| Elements of:                 |
|------------------------------|
| thermodynamics, kinetics and |
| Transport Phenomena in       |
| Dispersed Media              |

first edition

# **José Carlos Gubulin**

# Elements of: Thermodynamics, Kinetics and Transport Phenomena in Dispersed Media.

1st edition

Jose Carlos Gubulin

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## About the author

Jose Carlos Gubulin holds a degree in Physics from State University Júlio de Mesquita Filho/campus of Rio Claro - SP (1974), a Master's degree in Chemical Engineering from COPPE - Federal University of Rio de Janeiro (1977), and a PhD in Chemical Engineering (Génie Chimique) from the Institut National Polytechnique de Toulouse-France (1980). He was a full professor at the Federal University of São Carlos until his retirement in 2009, where he worked as a Volunteer until 2016. After that he to dedicated himself to your personal projects. Prof. Gubulin is one of the pioneers in the research field of adsorption and electrodeposition (Electrochemical Engineering) as active areas of research in Brazil, having experience in Chemical Engineering, with emphasis on Industrial Operations and Equipment for Chemical Engineering processes.

Dedicated to

Nilva

Tiago and Thais

Carolina, Enzo and Benjamin

Give to everyone what you owe them: If you owe taxes, pay taxes; if revenue, then revenue; if *respect*, then *respect*; if **honor**, then **honor**. (Romans 13:7)

to my dear masters

Jose Teixeira Freire

Satoshí Tobínaga

and in memory of

Gíulío Massaraní

#### - PROLOGUE -

In the 70s, the *Rational Continuum Mechanics* was adopted by the particulate system group of PEQ/COPPE-UFRJ by professors Afonso Silva Telles and Giulio Massarani. The brilliant way in which they developed theory and experimentation created a unique language in Particulate Systems and marked an entire generation of future researchers. If we add to these two names, in all fairness, that of professors José Teixeira Freire and Satoshi Tobinaga, we can certainly say that the entire Particulate System in Brazil descended from them, which can be confirmed by the ENEMP Proceedings, from the first one to the most recent edition. At that time, specific literature was scarce, but in 1982, during the X ENEMP, Freire and I edited the book entitled "Special Topics in Particulate System", bringing together the contribution of several national researchers. The book was a modest commemoration of the ten years of the traditional meetings on flow in porous media, ENEMP, and an attempt to unify the language of the various branches under development: flow in porous media, fluidization, hydraulic and pneumatic transport, sedimentation, heat transfer, etc... Recognizing the evolution of the fundamental and applied studies, mainly in the field of Chemical Engineering, it seemed opportune to continue this book, making it periodic every four years. In this sense, the content found in this book is a synthesis of what we have already presented in the Special Topics. The content that in this book is chapter 1 was the topic that I intended to present in the 1998's edition, however I preferred to complete the cycle of mass transfer that had begun in 1986. This topic was only discussed with our community in 2002, during the IV EBA (Brazilian Adsorption Meeting), when, as a speaker, I presented the topic: "some aspects of multicomponent adsorption" already with some data that justified the proposition. In this sense, the material shown here is not new and represents only an attempt to recover part of that material, since it is still current, as the reader will be able to verify.

#### – PREFACE –

Systems involving one continuous and one or more dispersed phases, finely divided, usually called Particulate System, are very abundant in industrial processes. In most of these processes, the dispersed phase is composed of solid particles or small bubbles. The continuous phase is commonly a liquid. In some cases, the continuous phase is a gas and the dispersed one consists of small particles. Such systems present a great degree of difficulty to be conveniently analyzed. The most common practice is the particle dynamics or dimensional analysis. Despite the complexity, systems containing multiple phases and multiple chemical species are particularly suitable for macroscopic treatment using Continuum Theories of Mixtures. These theories not only produce the fundamental equations but also provide the basis for the elaboration of the constitutive equations that embody the formulation. The scope and potential of use of these theories can be appreciated in the works of Silva Telles (1974) or Atkin and Craine (1976), among others. However, it is important to emphasize, that, depending on conception from which it comes, the observation of a macroscopically heterogeneous system, behaving as a continuous medium, the as presented theory, makes experimentation very laborious and uncomfortable, making it unable to fully meet the theoretical concept. However, a wide spectrum of applications to various areas, such as Biochemical Engineering (Gubulin, 1986), Chemical Engineering (Gubulin, 1990), Electrochemical Engineering (Gubulin, 1998), among others, opposes these possible limitations.

- Atkin, R.J. e Craine, R.E. (1976) Continuum theories of mixtures: basic theory and historical development". Q. Jl., Mech. Appl. Math., v.19, p. 209 - 244
- Silva Telles, A. (1974) Fenômenos de dispersão em meios porosos. Anais do II ENEMP, v. 1, p. 1 34.
- Gubulin, J.C. (1986) Transferência de massa em sistemas particulados: aplicações à produção de etanol em reatores de leito fixo contendo células imobilizadas; Cap. 4, p. 193 228. In: Tópicos especiais em sistemas particulados. Gráfica da UFSCar, 392p., Freire, J.T. e Gubulin J.C.(Editores).
- Gubulin, J.C. (1990) Transferência de massa em sistemas particulados: aspectos gerais do fenômeno de adsorção, Cap. 5, p. 203 - 291. In: Tópicos especiais em sistemas particulados. Gráfica da UFSCar, 382p., Freire, J.T. e Gubulin, J.C. (Editores).
- Gubulin, J.C. (1998) Transferência de massa em sistemas particulados: aplicações a sistemas eletroquímicos, Cap. 9, p. 319 - 366. In: Tópicos especiais em sistemas particulados. Gráfica da UFSCar, 370p., Freire, J.T. e Silveira, A.M. (Editores).

Mass Transfer Kinetics is a concept that naturally arises in the study of Transport Phenomena, so separating them in chapters imposed a difficulty in establishing which would be the Chapters 2 and 3. On the other hand, little emphasis was given to fluid dynamics and to heat transport. This reflects the internal structure of our research group at DEQ/UFSCar, where prof. Tobinaga was dedicated to polyphase flow and profs. Freire and Sartori to Heat Transfer. Vast literature can be found with their authorship. We could have treated fluid dynamics at least superficially, since we began our scientific adventure under the direction of prof. Massarani in the study of two-phase flow in porous media. Even it has been done, we could not even match the enviable work of Giulio, called: *Fluidodinâmica em Sistemas Particulados (1997)* and available on the internet.

https://www.academia.edu/6063322/FLUIDODINAMICA\_EM\_SISTEMAS\_PA RTICULADOS

Some of the heat and mass transfer can be appreciated in work by Rizzi Jr. (2008), supervised by prof. Freire, and also available on the internet.

