathbb{I}_*} \beta \mu_i a_i] Z_C,$$

where $\mu_i$ is the chemical potential of species $i$. In view of (2.6), the Leibniz formula leads to

$$Z^G = [1 + \sum_{i \in \mathbb{I}_*} \zeta_i e^{\beta \mu_i}]^{A_*},$$

so the grand potential $A$, which depends here on $T$, $A_*$ and $\mu_i$, $i \in \mathbb{I}_*$, is given by

$$A = -kT \log Z^G = -kT A_* \log[1 + \sum_{i \in \mathbb{I}_*} \zeta_i e^{\beta \mu_i}].$$

We shall be interested in the Helmholtz free energy $F$, which is the Legendre transform of $A$ with respect to $\mu_i$, $i \in \mathbb{I}_*$:

$$F(T, A_*, a_i) = A(T, A_*, \mu_i^*) - \sum_{i \in \mathbb{I}_*} \frac{\partial A}{\partial \mu_i^*} \mu_i^*,$$

where $\mu_i^*$ are solutions of $\frac{\partial A}{\partial \mu_i} = -a_i$, $i \in \mathbb{I}_*$. Resolution of these equations readily gives the chemical potential of species $i$, $i \in \mathbb{I}_*$:

$$\mu_i = kT \log \frac{1}{A} \frac{a_i}{\zeta_i(A_* - \sum_{i \in \mathbb{I}_*} a_i)}.$$
Considering (2.4) and (2.5), this formula becomes

\[ \mu_i = kT \log \frac{a_i}{A_* - \sum_{i \in I_*} a_i} - \log n_i e^{-\beta \varepsilon_i} + \sum_{m=1}^{M} i_m c_m ] . \tag{2.7} \]

From here one deduces easily the function \( F \):

\[ F(T, A_*, a_i) = -kT \log A_* - \sum_{i \in I_*} a_i \log a_i - \sum_{i \in I_*} a_i \xi(A_* - \sum_{i \in I_*} a_i) \]. \tag{2.8} \]

A straightforward computation gives

**Lemma 2.1** The function \( F \) is continuous, convex and homogenous of degree 1 with respect to \( A_* \), \((A_i)_{i \in I} \in \mathbb{R}^{M+1} \). It is of class \( C^1 \) on \( \mathbb{E}^{M+1} \).

The surface pressure is defined by

\[ \phi = -\frac{\partial F}{\partial A_*}, \]

which gives consequently

\[ \phi = -kT \left[ \log(A_* - \sum_{i \in I_*} a_i) - \log A_* \right] = -kT \log \frac{a_0}{A_*}. \tag{2.9} \]

The quantity \( \phi \) is thus related to the proportion of empty cells. It is nonnegative, since \( a_0 \leq A_* \), and is well defined if \( a_0 > 0 \). We shall see in the following section that the latter inequality is valid at the equilibrium.

### 2.2. Ideal solution

We recall here briefly how to obtain a classical model in statistical thermodynamics: the perfect monatomic gas. This model is usually designed for gaseous phases, or diluted liquid phases, where interactions are neglected. The component 0 can be considered here as the vector gas. For each molecule of species \( m \), the partition function \( \zeta_m \) is obtained by a three degrees of freedom particle model in the volume \( V \) (cf. Hill\(^6\)): \( \zeta_m = V(2\pi M_m/(\beta h^2))^{3/2} \), where \( M_m \) is the molecular mass of component \( m \), \( h \) the Planck constant, and \( \beta = 1/kT \), \( k \) the Boltzmann constant.

For a system of \( N_m \) independent and indistinguishable particles, \( 0 \leq m \leq M \), the canonical partition function \( Z^C \) is

\[ Z^C = \prod_{m=0}^{M} \frac{\zeta_m^{N_m}}{N_m!}. \tag{2.10} \]

We are interested in the grand partition function \( Z_G \) which is defined by

\[ Z^G = \sum_{N_1 \ldots N_M=0}^{\infty} \exp[\sum_{j=0}^{M} \beta \mu_j N_j] Z^C, \]

where \( \mu_j \) is the chemical potential of component \( j \). Replacing \( Z^C \) by its expression (2.10) in the preceding equation, we find the series expansion of the exponential, and thus we have

\[ Z^G = \exp[\sum_{m=0}^{M} \zeta_m e^{\beta \mu_m}]. \]
From that one can get the expression of the grand potential $A$:

$$A(T, V, \mu_0, \ldots, \mu_M) = -kT \log Z^G = -kT \sum_{m=0}^{M} \zeta_m e^{\beta \mu_m}.$$  

We shall be interested here in the free enthalpy $G$, since the gaseous phase is at isobaric-isothermal equilibrium. We obtain $G$ by computing the Legendre transform of $A$ with respect to $V$ and $\mu_0, \ldots, \mu_M$:

$$G(T, p, N_0, \ldots, N_M) = A(T, V^*, \mu^*_0, \ldots, \mu^*_M) - \frac{\partial A}{\partial V} V^* - M \sum_{m=0}^{M} \frac{\partial A}{\partial \mu_m} \mu^*_m,$$

where $V^*$ and $\mu^*_m, 0 \leq m \leq M$, are solutions of $\frac{\partial A}{\partial V} = -p$, $\frac{\partial A}{\partial \mu_m} = -N_m$. From the first equation one deduces $V^* = kT \sum_{m=0}^{M} N_m$, which is nothing but a formulation of the perfect gases law. The partition function $\zeta_m$ is now given by the following equation, which defines also the quantity $\alpha_m$:

$$\zeta_m = \frac{kT}{p} \left( \frac{2\pi M_m}{\beta h^2} \right)^{\frac{3}{2}} \sum_{j=0}^{M} N_j = \alpha_m \sum_{j=0}^{M} N_j.$$

As regards chemical potentials, one gets $\mu_m = kT \log \frac{N_m}{\zeta_m}$, so, replacing $\zeta_m$ by its value, the free enthalpy becomes

$$G(T, p, N_0, \ldots, N_M) = kT \sum_{m=0}^{M} N_m \log \frac{N_m}{\alpha_m \sum_{j=0}^{M} N_j}. \quad (2.11)$$

One can here make use of the concentration $c_m$ of component $m$, $c_m = N_m/V$, and introduce now a notation which will be useful only in the following section. Relation (2.4) defines the $M$ interaction energies of level 1, $E_1, \ldots, E_M$. Let $M_m$ be the molecular mass of component $m$, and set

$$K_m = \left( \frac{\beta h^2}{2\pi M_m} \right)^{\frac{3}{2}} e^{\beta E_m}.$$  

Obviously this coefficient $K_m$ is a positive constant at fixed temperature, and is homogenous to the inverse of a concentration. We shall call it the Langmuir coefficient of component $m$. We have

$$\frac{1}{\zeta_m} = \frac{1}{V} K_m e^{-\beta E_m}.$$  

Let us define an adimensional variable $w_m$ by $w_m = K_m c_m$. For $1 \leq m \leq M$, the chemical potential of component $m$ is then given by

$$\mu_m = kT \log \frac{N_m}{\zeta_m} = kT \log w_m - E_m. \quad (2.12)$$

The model described in this section is specifically designed for ideal solutions, that is for gases, or diluted liquids, so that interactions are negligible. However, we
applied it very often to model the mobile fluid phase of a chromatographic column, using the complex model only for the ad- or absorbed stationary phase, since this method leads to an explicit resolution of the equilibrium relations.