 $\underline{https://repositorio.ufscar.br/bitstream/handle/ufscar/3867/2215.pdf?sequence=1\&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?sequence=1&istream/handle/ufscar/3867/2215.pdf?$ 

We called these book topics of *Elements* due to the restrict scope, which we hope to have expanded by including the references suggested above, which can easily be obtained from the internet.

This book treats the *Elements* in a general way, applying them specifically in two parts within each chapter. The adoption of this strategy was to use as much of the readymade material as possible, being almost an insertion from the editing point of view, although it can be confusing in a certain aspect. This option clearly reflects our two main research lines: *adsorption* and *electroseparation of toxic metals*. This book was designed for free electronic access and only a few physical copies have been printed. It was fully typed and edited by me in times of COVID 19 (lockdown) and, in this sense, the only one responsible for the imperfection of the work.

> São Carlos, february 2023 Jose Carlos Gubulin

"The heavens declare the glory of God; and the firmament announce the work of your hands." (Psalm 19.1)

It is up to us to declare that, in the same way as expressed by other authors, we also recognize that the Second Principle of Thermodynamics has "philosophical implications" that point to the existence of a Creator of the Universe who also has the answer to the future destiny of man and of the universe (Van Wylen and Sonntag). We also recognize that this Creator has revealed His designs and purposes. "Nevertheless, there has been much reaction from the naturalistic current, which excels in defending materialism and atheism, against assertions made even in textbooks by authors who honestly recognize these metaphysical aspects embedded in the Second Principle."

"Overwhelming strong proofs of intelligent and benevolent design lies around us" William Thomson (Lord Kelvin)

Observe what scientist Isaac Newton says at a certain point in his life.

"The origin of the material world must be attributed to the intelligence and wisdom of a most powerful Being, always existing and present everywhere, who dominates, according to His will, all parts of the Universe, much more effectively than our soul dominates, through its will, the movements of the body united with it".

Since, until then, and even until today, it has never been possible to prove in any way the existence of any transcendental design, a supernatural reality, interventions or spiritual direction for humanity; where did Newton see the logical necessity of speculating on matters beyond human experience? Where did you get the firm conviction that, behind all external appearances, there is a supreme reality that penetrates the visible and tangible world?

"... I admire those intelligences that dominate matter to put it at the service of men. I rejoice in the progress of Science and Technology. I admire all those who, according to God's plans, enrich and complete the divine creation..." (physicist A. Tagliaro).

There is a phrase supposedly attributed to Einstein which is:

"Each new discovery of science is a new door through which I once again meet God, the author of it".

This magnificent phrase could be uttered by anyone who does science.

Science has already established that the universe was created, it would be wiser to accept a creator, who has revealed himself in a way: *general* (His creation), *precise* (His word) and *objective* (His son), which we desire and encourage greater interest in recognizing himself.

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#### CHAPTER 1 THERMODYNAMICS

In this Chapter we propose to present a modest contribution to the establishment of the thermodynamic bases of the Equilibrium Problem in Multicomponent Adsorption Systems. What is presented here summarizes the result of our work, supported by the relevant contribution of important researchers and the accumulation of knowledge generated in recent decades. The main characteristic of the proposed thermodynamic formulation is the gathering, in a single formalism, of the most significant multicomponent adsorptive processes: solid-gaseous, solid-liquid without electrolytes and solid-liquid with electrolytes (ion exchange).

In the different topics in which the subject will be developed, we will deal with the general problem of phase equilibrium and its importance for the adsorptive process and in particular the case of the isothermal system (adsorption isotherms). Attention will be given to the gas phase adsorption of a single component, with special emphasis on the Langmuir equation. Other important isotherms will also be addressed. Concerning the multicomponent adsorption, issues related to the main models and empirical correlations will be addressed.

Applications to problems of interest will be treated in two parts, as specific cases of the formulation:

- Part I- Electrolytic systems (ion exchange);
- Part II- Multicomponent adsorption in gas or liquid phase, ideal and non-ideal system;

In each of these parts, particular thermodynamic aspects will be discussed and various comparisons with literature data will be presented. The basic concepts and thermodynamic relationships to be developed here are mainly based on the work of Callen  $(1985)^1$  and Sandler  $(1989)^2$ .

*This essay is an attempt to accommodate within classical thermodynamics the adsorptive processes.* 

#### **1.1. Basic Postulates**

In presenting these elements, the mathematical formulation will be developed in terms of macroscopic coordinates (parameters: extensive, intensive, specific or molar, ...) and all attention will be restricted to the thermodynamic system, defined as a portion of matter, separated from the whole by real or fictitious boundaries, macroscopically homogeneous, isotropic and, not sufficiently extensive, with non-negligible boundary effects.

<sup>&</sup>lt;sup>1</sup>Callen, HB (1985) Thermodynamics and an Introduction to Thermostatistics. John Wiley & Sons 493 p. <sup>2</sup>Sandler, SI (1989). Chemical and Engineering Thermodynamics. John Wiley & Sons 622 p.

The system has a precise and defined amount of mass, subject to a precise and defined principle of conservation. The system also has a precise and defined amount of energy, subject to a precise and definite principle of conservation. An analogous postulate is admitted for electric charges.

The system boundaries have internal constraints (specific abilities) whose manipulation will allow the system to interact with its surroundings. These skills are *adiabaticity, rigidity and impermeability (or semi-permeability)*. A system whose boundaries are adiabatic, rigid and impermeable is said to be isolated.

The fundamental problem of *thermodynamics of reversible processes* is the determination of the equilibrium state that, eventually, results from the removal of some internal constraint in an isolated composite system. The composite system is the set of individual systems formed for analysis.

The system, in the absence of some internal constraint, will evolve, that is, it will have a tendency to assume states in which the macroscopic coordinates are determined by intrinsic factors and not by previously applied external influences. Each terminal state is, by definition, unique and does not depend on its recent history.

Thermodynamics can, in principle, describe these equilibrium states to which the system can tend and, through them, provide all conceivable information about the system.

For the development of the equations that will be useful in this work, it will be necessary to postulate that "there are particular states (called equilibrium states) of particular systems that, macroscopically, are completely characterized by the internal energy U, the volume V, the area A, the electric charge Q, and the mole numbers,  $N_1$ ,  $N_2$ , ...,  $N_m$ , of the m chemical components present in the system". These coordinates are parameters (properties) of the system and, with the exception of the area, they are all extensive.

On the other hand, the second law of thermodynamics postulates that "there exists an extensive coordinate (property), called entropy S, defined for all equilibrium states, a continuous and differentiable function of the variables (system parameters) that characterize the equilibrium state and having the following properties:

-entropy is a monotonically increasing function of internal energy;

- for an isolated composite system, in the absence of some internal constraint, the values assumed by the parameters of the individual constituent systems, are those that maximize the entropy of the isolated composite system, over the manifold of constrained equilibrium states".

Finally, the third law postulates (establishes) that: -the entropy of any system vanishes for the state in which:

$$\left(\frac{\partial U}{\partial S}\right)_{V,A,Q,N_1,\dots,N_n} = 0; \qquad (1.1)$$

#### 1.1.1. The Fundamental Equation of Thermodynamics (FET)

Denoting by  $\alpha$  the individual system and  $\kappa$  the chemical species present in the system, then, as a consequence of what has been exposed, we will have for a system constituted by  $\pi$  parts into constituents:

*i*) for the individual system:

$$S^{(\alpha)} = S^{(\alpha)} \Big( U^{(\alpha)}, V^{(\alpha)}, Q^{(\alpha)}, A^{(\alpha)}, N^{(\alpha)}_k, ... \Big); \alpha = 1, 2, ..., \pi \text{ and } \kappa = 1, 2, ..., m$$
(1.2)

*ii*) for the composite system:

$$U = \sum_{\alpha=1}^{\pi} U^{(\alpha)}; V = \sum_{\alpha=1}^{\pi} V^{(\alpha)}; Q = \sum_{\alpha=1}^{\pi} Q^{(\alpha)}; N = \sum_{\alpha=1}^{\pi} \sum_{k=1}^{m} N_{k}^{(\alpha)} e \quad S = \sum_{\alpha=1}^{\pi} S^{(\alpha)}$$
(1.3)

and the following criteria must be met:

$$(dS)_{U,V,Q,M} = 0$$
 e  $(d^2S)_{U,V,Q,M} = 0$ ; (1.4)

where M is the total mass of the system.

Equations that represent, respectively, the *equilibrium criterion* (existence) and the *stability criterion* (maximum existence).

The relation of Eq.1.2 is known as the *fundamental equation of thermodynamics* in *entropic* form. As a consequence of entropy being a monotonically increasing function of internal energy this relationship can be put in the form:

$$U^{(\alpha)} = U^{(\alpha)} \Big( S^{(\alpha)}, V^{(\alpha)}, A^{(\alpha)}, Q^{(\alpha)}, N^{(\alpha)}_k, ... \Big); \alpha = 1, 2, ..., \pi \text{ and } \kappa = 1, 2, ..., m$$
(1.5)

which is known as the *fundamental equation of thermodynamics* in the *energetic* form, this last form has been the most used.

Taking the total differential of the relation of Eq.1.5 will have:

$$dU^{(\alpha)} = \left(\frac{\partial U^{(\alpha)}}{\partial S^{(\alpha)}}\right)_{V^{(\alpha)}, A^{(\alpha)}, Q^{(\alpha)}, N^{(\alpha)}_{k}} dS^{(\alpha)} + \left(\frac{\partial U^{(\alpha)}}{\partial V^{(\alpha)}}\right)_{S^{(\alpha)}, A^{(\alpha)}, Q^{(\alpha)}, N^{(\alpha)}_{k}} dV^{(\alpha)} + \left(\frac{\partial U^{(\alpha)}}{\partial A^{(\alpha)}}\right)_{S^{(\alpha)}, V^{(\alpha)}, A^{(\alpha)}, N^{(\alpha)}_{k}} dQ^{(\alpha)} + \sum_{\kappa=1}^{m} \left(\frac{\partial U^{(\alpha)}}{\partial N^{(\alpha)}_{k}}\right)_{S^{(\alpha)}, V^{(\alpha)}, A^{(\alpha)}, Q^{(\alpha)}, N^{(\alpha)}_{j\neq k}} dN^{(\alpha)}_{k}$$

$$(1.6)$$

In this equation each one of the partial derivatives is an intensive parameter of the system and called *thermodynamic potential*.

The following notation is usual:

$$\left(\frac{\partial U^{(\alpha)}}{\partial S^{(\alpha)}}\right)_{V^{(\alpha)}, A^{(\alpha)}, N^{(\alpha)}_{k}} = T^{(\alpha)}; \text{ Thermal potential (absolute temperature)}$$
(1.7)

$$-\left(\frac{\partial U^{(\alpha)}}{\partial V^{(\alpha)}}\right)_{S^{(\alpha)},A^{(\alpha)},N^{(\alpha)}_{k}} = P^{(\alpha)} ; \text{ Mechanical potential (absolute pressure)}$$
(1.8)

$$\left(\frac{\partial \mathbf{U}^{(\alpha)}}{\partial \mathbf{Q}^{(\alpha)}}\right)_{S_{\alpha}, V_{\alpha}, N_{\kappa, \alpha}} = \Phi^{(\alpha)} ; \text{Electric potential}$$
(1.9)

$$-\left(\frac{\partial U^{(\alpha)}}{\partial A^{(\alpha)}}\right)_{S^{(\alpha)},V^{(\alpha)},N^{(\alpha)}_{k}} = \Pi^{(\alpha)}; \text{ Interfacial potential}$$
(1.10)

$$\left(\frac{\partial U^{(\alpha)}}{\partial N_k^{(\alpha)}}\right)_{S^{(\alpha)}, V^{(\alpha)}, A^{(\alpha)}, N_{j \neq k}^{(\alpha)}} = \mu_k^{(\alpha)}; \text{ Chemical potential}$$
(1.11)

Note that, in relation to the classical thermodynamics of solutions, the *electric potential* appears explicitly (due to the inclusion of electric charges), and, due to the inclusion of the new variable, the area, a new potential appears, denoted by *Interfacial potential* (Interfacial tension), which is the tension responsible for the restitution of the interface when an agent deforms it, in this case, the intermolecular interactions between the components lying on each side of the interface.

Introducing the Eqs. 1.7 to 1.11 in Eq. 1.6 results:

$$dU^{(\alpha)} = T^{(\alpha)} dS^{(\alpha)} - P^{(\alpha)} dV^{(\alpha)} - \Pi^{(\alpha)} dA^{(\alpha)} + \Phi^{(\alpha)} dQ^{(\alpha)} + \sum_{\kappa=1}^{m} \mu_{k}^{(\alpha)} dN_{k}^{(\alpha)}$$
(1.12)

and thus the state of the individual system can be completely characterized by entropy,  $S^{(\alpha)}$ , the volume,  $V^{(\alpha)}$ , the area,  $A^{(\alpha)}$ , the electric charge,  $Q^{(\alpha)}$ , and the mole numbers,  $N_k^{(\alpha)}$ .