Notice that this model can be at least formally interpreted in the formalism of the lattice-gas. Indeed the partition function is given by

\[ \zeta_m = \left( \frac{2\pi M_m}{\beta h^2} \right)^{3/2} = \frac{V}{K_m} e^{-\beta E_m} \]

with the previous definition of \( E_m \). Thus the coefficient \( V/K_m \) plays the same role as the degeneracy number \( n_i \). Considering a lattice model with degree \( q = 1 \), that is without interactions, we recover the properties of the ideal solution.

2.3. Internal constraints

Internal constraints depend on the behaviour of each phase: fluid or adsorbed on a solid. A first general principle is that a constraint such as constant temperature or pressure is dealt with by using the adequate thermodynamical potential. Usually, a thermodynamical system is characterized by several parameters, namely entropy \( S \), volume \( V \), energy \( U \), and a vector of quantities of matter \( \mathbf{N} \). It is said to be at equilibrium if there exists a smooth function \( f \) such that \( U = f(S,V,\mathbf{N}) \).

If we consider for instance the constraint of constant temperature, the potential we have to consider is the so-called Helmholtz free energy \( F \), which is defined as the Legendre transform of \( f \) with respect to \( S \). Since the temperature is defined as \( T = \partial f / \partial S \), the very construction of \( F \) shows that it minimizes \( f \) under the constraint \( T \) constant. For reasons which will appear more clearly in Section , this is precisely what we want to achieve.

2.3.1. Ideal solution

For such a phase, equilibrium occurs at constant pressure. The thermodynamical potential associated to constant temperature and pressure is the free enthalpy \( G^1 \).

In other respects, two interface constraints act on extensive variables. The first one means that the adsorbent (or absorbent) cannot pass in phase 1, that is \( N_{1\text{II}} = 0 \).

The expression of \( G^1 \) is therefore given by (2.11) (we drop the \( T \) and \( p \) dependance, and set \( N_0 = N_1^I \)). The second constraint comes from the fact we assume the amount of vector fluid to be constant (constraint (I) for Ideal):

\[ N_1^I = N_1^M = \text{constant}. \] (I)

We shall not explicit this constraint in the formulation of the equilibrium conditions. Instead, we set \( g^1(N_1^I,\ldots,N_M^I) = G^1(N_1^I,\ldots,N_M^I) \); a straightforward computation shows that \( g^1 \) is strictly convex – if \( N_1^I \) is non zero, that is if a vector fluid is present in phase 1. By (2.12), we have, for \( 1 \leq m \leq M \)

\[ \frac{\partial g^1}{\partial N_m^I} = \mu_m = -kT \log w_m + E_m. \] (3.3)
Notice that, when \( w_m \) (or \( c_m \)) goes to 0, then \( \mu^1_m \) goes to \(-\infty\).

### 2.3.2. General case

The stationary phase 2 is an adsorbed phase on a solid, or a liquid absorbed phase. The goal of these models of isotherms is precisely to take account of the interactions in the stationary phase, so we obviously make use of the complex model of sites. We have no constraints on the pressure here, so the associated thermodynamical potential is the Helmholtz free energy \( F^2 \) (2.8). Similarly to phase 1, we first state that the vector fluid cannot go in phase 2: \( N^2_{II} = 0 \). We have then to consider two cases: adsorbed or absorbed stationary phase.

- **solid phase.** We consider here a monolayer bidimensional lattice: a molecule “hides” the site on which it adsorbs. The species 0 represents the empty sites or, in a way, the “visible” molecules of adsorbent. The constraint acts in this case on the volume of the solid phase or, equivalently, on the total number of sites, which has to remain constant:

\[
q A^2_* = N^2_* = \text{constant.} \quad (S)
\]

- **liquid phase.** The species 0 of sites model interprets here as the absorbent itself (species II), the amount of which keeps constant. In a liquid absorbed phase, each absorbed molecule becomes a new absorption site: the lattice “inflates”, and the volume of the phase increases with the quantity of matter. One has therefore, by (2.3), the following constraint:

\[
q A^2_* - \sum_{i \in I_*} |i| a^2_i = N^2_{II} = \text{constant.} \quad (L)
\]

Notations \( L \) and \( S \) recall the type of phase: **Liquid** or **Solid**. The constraints \( L \) and \( S \), in contrast with the preceding case, will be of great importance in the computation of the isotherm, so we shall keep them explicit. The constraint \( N^2_{II} = 0 \) naturally disappears, and the Helmholtz free energy becomes a convex, homogenous of degree 1 function, which we still denote by \( F^2 \), of \( A^2_*; (a_i)_{i \in I_*} \). Its derivatives are given by

\[
\frac{\partial F^2}{\partial A^2_*} = kT \log \frac{A^2_* - \sum a^2_i}{A^2_*}, \quad \frac{\partial F^2}{\partial a^2_i} = kT \log \frac{1}{\zeta^2_i} \frac{a^2_i}{A^2_* - \sum a^2_i} \quad (3.4)
\]

and are a priori defined only if \( A^2_* - \sum_{i \in I_*} a^2_i = A^2_0 > 0 \). Moreover, since \( \sum_{i \in I_*} a^2_i \geq 0 \), we have \( \partial F^2 / \partial A^2_* \leq 0 \).

#### Remark 2.1

Notice that all the functions defined here are continuous on \( \mathbb{R}^{M+1}_+ \), and \( C^1 \) on \( E^{M+1}_+ \).

### 3. Diphasic Equilibrium

This section states the conditions of diphasic equilibrium. We consider now two phases, indexed by 1 and 2. Keeping in mind chromatography, the phase 1 would be the mobile phase, being thus gaseous or liquid, and phase 2 the ad- or absorbed
stationary phase 2. It seems natural to use a lattice model for the phase 2, since the interactions are not negligible, but both the ideal solution model and the lattice model can be used for phase 1.

$M+2$ species are distributed in the system: the $M$ components of the mixture we are interested in, the adsorbent (or absorbent), and finally the vector fluid, species we denote respectively by II and I. The notation recalls that the vector fluid I (resp. the adsorbent II) is in phase 1 (resp. 2). We set $\mathbf{I} = \{\text{I, II, 1, \ldots, } M\}$. Notice that the models we described above consider only $M+1$ species. But our $M+2$ component are in fact $M+1$ in each phase, since neither the adsorbent nor the vector fluid change phase. The species previously denoted by 0 will represent vector fluid I in the mobile phase, and adsorbent II in the stationary phase.

We shall use the following convention: a superscript will characterize the phase we are interested in. Thus, $V^j$ will denote the volume of phase $j$, $N^j_m$ the quantity of component $m$ in phase $j$, $j = 1, 2$, and so on.

3.1. Statement of the problem

Consider the following diphasic system: in phase 1, one has the $M+1$ basic components, in phase 2 the $K$ complex species defined in section 2. Assume this complex system to be at stable thermodynamic equilibrium. This means, according to Gibbs’ formulation,

1- for each phase, the free energy $U^j$ can be written as a smooth convex function of the other extensive variables, entropy $S^j$, volume $V^j$, and amount of matter $N^j$. Namely,

$$U^j = f^j(S^j, V^j, N^j), \quad j = 1, 2; \quad (3.1)$$

2- the free energy of the whole system is minimal with respect to all states satisfying several constraints to which the system is subjugated.

Usually, the constraints follow from the fact that the system is closed, which means that total volume, entropy and amount of matter are constant. Standard Lagrange multipliers arguments lead therefore to the so-called chemical potential equalities. Solving these equations characterizes the equilibrium states. We do not give any details here, since we shall do this below in a very similar context.

These constraints, that we shall fully explicit below, are the mathematical translation of the influence of the surroundings on the system (global constraints), and of the influence of each phase on the other (internal constraints). As we shall see, the latter constraints will lead us to make use of other representations than the energetic one (3.1) for each phase.

The first global constraint is common to both phases: the temperature $T$ is fixed, that is isothermal equilibrium. We deal with this constraint by choosing the correct thermodynamical potential for each phase (Gibbs free enthalpy, or Helmholtz free energy), and these were computed in section 2.

On the other hand, we assume the system to be closed with respect to our basic components, that is species $1, \ldots, M$. If we have complex species in both phases,
we use formula (2.2) to compute \( N_m^j, j = 1, 2 \). If we have a given total amount \( N_m \) of component \( m \), the constraints are given by
\[
\sum_{i \in \mathcal{I}} i_m a_1^i + \sum_{i \in \mathcal{I}^2} i_m a_2^i = N_m. \tag{3.2}
\]

Now we have internal constraints according to the type of phase we deal with: phase 1 is assumed to be liquid, so it is subdued to constraint (L), and the solid phase 2 is characterized by (S). So the Gibbs equilibrium state of the diphasic system is solution of the following constrained minimization problem:
\[
\inf \{ F^1(A_1^1, a_1^1) + F^2(A_2^2, a_2^2); q_1^{A_1} - \sum_{i \in \mathcal{I}^1} |i| a_1^i = N_1^1, \quad q_2^{A_2} = N_2^2, \quad \sum_{i \in \mathcal{I}^1} i_m a_1^i + \sum_{i \in \mathcal{I}^2} i_m a_2^i = N_m, \quad m = 1, \ldots, M \}. \tag{3.3}
\]

If the phase 1 is an ideal solution, formula (3.2) reduces to
\[
N_1^1 m + \sum_{i \in \mathcal{I}^2} i_m a_2^i = N_m. \tag{3.4}
\]

The constrained minimization problems leading to the equilibrium state become
\[
\inf \{ g^1(N^1) + F^2(A_2^2, a_2^2); q_2^{A_2} = N_2^2, \quad N_1^1 + \sum_{i \in \mathcal{I}^2} i_m a_2^i = N_m, \quad m = 1, \ldots, M \}. \tag{3.5}
\]
for gas-liquid equilibrium,
\[
\inf \{ g^1(N^1) + F^2(A_2^2, a_2^2); q_2^{A_2} = N_2^2, \quad N_1^1 + \sum_{i \in \mathcal{I}^2} i_m a_2^i = N_m, \quad m = 1, \ldots, M \}. \tag{3.6}
\]
for gas-solid equilibrium.

We leave to the reader the exercise of writing the minimization problem for a liquid-liquid equilibrium. Of course, all the results we are about to prove still hold in this case.

### 3.2. Existence and characterization of equilibrium states

We first state that the above problems have a unique solution. The proof of this follows from a classical result in convex analysis.

**Proposition 3.1** There exists a unique solution to problems (3.3), (3.5) and (3.6).

**Proof.** We have noticed in section 2.3.1 that the function \( g^1 \) is strictly convex. Thus the function we minimize for the problems (3.5) and (3.6), \( g^1 + F^2 \), is also strictly convex. Finally, the minimization domain is bounded, so the result follows. For the problem (3.3), we minimize a convex homogenous function on a bounded domain, under affine constraints. The restriction of the function to the affine subset defined by the constraints is strictly convex as soon as this set does not contain the origin. This is the case provided one of the constants \( N_1^1 \) or \( N_2^2 \) is not zero. So we can rewrite (3.3) as the minimization of a strictly convex function on a bounded domain, which gives the existence and uniqueness of the minimum. \( \square \)
Proposition 3.1 ensures the existence and uniqueness of the diphasic constrained equilibrium state for the complex model. We wish now to go back to our basic components, that is to the vectors $\mathbf{N}^i = (N_1^i, \ldots, N_M^i)$. We shall state and prove such a result for the problem (3.3). The proof for the other two problems goes in the same way, but the work is half done since the function $g^1$ is already explicit. First define two vectors $\mathbf{N}_1^*$ by using formula (2.2):

$$N_{1m}^* = \sum_{i \in I} i_m a_i^*, \quad 1 \leq m \leq M.$$

**Proposition 3.2** There exist two strictly convex functions $\mathcal{F}^j : \mathbb{R}_+^M \to \mathbb{R}_+^M$, $j = 1, 2$, such that $\mathbf{N}_1^*$ and $\mathbf{N}_2^*$ are solutions of the following problem:

$$\inf \{ \mathcal{F}^1(\mathbf{N}_1) + \mathcal{F}^2(\mathbf{N}_2); N_{1m}^1 + N_{2m}^2 = N_m, \quad 1 \leq m \leq M \}. \quad (3.7)$$

The functions $\mathcal{F}^i$ are continuous on $\mathbb{R}_+^M$ and $C^1$ on $E^M$.

**Proof.** First define a function $\tilde{f}^1 : \mathbb{R}_+^{M+1} \to \mathbb{R}_+^M$:

$$\tilde{f}^1(N_1^1, N_1^2, \ldots, N_M^1) = \inf \{ \mathcal{F}^1(A_1^1, a_1^1); \sum_{i \in I} i_m a_i^1 = N_{1m}^1, q^1 A_1^1 - \sum_{i \in I} q_i a_i^1 = N_1^1 \}. $$

The function $\tilde{f}^1$ is convex, homogenous of degree 1, and has the same regularity as $F^1$. Define $\tilde{f}^2$ in the same way, it enjoys the same properties. These two functions represent the stable equilibrium of the complex system in each phase. Obviously, the problem (3.4) reduces to

$$\inf \{ \tilde{f}^1(N_1^1, \mathbf{N}_1^1) + \tilde{f}^2(N_1^2, N_2^2, \ldots, N_M^2); \quad N_1^1 = N_1^1, \quad \sum_{j=1} M N_j^2 = N_2^2, \quad N_{1m}^1 + N_{2m}^2 = N_m, \quad m = 1, \ldots, M \}.$$ 

If we define now

$$\mathcal{F}^1(\mathbf{N}_1) = \tilde{f}^1(N_1^1, N_1^2, \ldots, N_M^1), \quad \mathcal{F}^2(\mathbf{N}_2) = \tilde{f}^2(N_2^2 - \sum_{m=1}^M N_{2m}^2, N_2^2, \ldots, N_M^2),$$

we obtain the desired result. By construction, the functions $\mathcal{F}^i$ have the same regularity as $F^i$, which are $C^1$ by Remark 2.1. □

Notice that the operation performed in (3.7) is well-known in convex analysis and optimization: the so-called infimal convolution.