Eq. 1.12 can also be expressed in entropy form by:

$$dS^{(\alpha)} = \frac{dU^{(\alpha)}}{T^{(\alpha)}} + \frac{P^{(\alpha)}}{T^{(\alpha)}} dV^{(\alpha)} + \frac{\Pi^{(\alpha)}}{T^{(\alpha)}} dA^{(\alpha)} - \frac{\Phi^{(\alpha)}}{T^{(\alpha)}} dQ^{(\alpha)} - \sum_{\kappa=1}^{m} \frac{\mu_{k}^{(\alpha)}}{T^{(\alpha)}} dN_{k}^{(\alpha)}$$
(1.13)

#### 1.1.2. Integration of the Fundamental Equation of Thermodynamics

Using Euler's theorem of homogeneous functions (Callen, 1985) for the integration of Eq. 1.12 results:

$$U^{(\alpha)} = T^{(\alpha)}S^{(\alpha)} - P^{(\alpha)}V^{(\alpha)} - \Pi^{(\alpha)}A^{(\alpha)} + \Phi^{(\alpha)}Q^{(\alpha)} + \sum_{\kappa=1}^{m}\mu_{k}^{(\alpha)}N_{k}^{(\alpha)}$$
(1.14)

It is important to note that the products  $T^{(\alpha)}S^{(\alpha)}$ ,  $P^{(\alpha)}V^{(\alpha)}$ ,  $\Pi^{(\alpha)}A^{(\alpha)} \in \Phi^{(\alpha)}Q^{(\alpha)}$  are energies similar in nature to U<sub> $\alpha$ </sub>. Thus, through the combination of these energies it is possible to define others.

The complete development of this formulation although it can be done without great difficulties, it does not present advantages of real interest and, in this sense, we will deal with particular cases, of more immediate interest and less loaded with information. In part I we will deal with systems with electrical charges (electrochemical systems) not taking into account the area and in part II only the dependence of the area not taking into account electrical charges.

#### **1.2. Other considerations**

Some concepts, due to their relevance in the thermodynamics of solutions, are widely used, among them the most recurrent are: the *standard state* and the *ideal solution*; and as they will certainly be needed, an immediate conceptualization is opportune. In what follows **M** is the symbolic representation of any thermodynamic property of interest.

#### **1.2.1. standard state**

The standard state is a state of the solution, real or fictitious, at the *temperature* and *Interfacial potential* of the solution of interest, but at an arbitrarily fixed pressure and composition, and usually symbolized by a superscript index (o), to indicate the arbitrariness of State.

$$M^{0(\alpha)} = M^{0(\alpha)} \Big( T^{(\alpha)}, \Pi^{(\alpha)}, P^{0(\alpha)}, \dots, N_k^{0(\alpha)}, \dots \Big)$$
(1.15)

The arbitrariness of the composition leads to a fundamental simplification which is the choice of the pure component for the standard state.

#### 1.2.2. ideal solution

The ideal solution is a solution for which, under the same conditions of temperature, Interfacial potential, pressure and composition of the real system, one has, by definition:

$$\overline{v}_k^{(\alpha)} = v_k^{0(\alpha)} \tag{1.16}$$

that is, the molar volume of the k component in solution is assumed to be that of the pure component in the standard state, and, usually, symbolized by a superscript index (ID), for the identification of the state.

$$M^{ID(\alpha)} = M^{ID(\alpha)} \Big( T^{(\alpha)}, \Pi^{(\alpha)}, P^{(\alpha)}, ..., N_k^{(\alpha)}, ... \Big)$$
(1.17)

#### 1.2.3. excess function

An excess property is defined as the difference between the property value in the real solution and the property value if the solution behaved as ideal, and, usually, symbolized by a superscript index (E), for the identification of the state.

$$M^{E} = M(T, P, N_{1},...) - M^{ID}(T, P, N_{1},...)$$

$$m^{E} = m(T, P, x_{1},...) - m^{ID}(T, P, x_{1},...)$$

$$\overline{m}_{j}^{E} = \overline{m}_{j} - \overline{m}_{j}^{ID} \quad e \quad m^{E} = \sum_{j}^{n} x_{j} \overline{m}_{j}^{E}$$
(1.18)

#### 1.2.4. Mixture or mixture quantity Function

A mixture property is, by definition, the difference between the value of a thermodynamic property in the actual mixture and its value based on a mixture constructed with values of the standard state, and, usually, symbolized by a superscript index (mix), for the identification of the state.

$$M^{mix} \equiv M(T, P, N_1, N_2, ..., N_n) - \sum_{k=1}^n N_j m_j^o(T, P^o, x_1^o, x_2^o, ..., x_n^o)$$
  

$$m^{mix} \equiv m(T, P, x_1, x_2, ..., x_n) - \sum_{j=1}^n x_j m_j^o(T, P^o, x_1^o, x_2^o, ..., x_n^o)$$
  

$$\overline{m}_j^{mix} = (\overline{m}_j - m_j^o) \quad e \quad m^{mix} = \sum_{j=1}^n x_j \overline{m}_j^{mix}$$
(1.19)

#### 1.2.5. fugacity and activity

In virtue of which the *chemical potential* is not a convenient parameter (from a mathematical point of view) to work with, the following change of variable, by definition, is almost always useful:

$$d\mu_k^{(\alpha)} \equiv RT^{(\alpha)} d\ln(\hat{f}_k^{(\alpha)}) \text{ at constant } \mathbf{T}^{(\alpha)}$$
(1.20)

in which:

$$\lim_{p(\alpha) \to 0} \hat{\varphi}_k^{(\alpha)} = 1 \text{ where } \hat{\varphi}_k^{(\alpha)} \equiv \frac{\hat{f}_k^{(\alpha)}}{x_k^{(\alpha)} P^{(\alpha)}}$$
(1.21)

On the other hand, by definition:

$$\gamma_k^{(\alpha)} \equiv \frac{\hat{f}_k^{(\alpha)}}{x_k^{(\alpha)} f^{0(\alpha)}} = \frac{\hat{f}_k^{(\alpha)}}{f_k^{(D(\alpha)}}$$
(1.22)

and, depending on choice of standard state:

$$\lim_{x_k^{(\alpha)} \to 1} \gamma_k^{(\alpha)} = 1 \quad \text{or} \quad \lim_{x_k^{(\alpha)} \to 0} \gamma_k^{(\alpha)} = 1$$
(1.23)

The following definition is also usual:

$$\hat{a}_{k}^{(\alpha)} \equiv \frac{\hat{f}_{k}^{(\alpha)}}{f_{k}^{0(\alpha)}} = \gamma_{k}^{(\alpha)} x_{k}^{(\alpha)}$$
(1.24)

In these equations  $\hat{f}_k^{(\alpha)}$ ,  $\hat{\varphi}_k^{(\alpha)}$ ,  $\gamma_k^{(\alpha)}$ ,  $a_k^{(\alpha)} \in \hat{f}_k^{o(\alpha)}$  are, respectively, inside the  $\alpha$ , phase: the *fugacity* of the k component, the *fugacity coefficient* of the k component, the *activity coefficient* of the k component, the *activity* of the k component, and the *fugacity* of the pure k component, in the standard state.

The integration of Eq. 1.20 between the states of the k component, inside the phase  $\alpha$ , and that of the k component, inside the  $\beta$  phase at  $T^{(\alpha)} = T^{(\beta)} = T$  results:

$$\mu_k^{(\beta)} - \mu_k^{(\alpha)} = RT \ln(\frac{\hat{f}_k^{(\beta)}}{\hat{f}_k^{(\alpha)}})$$

and how, in equilibrium,

$$\mu_k^{(\beta)} - \mu_k^{(\alpha)} = 0$$

then:

$$\hat{f}_k^{(\beta)} = \hat{f}_k^{(\alpha)} \tag{1.25}$$

which is equivalent to  $\mu_k^{(\beta)} = \mu_k^{(\alpha)}$  equilibrium can be treated in terms of fugacity rather than chemical potentials with the already known advantages.

#### CHAPTER 1 Part I. Electrolyte Thermodynamics

In part I we will deal with systems with electrical charges (electrochemical systems) not taking into account, the area, at the time.

#### 1.I.1. The fundamental equation and thermodynamic potentials

Thus, based on what has already been presented, we can start by postulating a fundamental relationship of thermodynamics in the energetic form as:

$$U^{(\alpha)} = U^{(\alpha)}(S^{(\alpha)}, V^{(\alpha)}, Q^{(\alpha)}, ..., N_k^{(\alpha)}, ...)$$
(1.I.1)

and your total differential like:

$$dU^{(\alpha)} = \left(\frac{\partial U^{(\alpha)}}{\partial S^{(\alpha)}}\right) dS^{(\alpha)} + \left(\frac{\partial U^{(\alpha)}}{\partial V^{(\alpha)}}\right) dV^{(\alpha)} + \left(\frac{\partial U^{(\alpha)}}{\partial Q^{(\alpha)}}\right) dQ^{(\alpha)} + \sum_{\kappa=1}^{m} \left(\frac{\partial U^{(\alpha)}}{\partial N_{k}^{(\alpha)}}\right) dN_{k}^{(\alpha)}$$
(1.I.2)

and potentials like:

$$\begin{pmatrix} \frac{\partial}{\partial} \mathbf{U}^{(\alpha)} \\ \frac{\partial}{\partial} \mathbf{S}^{(\alpha)} \end{pmatrix}_{V^{(\alpha)}, Q^{(\alpha)}, N_{k}^{(\alpha)}} = T^{(\alpha)}; \text{Thermal potential (absolute temperature)}$$

$$\begin{pmatrix} \frac{\partial}{\partial} \mathbf{U}^{(\alpha)} \\ \frac{\partial}{\partial} \mathbf{V}^{(\alpha)} \end{pmatrix}_{S^{(\alpha)}, Q^{(\alpha)}, N_{k}^{(\alpha)}} = -P^{(\alpha)}; \text{Mechanical potential (absolute pressure)}$$

$$\begin{pmatrix} \frac{\partial}{\partial} \mathbf{U}^{(\alpha)} \\ \frac{\partial}{\partial} \mathbf{Q}^{(\alpha)} \end{pmatrix}_{S^{(\alpha)}, V^{(\alpha)}, N_{k}^{(\alpha)}} = \Phi^{(\alpha)}; \text{Electric potential}$$

$$\begin{pmatrix} \frac{\partial}{\partial} \mathbf{U}^{(\alpha)} \\ \frac{\partial}{\partial} \mathbf{N}_{k}^{(\alpha)} \end{pmatrix}_{S^{(\alpha)}, V^{(\alpha)}, Q^{(\alpha)}, N_{j, j \neq k}^{(\alpha)}} = \mu_{k}^{(\alpha)}; \text{Chemical potential}$$

whose relations functionals (equations of state) are:

$$T^{(\alpha)} = T^{(\alpha)} \Big( S^{(\alpha)}, V^{(\alpha)}, Q^{(\alpha)}, \dots, N_{K}^{(\alpha)}, \dots \Big)$$

$$P^{(\alpha)} = P^{(\alpha)} \Big( S^{(\alpha)}, V^{(\alpha)}, Q^{(\alpha)}, \dots, N_{K}^{(\alpha)}, \dots \Big)$$

$$\Phi^{(\alpha)} = \Phi^{(\alpha)} \Big( S^{(\alpha)}, V^{(\alpha)}, Q^{(\alpha)}, \dots, N_{K}^{(\alpha)}, \dots \Big)$$

$$\mu_{k}^{(\alpha)} = \mu_{k}^{(\alpha)} \Big( S^{(\alpha)}, V^{(\alpha)}, Q^{(\alpha)}, \dots, N_{K}^{(\alpha)}, \dots \Big)$$
(1.I.4)

In terms of the equations of state the relationship of Eq. 1.I.2 takes the form:

$$dU^{(\alpha)} = T^{(\alpha)} dS^{(\alpha)} - P^{(\alpha)} dV^{(\alpha)} + \Phi^{(\alpha)} dQ^{(\alpha)} + \sum_{\kappa=1}^{m} \mu_{k}^{(\alpha)} dN_{k}^{(\alpha)}$$
(1.I.5)

It is clearly noted that in a reversible change of state the change in internal energy is consequence of the exchange of heat and work (mechanical, electrical and chemical) between the system and its surroundings.

#### 1.I.1.1. electrochemical potential

On the other hand, if F (Faraday's constant) represents one mole of electrical charges and if each "individual" of the chemical species  $\kappa$  has an amount of charge  $z_{\kappa}$ , then the total charge associated with this chemical species will be given by:

$$Q_k^{(\alpha)} = z_\kappa F N_k^{(\alpha)} \tag{1.I.6}$$

and the total system electrical charges,  $Q^{(\alpha)}$ , will be given by:

$$Q^{(\alpha)} = \sum_{\kappa=1}^{m} Q_{k}^{(\alpha)} = \sum_{\kappa=1}^{m} z_{\kappa} F N_{k}^{(\alpha)}$$
(1.I.7)

whose differentiation gives the result:

$$dQ^{(\alpha)} = \sum_{\kappa=1}^{m} z_{\kappa} F dN_{k}^{(\alpha)}$$
(1.I.8)