We denote by $\mu_i$, the gradient of $\mathcal{F}^i$, $i = 1, 2$, and we set $\lambda = (\lambda_1, \ldots, \lambda_M)$: these are vectors of $R^M$. Since $\mathcal{F}^i$ is strictly convex, $\mu^i$ is a monotone operator.

**Theorem 3.1** The equilibrium states are characterized on $E^M$ by the system of equations

$$\mu^1(\mathbf{N}_1) = \mu^2(\mathbf{N}_2) \quad (3.8)$$

There exists a function $h$ from $E^M$ in $E^M$, of class $C^1$, such that the equilibrium state between the two phases is characterized by $N^2 = h(N^1)$. Moreover, this function verifies the thermodynamic consistency property.
Proof. We give here but a sketch of the proof of the existence of the function $h$. The details of the proof, especially for the thermodynamical consistency, can be found in Ref.\textsuperscript{10,7}. Let $(\mathbf{N}^{1*},\mathbf{N}^{2*})$ be a solution in $\mathbb{E}^M \times \mathbb{E}^M$ to the problem (3.7). The function we minimize (that is $(\mathbf{N}^1,\mathbf{N}^2) \mapsto \mathcal{F}^1(\mathbf{N}^1) + \mathcal{F}^2(\mathbf{N}^2)$) is $C^1$ on $\mathbb{E}^M$. The constraints are affine, so they are also $C^1$. We are thus in position to use the Lagrange multipliers characterization of the infimum (see Rockafellar\textsuperscript{16}). Therefore there exists $\lambda \in \mathbb{R}^m$ such that the relations $\mu_1(\mathbf{N}^{1*}) = \lambda$, and $\mu_2(\mathbf{N}^{2*}) = \lambda$ hold true. We have thus at equilibrium the equality $\mu_1(\mathbf{N}^1) = \mu_2(\mathbf{N}^2)$. Since $g^1$ is strictly convex, one can solve equation (3.8) with respect to $\mathbf{N}^1$, which implies the existence of the function $h$.

Next, rewrite equation (3.8) in the form $\mu_1(\mathbf{N}^1) = \mu_2(h(\mathbf{N}^1))$, then differentiate with respect to $\mathbf{N}^1$. We obtain an expression of the jacobian matrix $h'$ as a product of two symmetric definite positive matrices (namely the Hessian matrices of $\mathcal{F}^i$), from which we can deduce that $h'$ is self-adjoint with respect to a certain scalar product in $\mathbb{R}^M$. This last property implies that $h'$ is diagonalisable, its eigenvalues being positive.

The system of equations (3.8) can be understood as “chemical potential” equalities, although $\mu_i$ is not exactly a vector of chemical potential in the classical sense, because of the constraints.

Remark 3.1. The thermodynamical consistency results from the strict convexity of the energetic phase representations, which follows from the existence of constraints on both phases. Namely, the fact that there exists a species which does not change phase is fundamental. For chromatography, it means that the existence of a non adsorbed vector fluid in the mobile phase, or of an adsorbent in the stationary phase is fundamental to get well-posed equations.

Remark 3.2 Notice that this result does not give the behaviour of $h$ on the boundary of the domain of definition, that is when one of variables tends to 0.

4. Computation of the Isotherms

Our purpose is now to give a way to compute these isotherms. This will be done by using the characterization of the constrained minimum in terms of Lagrange multipliers (see Ref.\textsuperscript{16} for precise statements). In this section, $\lambda_m$ will denote the Lagrange multiplier associated to the global constraint (3.2) or (3.3), and $\eta^j$ the one associated, according to the case, to $(L)$ or to $(S)$ in phase $j$. Once again, the existence of Lagrange multipliers is ensured by the regularity of the constraints. Recall that the first two problems will be (almost) explicitely solved, but the third one needs a numerical resolution.

4.1. Gas-solid equilibrium

The optimality conditions for the minimum are given by

$$\frac{\partial \mathcal{F}^1}{\partial N^1_m} - \lambda_m = 0, \quad \frac{\partial \mathcal{F}^2}{\partial u^2_i} - \sum_{m=1}^{M} i_m \lambda_m = 0, \quad \frac{\partial \mathcal{F}^2}{\partial A^2_i} - \eta^2 = 0 \quad (4.1)$$
By using (3.3), we obtain
\[ \lambda_m = kT \log w_m - E_m, \] (4.2)
so that
\[ \sum_{m=1}^{M} i_m \lambda_m = kT \log \prod_{m=1}^{M} w_m^{i_m} - \sum_{m=1}^{M} i_mE_m. \] (4.3)
The third relation in (4.1) implies in view of (3.4)
\[ A^*_2 - \sum_{i \in I} a^*_i = A^*_0 = A^*_2 e^{\eta_2/kT}, \] (4.4)
so the number \( a^*_0 \) of empty cells at equilibrium is strictly positive. By using (2.7) and (4.3), the second relation in (4.1) can be written
\[ \log \frac{a^*_i}{A^*_0} = \log \prod_{m=1}^{M} w_m^{i_m} + \log n_1 e^{-\beta_1}. \]
One deduces easily from the definition of \( a^*_0 \) the proportion of type \( i \) cells:
\[ a^*_i = \frac{n_1 e^{-\beta_1} \prod_{m=1}^{M} w_m^{i_m}}{1 + \sum_{i \in I} n_1 e^{-\beta_1} \prod_{m=1}^{M} w_m^{i_m}}. \]
In order to simplify the notations, we define a polynomial \( P \) of degree \( q^2 \) with respect to \( w_1, \ldots, w_M \):
\[ P(w_1, \ldots, w_M) = 1 + \sum_{i \in I} n_1 e^{-\beta_1} \prod_{m=1}^{M} w_m^{i_m}. \] (4.4)
The number of type \( i \) cells is thus completely determined by
\[ a^*_i = N^*_s \frac{n_1 e^{-\beta_1} \prod_{m=1}^{M} w_m^{i_m}}{q^2 P}. \]
To get the mole number of component \( m \) in phase 2, we simply use (2.2):
\[ N^*_m = \frac{N^*_s}{q^2 P} \sum_{i \in I} n_1 e^{-\beta_1} \prod_{m=1}^{M} w_m^{i_m}, \]
which can be given in a more compact way by using the polynomial \( P \):
\[ N^*_m = N^*_s \frac{w_m}{q^2 P} \frac{\partial P}{\partial w_m} = \frac{N^*_s}{q^2 w_m} \frac{\partial \log P}{\partial w_m}. \] (4.5)

**Remark 4.1.** The resolution of the equations is here fully explicit. We shall see in the next section that this advantage disappears in the case of gas-liquid equilibrium.
Remark 4.2. Let us define the coverage rate $\theta_m$ of component $m$ by $\theta_m = N_{2m}/N_m$. This quantity is readily given by formula (4.5).