Introducing Eq. 1.I.8 in Eq. 1.I.5 results:

$$dU^{(\alpha)} = T^{(\alpha)} dS^{(\alpha)} - P^{(\alpha)} dV^{(\alpha)} + \Phi^{(\alpha)} \sum_{\kappa=1}^{m} z_{\kappa} F dN_{k}^{(\alpha)} + \sum_{\kappa=1}^{m} \mu_{k}^{(\alpha)} dN_{k}^{(\alpha)}$$
(1.I.9)

whose rearrangement gives the result:

$$dU^{(\alpha)} = T^{(\alpha)} dS^{(\alpha)} - P^{(\alpha)} dV^{(\alpha)} + \sum_{\kappa=1}^{m} \left[ \Phi^{(\alpha)} z_{\kappa} F + \mu_{k}^{(\alpha)} \right] dN_{k}^{(\alpha)}$$
(1.I.10)

Eq. 1.I.10 is a consequence of the existence of a linear relationship between the charge  $Q_k^{(\alpha)}$  and the number of moles  $N_k^{(\alpha)}$ , given by Eq. 1.I.6. Under these conditions, if an amount  $\eta_k^{(\alpha)}$ , defined by:

$$\eta_k^{(\alpha)} = \mu_k^{(\alpha)} + z_\kappa F \Phi^{(\alpha)} \tag{1.I.11}$$

is introduced in Eq. 1.I.10, one can write:

$$dU^{(\alpha)} = T^{(\alpha)} dS^{(\alpha)} - P^{(\alpha)} dV^{(\alpha)} + \sum_{k=1}^{m} \eta_k^{(\alpha)} dN_k^{(\alpha)}$$
(1.I.12)

and thus, the state of the system can be characterized completely by entropy  $S^{(\alpha)}$ , the volume  $V^{(\alpha)}$ , and the number of moles  $N_k^{(\alpha)}$ . The charge  $Q_{\alpha}$ , will be known from Eq. 1.I.6.

In Eq. 1.I.12 is defined:

$$\left(\frac{\partial \mathbf{U}^{(\alpha)}}{\partial \mathbf{N}_{k}^{(\alpha)}}\right)_{S^{(\alpha)}, V^{(\alpha)}, N_{j, j \neq k}^{(\alpha)}} = \eta_{k}^{(\alpha)} \quad \text{Electrochemical potential}$$
(1.I.13)

Eq. 1.I.12 is thus the most useful form of the thermodynamic fundamental equation for electrochemical systems.

The use of *electrochemical potential*, introduced by Guggenheim (1929)<sup>3</sup> is much more advantageous than the separate use of electrical potential and chemical potential.

<sup>&</sup>lt;sup>3</sup>Guggenheim, EA (1929). J.Phys. Chem. 33, 842.

#### **1.I.1.2.** the free energies

Using Euler's theorem of homogeneous functions (Callen, 1985) for the integration of Eq. 1.I.12 results:

$$U^{(\alpha)} = T^{(\alpha)}S^{(\alpha)} - P^{(\alpha)}V^{(\alpha)} + \sum_{\kappa=1}^{m} \eta_{k}^{(\alpha)}N_{k}^{(\alpha)}$$
(1.I.14)

combining similar energies, one arrives at others such as:

$$H^{(\alpha)} = U^{(\alpha)} + P^{(\alpha)}V^{(\alpha)} ; \text{ enthalpy}$$
  

$$F^{(\alpha)} = U^{(\alpha)} - T^{(\alpha)}S^{(\alpha)} ; \text{ Helmholtz free energy}$$
(1.I.15)  

$$G^{(\alpha)} = U^{(\alpha)} - T^{(\alpha)}S^{(\alpha)} + P^{(\alpha)}V^{(\alpha)}; \text{ Gibbs free energy}$$

These settings allow rewrite Eq. 1.I.12 in more convenient ways, such as:

$$dH^{(\alpha)} = T^{(\alpha)} dS^{(\alpha)} + V^{(\alpha)} dP^{(\alpha)} + \sum_{\kappa=1}^{m} \eta_{k}^{(\alpha)} dN_{k}^{(\alpha)}$$
  

$$dF^{(\alpha)} = -S^{(\alpha)} dT^{(\alpha)} - P^{(\alpha)} dV^{(\alpha)} + \sum_{\kappa=1}^{m} \eta_{k}^{(\alpha)} dN_{k}^{(\alpha)}$$
  

$$dG^{(\alpha)} = -S^{(\alpha)} dT^{(\alpha)} + V^{(\alpha)} dP^{(\alpha)} + \sum_{\kappa=1}^{m} \eta_{k}^{(\alpha)} dN_{k}^{(\alpha)}$$
  
(1.I.16)

It is easy to verify that, for the purposes of the equilibrium criterion, the following relations are collectively null:

$$(dS)_{U,V,M} = (dU)_{S,V,M} = (dH)_{S,P,M} = (dF)_{T,V,M} = (dG)_{T,P,M} = 0$$
(1.I.17)

#### 1.I.1.3. Gibbs-Duhen and Gibbs-Helmholtz relationships

To complete it is important to present the Gibbs-Duhen Relation and the Gibbs-Helmholtz Relation.

The integration of the equation 1.I.16c will result, in terms of Gibbs free energy:

$$G^{(\alpha)} = \sum_{k=1}^{m} \eta_k^{(\alpha)} dN_k^{(\alpha)} \text{ at constants } T^{(\alpha)} \text{ and } P^{(\alpha)}$$
(1.I.18)

Differentiating Eq. 1.I.18 and comparing with Eq. 1.I.16 will result in the Gibbs-Duhen relationship:

$$S^{(\alpha)}dT^{(\alpha)} - V^{(\alpha)}dP^{(\alpha)} + \sum_{\kappa=1}^{m} N_{k}^{(\alpha)}d\eta_{k}^{(\alpha)} = 0$$
(1.I.19)

it is like:

$$G^{(\alpha)} = H^{(\alpha)} - T^{(\alpha)} S^{(\alpha)}$$
(1.I.20)

and still:

$$-S^{(\alpha)} = \left(\frac{\partial \mathbf{G}^{(\alpha)}}{\partial \mathbf{T}^{(\alpha)}}\right)_{P_{\alpha}, N_{\kappa, \alpha}}$$
(1.I.21)

will result in the Gibbs-Helmholtz relation.

$$\left[\frac{\partial}{\partial \mathbf{T}^{(\alpha)}} \left(\frac{G^{(\alpha)}}{T^{(\alpha)}}\right)\right]_{P^{(\alpha)}, N_k^{(\alpha)}} = -\frac{H^{(\alpha)}}{(T^{(\alpha)})^2}$$
(1.I.22)

which is of particular importance in chemical thermodynamics.

#### **1.I.1.4.** the problem of electrochemical equilibrium

To find the equilibrium conditions for a closed composite system at constant pressure and temperature, take is based on Eq. 1.I.18 and the fact that the function G (extensive property) admits a minimum at equilibrium. So, you will have:

$$(dG)_{T,P,M} = \sum_{\alpha=1}^{\pi} (dG^{(\alpha)})_{T^{(\varepsilon)},P^{(\alpha)}} = 0$$
(1.I.23)

When the system is not the site of chemical reactions (non-reactive systems) the total number of moles of each chemical species remains constant and is given by:

$$N_{\kappa} = \sum_{\alpha=1}^{\pi} N_k^{(\alpha)} \tag{1.I.24}$$

whence:

$$\sum_{\alpha=1}^{\pi} dN_k^{(\alpha)} = 0$$
 (1.I.25)

making  $T^{(\alpha)}$  and  $P^{(\alpha)}$  constants in Eq. 1.I.16 and substituting in Eq. 1.I.23 results as a criterion of equilibrium the equation:

$$\sum_{\alpha=1}^{\pi} \sum_{\kappa=1}^{m} \eta_{\kappa,\alpha} dN_{\kappa,\alpha} = 0$$
(1.I.26)

The use of Eq. 1.I.25 (constancy of the total number of moles of each chemical species) in Eq. 1.I.26 presents the equation as a result:

$$\sum_{k=1}^{m} \left[ \sum_{\alpha=2}^{\pi} \left( \eta_{k}^{(\alpha)} - \eta_{k}^{(1)} \right) dN_{k}^{(\alpha)} \right] = 0$$
(1.I.27)

Due to the linear structure of Eq. 1.I.27 and the fact that  $N_k^{(\alpha)}$  is a system variable and therefore  $dN_k^{(\alpha)}$  is not the null term, then as a consequence of the equilibrium criterion it results:

$$\eta_{\kappa,\alpha} - \eta_{\kappa,1} = 0;$$
 for any  $\alpha$  and  $\kappa.$  (1.I.28)

So, in *phase equilibrium* in non-reactive systems with constant temperature and pressure *the electrochemical potential of a particular chemical species is identical in all phases.* 

When the system is host to chemical reactions, the total number of moles of each chemical species does not necessarily remain constant.

If the reactive system moves towards equilibrium, at constant temperature and pressure, according to r independent reactions given by the relation:

$$\sum_{\kappa} v_{j\kappa} A_{\kappa} = 0 \qquad j = 1, 2, ..., r \qquad (1.I.29)$$

Where  $v_{j\kappa} \in A_{\kappa}$  are, respectively, the stoichiometric numbers (numerically equal to the coefficients stoichiometric, but affected with a negative sign if k chemical species is a reactant and positive if a product of the reaction) and k chemical species participating in reaction j.

If  $\xi_j$  is the reaction coordinate (molar extent of chemical reaction) for reaction j, then at each instant the total number of moles of the k chemical species in the whole system will be given by:

$$N_{\kappa} = \sum_{\alpha=1}^{\pi} N_{k}^{(\alpha)} = N_{\kappa0} + \sum_{j=1}^{r} v_{\kappa j} \xi_{j}$$
(1.I.30)

where  $N_{\kappa 0}$  is the value of the number of moles of the k chemical species, at the beginning of the reaction ( $\xi_j = 0$ ).

The Gibbs free energy for a system containing  $\pi$  phases is given by:

$$G = \sum_{\alpha=1}^{\pi} G^{(\alpha)} \tag{1.I.31}$$

it is like:

$$G^{(\alpha)} = \sum_{k=1}^{m} \eta_k^{(\alpha)} N_k^{(\alpha)}$$
(1.I.32)

results:

$$G = \sum_{\alpha=1}^{\pi} \sum_{\kappa=1}^{m} \eta_k^{(\alpha)} N_k^{(\alpha)}$$
(1.I.33)

The equilibrium state at constant temperature and pressure is one for which G reaches a minimum value from all states consistent with the stoichiometry of the reactions. The identification of the equilibrium state coincides with the Gibbs free energy minimization problem subject to the constraint equations given by Eq. 1.I.30.

Since the simplest way to solve constrained maximum and minimum problems is to apply the Lagrange multipliers method, a set of Lagrange multipliers is defined  $\lambda_1, \lambda_2, ..., \lambda_m$ , one for each chemical species and a new function F is constructed given by:

$$F = \sum_{\alpha=1}^{\pi} \sum_{\kappa=1}^{m} \eta_{\kappa,\alpha} N_{\kappa,\alpha} + \sum_{\kappa=1}^{m} \lambda_{\kappa} \left[ \sum_{\alpha=1}^{\pi} N_{\kappa,\alpha} + N_{\kappa 0} + \sum_{j=1}^{r} v_{\kappa j} \xi_j \right]$$
(1.I.34)

This new function is identical to G, since the added term is null (see Eq. 1.I.30. Thus, the minimization of F implies the minimization of G.

The minimum value of F must be sought in a domain of independent variables of this function, that is,  $N_k^{(\alpha)} \lambda_k$  and  $\xi_j$  where  $\kappa = 1, 2, ..., m$ ;  $\alpha = 1, 2, ..., \pi$  and j = 1, 2, ..., r.

When an expression of the electrochemical potential is known  $\eta_k^{(\alpha)}$  as a function of temperature and composition, the search process leads to the minimum and, consequently, to the complete knowledge of the equilibrium state. Even if this relationship is not available at the moment, it is possible to obtain the following general criteria for phase equilibrium for multireactives systems (Sandler, 1989). Of the minimum conditions:

$$\left(\frac{\partial \mathbf{F}}{\partial \mathbf{N}_{\mathbf{k}}^{(\alpha)}}\right) = 0 \left(\frac{\partial \mathbf{F}}{\partial \xi_{j}}\right) = 0 \left(\frac{\partial \mathbf{F}}{\partial \lambda_{\kappa}}\right) = 0$$
(1.I.35)

result, respectively:

$$\eta_{\kappa,\alpha} + \lambda_{\kappa} = 0$$
; to any  $\kappa$  and  $\alpha$ . (1.I.36)

$$\sum_{k=1}^{m} v_{jk} \eta_k^{(\alpha)} = 0 \text{ ; to any j and } \alpha$$
(1.I.37)

$$\sum_{\alpha=1}^{\pi} N_{\kappa,\alpha} = N_{\kappa 0} + \sum_{j=1}^{r} \nu_{\kappa j} \xi_j \qquad ; \text{ to any } \kappa \qquad (1.I.38)$$