Remark 4.3. The third relation in (4.1) establishes that minimization happens at constant surface pressure. The Lagrange multiplier $\eta^2$ has thus a precise physical meaning.

4.2. Gas-liquid equilibrium

The optimality conditions for the minimum related to the constraint $(L)$ are now

$$\frac{\partial \phi^1}{\partial N_m} - \lambda_m = 0, \quad \frac{\partial F^2}{\partial a^2_i} - \sum_{m=1}^M i_m \lambda_m + \eta^2 |i| = 0, \quad \frac{\partial F^2}{\partial A^*_2} - \eta^2 = 0 \quad (4.6)$$

Relations (4.2) and (4.3) are still valid. The second and third relations in (4.6) give respectively

$$\frac{q_1^2}{A^2_0} = n_i e^{-\beta \epsilon_i \Sigma_i e^{-|i|} q^2 / kT} \quad (4.7)$$

$$\frac{A^2_0}{A^2_2} = e^{q^2 \eta^2 / kT}. \quad (4.8)$$

From (4.8), one can see in particular that $a^2_0$ is strictly positive. Relation (4.7) holds therefore for every equilibrium point. We obtain in other respects by replacing (4.8) in (4.7)

$$\frac{q_1^2}{A^2_2} = n_i e^{-\beta \epsilon_i \Sigma_i e^{-|i|} q^2 / kT} \prod_{m=1}^M w_{i_m}^m, \quad (4.9)$$

but, in contrast with the previous case, $A^2_2$ is no longer a known quantity. The Lagrange multiplier $\eta^2$ is determined by summing the equations in (4.7) for $i \in I_*$, and by using (4.8). We obtain the following equation:

$$1 = e^{q^2 \eta^2 / kT} + \sum_{i \in I_*} n_i e^{-\beta \epsilon_i (q^2 - |i|) \eta^2 / kT} \prod_{m=1}^M w_{i_m}^m. \quad (4.10)$$

We define a new variable $w_0$ by $w_0 = e^{q^2 / kT}$. This is an adimensional quantity related to the proportion of empty cells by equation (4.8). Since $\partial F^2 / \partial A^2_2 \leq 0$, we have from the third equality in (4.6) $\eta^2 \leq 0$, and thus $w_0$ has to satisfy $0 < w_0 \leq 1$. The right hand side of (4.10) defines a polynomial $P$ of the $M + 1$ variables $w_0, \ldots, w_M$:

$$P(w_0, \ldots, w_M) = w_0^2 + \sum_{i \in I_*} n_i e^{-\beta \epsilon_i (q^2 - |i|) \eta^2 / kT} \prod_{m=1}^M w_{i_m}^m.$$

The question is now: is there a root of $P$ in $[0, 1]$? To check whether it is the case or not, fix $w_1 \geq 0, \ldots, w_M \geq 0$, and set $\varphi(w_0) = P(w_0, w_1, \ldots, w_M)$. One has

$$\varphi'(w_0) = q^2 w_0^{q^2 - 1} + \sum_{i \in I_*} n_i e^{-\beta \epsilon_i (q^2 - |i| - 1) w_0^{q^2 - |i| - 1}} \prod_{m=1}^M w_{i_m}^m,$$
so that \( \varphi'(w_0) > 0 \) for \( w_0 > 0 \). Since we are looking for a root in \([0, 1]\), we notice that

\[
\varphi(0) = \sum_{|i| = q^2} n_i e^{-\beta \epsilon_i} \prod_{m=1}^{M} w_m^{i_m}
\]

and

\[
\varphi(1) = 1 + \sum_{i \in I^*} n_i e^{-\beta \epsilon_i} (q^2 - |i| - 1) \prod_{m=1}^{M} w_m^{i_m},
\]

so clearly \( \varphi(1) \geq 1 \). We have a unique root in \([0, 1]\) if and only if \( \varphi(0) < 1 \), that is

\[
\sum_{|i| = q^2} n_i e^{-\beta \epsilon_i} \prod_{m=1}^{M} w_m^{i_m} < 1.
\]

Thus the isotherm is no longer defined on the whole space \( \{w_i \geq 0; 1 \leq i \leq M\} \).

We shall see in the next section simpler forms of (4.11).

The total number of cells \( A_2^* \) is determined by using the constraint \((L)\). Noticing

first that

\[
\sum_{i \in I} |i| a_i = A_2^* \sum_{m=1}^{M} w_m \frac{\partial P}{\partial w_m},
\]

we obtain

\[
A_2^* = \frac{N_2^*}{q^2 P} - \sum_{m=1}^{M} w_m \frac{\partial P}{\partial w_m}.
\]

The quantity \( a_i \) is thus totally determined by replacing the latter equality in (4.9). To obtain the quantity of component \( m \), we use again (1.2) and, by (4.12), we have:

\[
N_m^2 = \frac{N_2^*}{q^2 P - \sum_{i=1}^{M} w_i \frac{\partial P}{\partial w_i}}
\]

Quantities \( N_m^2 \), for \( 1 \leq m \leq M \), are thus completely determined by equations (4.10) and (4.13).

Notice that the equation (4.8), \( P(w_0, \ldots, w_M) = 1 \), defines implicitly \( w_0 \) as a function of \( w_1, \ldots, w_M \), the derivatives of which are given by

\[
\frac{\partial w_0}{\partial w_j} = \frac{1}{q^2 P} \frac{\partial P}{\partial w_0} \frac{\partial P}{\partial w_j}.
\]

A straightforward calculation shows then that

\[
q^2 P - \sum_{m=1}^{M} w_m \frac{\partial P}{\partial w_m} = q^2 w_0 \frac{\partial P}{\partial w_0}.
\]

Replacing the last formula in (4.13), and using (4.14) leads to

\[
N_m^2 = \frac{N_2^*}{q^2 w_m} \frac{\partial \log w_0}{\partial w_m}.
\]

**Remark 4.4.** The algebraic equation (4.10) is here implicit, in contrast with the case of gas-solid adsorption. However, if \( w_1, \ldots, w_M \) are fixed nonnegative quantities, one shows that the function \( w_0 \mapsto P(w_0, \ldots, w_M) \) is strictly increasing.
for \( w_0 > 0 \). Thus we have the existence and uniqueness of the positive root \( w_0 \) we are looking for. Moreover, the numerical determination of \( w_0 \) remains quite simple, by a Newton method for instance.

**Remark 4.5.** By analogy with gas-solid adsorption, we define a coverage rate \( \theta_m \), which is the rate between the quantity of component \( m \) in adsorbed phase and the quantity of adsorbent (which is assumed to be constant): \( \theta_m = N_m^2/N_1^2 \). Once again, this quantity is readily given by the polynomial \( P \).

**Remark 4.6.** In the case of gas-solid adsorption, the polynomial \( P \) has no roots on the physical domain \( w_m \geq 0, 1 \leq m \leq M \). This ensures the coverage rate to be well defined for every \((w_1, \ldots, w_M)\). This no longer the case here, as we shall see from formula (4.13) on particular cases in the next section.

**Remark 4.7.** Notice the particular form of formulæ (4.5) and (4.15). The quantities \( N_m^2 \) are given in the form

\[
N_m^2 = \alpha w_m \frac{\partial f(w)}{\partial w_m},
\]

where \( \alpha \) is a constant, and \( f \) a given scalar function. This has important consequences on the mathematical study of the isotherm from the point of view of partial differential equations.

### 4.3. Liquid-solid equilibrium

The optimality conditions associated with the problem (3.3) are now

\[
\frac{\partial F^1}{\partial a_i} - \sum_{m=1}^{M} i_m \lambda_m + \eta^1 |i| = 0, \quad \frac{\partial F^1}{\partial A^*_1} - \eta^1 = 0, \quad \text{(4.16)}
\]

\[
\frac{\partial F^2}{\partial a_i} - \sum_{m=1}^{M} i_m \lambda_m = 0, \quad \frac{\partial F^2}{\partial A^*_2} - \eta^2 = 0. \quad \text{(4.17)}
\]

Practically, the computation of this isotherm will split in two parts. The first one consists in computing the quantities in phase 2 in terms of the Lagrange multipliers \( \lambda_m \) and \( \eta_1 \). This is the same explicit computation as in the previous section: we introduce some new variables \( \chi_0 = e^{\eta_1}, \chi_m = e^{\lambda_m}, m = 1, \ldots, M \), and a polynomial \( P \) in the \((M + 1)\)-variables \( \chi^i = (\chi_0, \ldots, \chi_M) \):

\[
P(\chi') = \frac{1}{q_2} \sum_{|j| \leq q_2} \eta_1^j e^{-\beta E_2} \chi_1^{i_1} \cdots \chi_M^{i_M}.
\]

Eq. (4.17) give readily the following expression for the quantities in phase 2:

\[
N_m^2 = N_2^* \frac{\sum_{|j| \leq q_2} \eta_1^j e^{-\beta E_2} \chi_1^{i_1} \cdots \chi_M^{i_M}}{q_2} = N_2^* \frac{\chi_m \frac{\partial P}{\partial \chi_m}(\chi')}{q_2 P(\chi')}, \quad m = 1, \ldots, M,
\]

where \( N_2^* \) is a constant.
It remains now to compute the $\chi_m$-s in terms of the quantities in phase 1. This was obvious when the phase 1 was an ideal solution, it becomes a little tougher here. Indeed, if we define another polynomial $Q$ by

$$Q(\chi_0, \ldots, \chi_M) = \frac{1}{q_1} \sum_{|i| \leq q_1} n_1^i e^{-\beta E_1^i} \chi_0^{(q_1 - |i|)} \chi_1^i \ldots \chi_M^i,$$

we can rewrite the optimality conditions (4.16):

$$\frac{N_m^1}{N_1^1} = \chi_m \frac{\partial Q}{\partial \chi_m}, \quad m = 0, \ldots, M. \tag{4.19}$$

Thus we obtain the molar fractions $\frac{N_0^1}{N_1^1}, \ldots, \frac{N_M^1}{N_1^1}$ in terms of the variables $\chi_0, \ldots, \chi_M$ by a polynomial mapping:

$$\left(\frac{N_0^1}{N_1^1}, \ldots, \frac{N_M^1}{N_1^1}\right) = \Phi(\chi_0, \ldots, \chi_M).$$

We already know by the general result in the preceding section that the function $\Phi$ is invertible. But we can see it directly on formula (4.19). Indeed we sum the $M + 1$ equations in (4.19), so that

$$\sum_{m=0}^{M} \frac{N_m^1}{N_1^1} = 1.$$

Using this identity and noticing that all the coefficients in $Q$ are nonnegative, an easy computation shows that

$$\sum_{m=0}^{M} \left( \chi_m \frac{\partial Q}{\partial \chi_m}(\chi') - \chi_m'' \frac{\partial Q}{\partial \chi_m}(\chi'') \right) (\chi' - \chi''_m) > 0,$$

so that $\Phi$ is a monotone operator on $\mathbb{R}^{M+1}_+$. This proves that $\Phi$ is invertible.

Finally, the isotherm for the liquid-solid equilibrium is given by the following set of formulae:

$$(N_1^2, \ldots, N_M^2) = \Psi \circ \Phi^{-1}(1 - \sum_{m=1}^{M} N_m^1, N_1^1, \ldots, N_M^1),$$

$$\left\{
\begin{array}{l}
\Psi_m(\chi') = N_2^m \frac{\chi_m \frac{\partial P}{\partial \chi_m}(\chi')}{q_2 P(\chi')}, \quad m = 1, \ldots, M,
\Phi_m(\chi_0, \chi') = \chi_m \frac{\partial Q}{\partial \chi_m}(\chi_0, \chi'), \quad m = 0, \ldots, M.
\end{array}
\right.$$
We show here a few simple examples of our models. First, we consider for the stationary phase the model obtained either by setting $q^2 = 1$, or by choosing all the interaction energies $\varepsilon_i$ equal to 0, for every $|i| > 1$. This will lead us to Langmuir-like isotherms. Next, we shall limit ourselves to the single-component adsorption, and show how inflexion points arise in the isotherm when $q^2 > 1$. Finally, to fix the ideas, we give the explicit formulæ in the case of a binary mixture.

5.1. Langmuir-like models

We limit ourselves to the case of an ideal solution in the adsorbed phase, which is physically not very realistic, but simplifies the equations. In the case of gas-solid adsorption, we find the classical Langmuir isotherm. For the gas-liquid absorption, we find a function quite analogous, but having singularities. The Langmuir isotherm allows a thorough mathematical study of the equations of chromatography (cf. Refs. 14, 15, 7) and distillation (Refs. 2, 1).

If all interaction energies are taken equal to zero, the polynomials defined by (4.4) and (4.10) simplify and become respectively, by the Leibniz formula:

$$P(w_1, \ldots, w_M) = (1 + \sum_{m=1}^{M} w_m) q^2, \quad \text{and} \quad P(w_0, \ldots, w_M) = \left( \sum_{m=0}^{M} w_m \right)^q.$$

Partial derivatives of $P$ with respect to $w_m$, $1 \leq m \leq M$, are now particularly simple to compute. In the first case, we have

$$\frac{\partial P}{\partial w_m} = q^2 \frac{P}{1 + \sum_{i=1}^{M} w_i}.$$  

Formula (4.5) which gives $N_2^m$ takes thus the following form:

$$N_2^m = N_2 \frac{w_m}{1 + \sum_{i=1}^{M} w_i} \quad (5.1)$$

which, replacing $w_m$ by its value, $w_m = K_m c_m$, gives the classical Langmuir isotherm (Refs. 11, 5, 6, 14, 15).

In the second case, the constraint (4.10) $P(w_0, \ldots, w_M) = 1$ implies, since all the $w_m$ are nonnegative, $\sum_{m=1}^{M} w_m = 1$. Therefore, we have $\partial P/\partial w_m = q^2$, and the relation (4.13) finally reduces to

$$N_2^m = N_2^\Pi \frac{w_m}{1 - \sum_{i=1}^{M} w_i} \quad (5.2)$$

Notice that this isotherm is the inverse function of Langmuir isotherm.

One can also find these results by setting $q^2 = 1$, which is nothing but another way to say that there are no interactions between species. The set $I$ is then given by $I = \{(0, \ldots, 0), (1, 0, \ldots, 0), \ldots, (0, \ldots, 0, 1)\}$, so that $|i| = 1$ except for $i = 0$. One has obviously $a_0 = N_0^\Pi$ and, if $i$ has an 1 in the $m$-th position, then $a_i = N_m^2$. We have also $n_i = 1$ for every $i$, so the polynomials defined by (4.4) and (4.10)
become respectively: \( P(w_1, \ldots, w_M) = 1 + w_1 + \cdots + w_M \) and \( P(w_0, \ldots, w_M) = w_0 + w_1 + \cdots + w_M \). The result follows easily.

As we said before, the gas-liquid absorption isotherm shows a discontinuity on the set \( K e_1 + \cdots + K e_M = 1 \), which is the form taken by (4.11) in this particular case. From a physical point of view, one can say that, when the total amount of matter in the gaseous phase tends to infinity, the stationary phase behaves like the mixture of all the components. The relevant physical model should be the condensation of the mixture, and not the absorption by a liquid phase.

### 5.2. Gas-solid binary adsorption

We briefly give here the form that take formulæ (4.4) and (4.5) in the case of binary adsorption, that is when \( \mathcal{I} = \{(0,0), (0,1), (1,0), (2,0), (2,1), \ldots, (0,q^2)\} \). The multi-index \( i \) is now given by \( i = (i, j) \), \( 0 \leq i, j \leq q^2 \), \( i + j \leq q^2 \), the degeneracy number \( n_{ij} \) is

\[
n_{ij} = \frac{q^{2i}}{i!j!(q^2-i-j)!}.
\]

and we set \( b_{ij} = \exp(-\epsilon_{ij}/(RT)) \). The coverage rates \( \theta_1 \) and \( \theta_2 \) are given by:

\[
\begin{align*}
\theta_1 &= \frac{\sum_{i,j \in \mathcal{I}} i n_{ij} b_{ij} w_1^i w_2^j}{q^2 \sum_{i,j \in \mathcal{I}} n_{ij} b_{ij} w_1^i w_2^j}, \\
\theta_2 &= \frac{\sum_{i,j \in \mathcal{I}} j n_{ij} b_{ij} w_1^i w_2^j}{q^2 \sum_{i,j \in \mathcal{I}} n_{ij} b_{ij} w_1^i w_2^j}.
\end{align*}
\tag{5.3}
\]

These formulæ readily extend to more than two components. By using combination rules for energies, such as \( \epsilon_{ij} = (\epsilon_{i0} + \epsilon_{0j})/2 \), one may reduce the number of parameters needed in (5.3). It becomes easier to choose these parameters to fit the isotherm to experimental data, and one can also deduce multicomponent isotherms from single component isotherms.

Notice also that for \( q = 2 \), and for two components, our models allow to recover a classical isotherm, namely the “bi-Langmuir” isotherm, which is usually given in the form:

\[
\begin{align*}
\theta_1 &= \frac{\alpha_1 w_1}{1 + \alpha_1 w_1 + \alpha_2 w_2} + \frac{\beta_1 w_1}{1 + \beta_1 w_1 + \beta_2 w_2} \\
\theta_2 &= \frac{\alpha_2 w_2}{1 + \alpha_1 w_1 + \alpha_2 w_2} + \frac{\beta_2 w_2}{1 + \beta_1 w_1 + \beta_2 w_2}.
\end{align*}
\]

A trivial computation gives for \( \theta_1 \)

\[
\theta_1 = w_1 \frac{Q(w_1, w_2)}{P(w_1, w_2)},
\]

where \( P(w_1, w_2) = 1 + (a_1 + b_1) w_1 + (a_2 + b_2) w_2 + (a_1 b_2 + a_2 b_1) w_1 w_2 + a_1 b_1 w_1^2 + a_2 b_2 w_2^2 \), and \( Q(w_1, w_2) = \alpha_1 + \beta_1 + (\alpha_1 b_1 + \beta_1 a_1) w_1 + (\alpha_1 b_2 + \beta_1 a_2) w_2 \). In order to have \( Q = \partial P/\partial w_1 \), the constants must satisfy

\[
a_1 + \beta_1 = a_1 + b_1, \quad 2a_1 b_1 = \alpha_1 b_1 + \beta_1 a_1, \quad a_1 b_2 + a_2 b_1 = \alpha_1 b_2 + \beta_1 a_2,
\]

and
and similar relations are obtained by computing \( \theta_2 \). With our notations, we have 
\[ b_{10} = (a_1 + b_1)/2, b_{01} = (a_2 + b_2)/2, b_{11} = (a_1 b_2 + a_2 b_1)/2, b_{20} = a_1 b_1 \text{ and } b_{02} = a_2 b_2. \]

### 5.3. Comparison with experiment

Figure 1 shows the comparison between an experimental result obtained by Rouchon & al.\textsuperscript{18}, and an numerical simulation based on the modelling of chromatographic columns by nonlinear hyperbolic systems, see Refs.\textsuperscript{18,7}. The experiment was gas-solid adsorption of N-hexane on graphitized carbon, the coefficient \( K \) has been taken equal to 1286 l./mol. The model of isotherm we used is of degree 4, the energies (in cal./mol.) are the following: \( e_2 = -359, e_3 = -1251, e_4 = -9.1 \).

Actually, the value of \( e_4 \) is not very important, it could be taken equal to 0, but the fact that the isotherm is of degree 4 is important.

![Fig. 1. Gas-solid adsorption – Experiment (···) vs simulation (—)](image_url)

### 6. Single Component Isotherms

We give in this section some examples of isotherms for the gas-solid adsorption, the gas-liquid absorption and liquid-liquid equilibrium for a single component. The set \( I \) is simply given now by \( I = \{0, 1, \ldots, q^2\} \), and we obviously replace the multi-index \( i \) by an index \( i \). The quantity \( w_1 \) is denoted now by \( w \), and we keep the notation \( w_0 \) for the adsorbent (or absorbent). We set also \( b_i = \exp(-\varepsilon_i/(RT)) \), and notice that \( n_i \) is the classical binomial coefficient \( C_i^j \):

\[ C_i^j = \frac{q^2!}{j!(q^2 - j)!}. \]
For gas-solid adsorption, we obtain the coverage rate $\theta$ by using formulæ (4.4) and (4.5). The latter becomes, since the coefficients in the numerator $C_q^j$ simplify by $q$:

$$\theta = \frac{w \sum_{j=1}^{q-1} C_q^j b_{j+1} w^j}{\sum_{j=1}^{q} C_q^j b_j w^j}.$$ 

On this formula, it is clear that $\lim_{w \to \infty} \theta = 1$, and a straightforward computation shows that $\theta'(0) = 1$ and $\theta''(0) = (q - 1)b_2 - q$. Thus one has an inflexion point at the origin if $q''(0) = 0$, that is $b_2 = q/(q - 1)$. This is a simple example to show that the values of parameters $b_i$ can be fixed to match remarkable points of a given isotherm: inflexion points, asymptotes, ...

We turn now to the case of gas-liquid absorption, which is no longer explicit, as we noticed before. The coverage rate $\theta$ is given by two equations we deduce from (4.10) and (4.12). The polynomial $P$ is given by

$$P = w^q + \sum_{j=1}^{q} C_q^j b_j w^{q-j} w^j,$$

so we have to solve the following equations for $\theta$

$$\theta = \frac{wP'(w)}{qP - wP'(w)}, \quad P = 1$$

where $P'(w)$ stands for the derivative of $P$ with respect to $w$.

The resolution of the equation $P = 1$ is usually not explicit, especially when $q$, that is the degree of $P$, is high. However, as we noticed before, the numerical resolution by a Newton method is very efficient.

The analogous of formula (4.11) becomes here very simple: $b_q w_q < 1$. This gives us explicitly the position of the vertical asymptote in terms of interaction energies, that is

$$w = \left(\frac{1}{b_q}\right)^{\frac{1}{q}} = \exp\left(\frac{\varepsilon_q}{qRT}\right).$$

Here again, the parameters $b_i$ happen to determine some remarkable points of the isotherm, the former being the simplest example.

We give now a few examples of isotherms for one component, based on several set of energies $\varepsilon_i$, which are given in cal./mol. in Table 1, 2 and 3.

<table>
<thead>
<tr>
<th>Table 1. Energies for gas-solid adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energies</td>
</tr>
<tr>
<td>Langmuir</td>
</tr>
<tr>
<td>degree 2</td>
</tr>
<tr>
<td>degree 3 (a)</td>
</tr>
<tr>
<td>degree 3 (b)</td>
</tr>
<tr>
<td>degree 4</td>
</tr>
</tbody>
</table>
6.1. Gas-solid adsorption

In this section and in the following one, the Langmuir coefficient $K_1$ has been taken equal to 1286 L./mol., and the pressure $p$ has been taken equal to 760 mm Hg. The derivatives of the isotherms appear on Figure 2, the isotherms themselves on Figure 3.

Our set of examples includes the Langmuir isotherm. Notice how inflexion points arise when the degree increases: they can hardly be seen on the isotherms, but appear clearly on the derivatives.

6.2. Gas-liquid absorption

We turn on now gas-liquid isotherms, the derivative of which blow up.

Table 2. Energies for gas-liquid absorption

<table>
<thead>
<tr>
<th>Energies</th>
<th>$\varepsilon_2$</th>
<th>$\varepsilon_3$</th>
<th>$\varepsilon_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>No interactions</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>degree 2</td>
<td>-600</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>degree 3 (a)</td>
<td>-3000</td>
<td>-700</td>
<td>-</td>
</tr>
<tr>
<td>degree 3 (b)</td>
<td>-1500</td>
<td>-1000</td>
<td>-</td>
</tr>
<tr>
<td>degree 4</td>
<td>214</td>
<td>-1500</td>
<td>2000</td>
</tr>
</tbody>
</table>

Similarly to the preceding case, we show in Figs. 4 and 5 the model with no interaction, analogous to the Langmuir isotherm: it blows up very slowly. As soon as the degree increases, the blowing up is more violent, and inflexion points appear.
Fig. 3. Gas-solid adsorption – Isotherms

Fig. 4. Gas-liquid absorption – Derivative of the isotherms
6.3. Liquid-liquid equilibrium

We now turn to liquid-liquid isotherms, and give a set of five examples, four of them being obtained just by exchanging the coefficients between phase 1 and phase 2. The fifth one is merely the model without any interaction in the two phases (degree 0). Making this particular choice of coefficients leads us to expect a kind of symmetry of the isotherms with respect to the model without interactions.

More precisely, we first consider two lattice models for phase 1, and an ideal solution for phase 2. The models are of order 7 and 10, with the following sets of interaction energies:

- For degree 7: 
  \[ E_7 = (\varepsilon_2 = -3419; \varepsilon_3 = 6015; \varepsilon_4 = 3998; \varepsilon_5 = 1263.2; \varepsilon_6 = -3973; \varepsilon_7 = 124.57), \]

- For degree 10: 
  \[ E_{10} = (\varepsilon_2 = -5735; \varepsilon_3 = 5945; \varepsilon_4 = 3689; \varepsilon_5 = 1481; \varepsilon_6 = -914.9; \varepsilon_7 = -10910; \varepsilon_8 = -1432; \varepsilon_9 = -7.434; \varepsilon_{10} = -0.1327). \]

The Langmuir coefficients are \( k_1 = 1.7239 \) for degree 7, \( k_2 = 5.8869 \) for degree 10.

Next, we consider the phase 1 as an ideal solution, and model the phase 2 with the above lattice models, the only modification being in the Langmuir coefficients: we take respectively \( 1/k_1 \) and \( 1/k_2 \) (see Table 3).

<table>
<thead>
<tr>
<th>Isotherms</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K )</td>
<td>1</td>
<td>( k_1 )</td>
<td>( k_2 )</td>
<td>( 1/k_1 )</td>
<td>( 1/k_2 )</td>
</tr>
<tr>
<td>( \varepsilon_i ) mobile phase</td>
<td>-</td>
<td>( \varepsilon_7 )</td>
<td>( \varepsilon_{10} )</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \varepsilon_i ) stationary phase</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>( \varepsilon_7 )</td>
<td>( \varepsilon_{10} )</td>
</tr>
</tbody>
</table>
We obtain a family of isotherms, which is symmetric with respect to the model without interactions (see Figs. 6 and 7). This was expected since the choice of the energies is in a way symmetric.

7. Conclusion

The use of a statistical models for phases allows us to give a general framework for the computation of several adsorption equilibria. The coefficients which arise in the formulation—interaction energies in the adsorbed phase—are physically meaningful, although they may reflect rather crude approximations. The concept of synergy ($\varepsilon_i < 0$) and antisymmetry ($\varepsilon_i > 0$) of adsorption can be naturally introduced, and its interpretation in terms of remarkable points of the isotherm (inflexion points, asymptotes) should be investigated.

The main restriction for the moment is that we assume an inert component in each phase (vector fluid or adsorbent), which forbids us the study of phase transition (condensation in the adsorbed phase). However, by using a lattice model for both phases, we can extend to liquid-liquid equilibria. Let us mention also a possible generalization to the case of molecules of different sizes: the definition of $I$ for two components should become $I = \{(i, j); 0 \leq i, j \leq q; \sigma_i + \sigma_j \leq s\}$, where $\sigma_m$ is the surface occupied by the component $m = 1, 2$, and $\sigma$ is the size of the cell. The degeneracy numbers will take a form analogous to the one we gave previously, but involving Euler’s Gamma function.

References