Eq. 1.I.36 is equivalent to Eq. 1.I.28 and also establishes that in a multiple reaction system the chemical potential of any k species, at equilibrium, is identical in all phases. The condition presented by Eq. 1.I.37 states that each reaction must be in equilibrium in all phases. In fact, since the electrochemical potential of each species is the same in all phases if Eq. 1.I.36 is satisfied for a particular phase will be satisfied in all phases. The equilibrium state is therefore the state for which Eqs. 1.I.36, 1.I.37 and 1.I.38 must be satisfied simultaneously; for known expressions of:

$$\eta_k^{(\alpha)} = \mu_k^{(\alpha)} + z_\kappa F \Phi^{(\alpha)}$$

from the definition of fugacity seen earlier:

$$d \mu_k^{(\alpha)} = RT^{(\alpha)} d \ln \hat{f}_k^{(\alpha)} \quad ; \text{ at constant } T^{(\alpha)} \tag{1.I.39}$$

The integration of Eq. 1.I.39 from a standard state of the k pure component at system temperature to a state of the k component in solution in  $\alpha$  phase results:

$$\mu_k^{(\alpha)} = \mu_\kappa^{0(\alpha)} + RT_\alpha \ln \frac{\hat{f}_k^{(\alpha)}}{f_\kappa^{0(\alpha)}}$$
(1.I.40)

what if:

$$\hat{a}_{k}^{(\alpha)} = \frac{\hat{f}_{k}^{(\alpha)}}{f_{\kappa}^{0(\alpha)}} = \gamma_{k}^{(\alpha)} x_{k}^{(\alpha)}$$
(1.I.40b)

then,

$$\eta_k^{(\alpha)} = \mu_\kappa^{0(\alpha)} + z_\kappa F \Phi^{(\alpha)} + RT^{(\alpha)} d\ln \hat{a}_{\kappa,\alpha}$$
(1.I.41)

In electrochemical systems, when one mole of a neutral k chemical species, in a phase  $\alpha$ , dissociates into  $a_{\kappa+} e a_{\kappa-}$  gram ions of a positively and negatively charged k chemical species, respectively, the chemical potential can be expressed as:

$$\mu_k^{(\alpha)} = a_{\kappa+} \mu_{k+}^{(\alpha)} + a_{\kappa-} \mu_{k-}^{(\alpha)}$$
(1.I.42)

Where  $\mu_{k+}^{(\alpha)}$  and  $\mu_{k-}^{(\alpha)}$  are the chemical potentials of the charged chemical species and depend on the temperature, pressure, composition and electrical state of the  $\alpha$  phase. Since the k chemical species is electrically neutral, the coefficients  $a_{k+} e a_{k-}$  are subject to the restriction:

$$z_{\kappa+}a_{\kappa+} + z_{\kappa-}a_{\kappa-} = 0 \tag{1.I.43}$$

Where  $z_{\kappa+} \in z_{\kappa-}$  are, respectively, the number of charges of the positive and negative ions. The chemical potential of a pure, electrically neutral metal can be expressed in terms of positive ions and electrons in the form:

$$\mu_m = a_{m+}\mu_{m+} + a_{m-}\mu_{e^-} \tag{1.I.44}$$

#### 1.I.1.5. The electrochemical electrode and the electrochemical cell

According to Vetter  $(1967)^4$  An electrode consists of several conducting phases, in series, with one of the terminal phases being a metal and the other a solution containing electrolytes (electrolyte solution). In its simplest form, a metal immersed in an electrolyte solution consists of an electrode.

The simplest electrochemical cell consists of two metals with a common electrolyte solution closing the electrical circuit between they; it is, therefore, two electrodes in contact by the common solution.

The difference in electric potential between the terminal phases of an electrode is called the *electrode potential*. The electrical potential difference between the terminal phases of an electrochemical cell is called the cell voltage, and it is absolutely necessary that the terminal phases be of the same metal. Fig. 1a, 1b and 1c show a schematic of the simplest electrochemical cell with its two electrodes A and B.

<sup>&</sup>lt;sup>4</sup>Vetter, KJ (1967). Electrochemical Kinetics. Academic Press 789 p.



FIGURE 1.1.1 - Schematic diagram of electrical potential  $\Phi$  in a galvanic cell.

Fig. 1.I.1c shows, in arbitrary units, the electrical potential of each phase and its discontinuity at the phase separation interface. Figure 1.I.1b schematically shows the phases in contact.

The electrode potential A is given by:

$$E_{A} = \Phi_{12} = (\Phi_{1} - \Phi_{2}) \tag{1.I.45}$$

The electrode potential B is given by

$$E_{B} = \Phi_{32} = (\Phi_{3} - \Phi_{2}) \tag{1.I.46}$$

The cell voltage, E, is equal to the sum of all potential differences between successive phases and given by:

$$E = \Phi_{1\pi} = \sum_{\alpha=1}^{\pi-1} (\Phi_{\alpha} - \Phi_{\alpha+1}) = (\Phi_{1} - \Phi_{\pi})$$
(1.I.47)

The application of Eq. 1.I.47 to the system of Fig. 1 confirms this result.

$$E = (\Phi_1 - \Phi_2) + (\Phi_2 - \Phi_3) + (\Phi_4 - \Phi_5) = (\Phi_1 - \Phi_5)$$
(1.I.48)

or

$$E = \Phi_{12} - \Phi_{32} + (\Phi_4 - \Phi_5)$$
(1.I.49)

The potential difference between metal II and metal I ( $\Phi_4$ - $\Phi_5$ ) is practically zero, so the cell voltage is simply given by:

$$E = E_A - E_B \tag{1.I.50}$$

It should be noted that only the *cell voltage* is an electrically measurable quantity, since any attempt to place the metallic terminals of the measuring instrument between the solution and the metal will create a new electrode and, consequently, a new electrode potential in series with the one you want to measure. To determine the *electrode potential*, it is therefore necessary to use a *reference electrode* whose electrode potential is arbitrated by default. Under these conditions, the voltage measurement of the cell constituted by the electrode of unknown potential and by the *reference electrode*, having the common electrolyte solution, coincides with the value of the electrode potential to be measured. So, for example, if in the cell shown in Fig. 1 the electrode potential A is known (default) and the voltage of cell E is then measured by Eq. 1.I.50 the electrode potential of electrode B is determined.

More complex cells, such as those in which one of the metals is covered with a layer of another material and a porous wall separates two distinct electrolyte solutions, will constitute a galvanic cell that has six potential differences.

Depending on the value of the electrical potentials in the terminal phases, that is, on the value of E, an *electric current* through the galvanic cell and is defined in terms of its value and its direction (the direction is that of positive charges). When positive charges flow from the metal into solution, the electrode acts as an anode. The local current is said to be anodic and the local reaction is called anodic. When positive charges flow from solution to metal, the electrode acts as a cathode. The local current is called cathodic and the local reaction is called cathodic.

The electric current flowing through a galvanic cell is consequence of electron exchange reaction activities at the electrode interface. When current flows through the cell, either by applying an adequate voltage across its terminals or by closing the circuit through an adequate resistance, the electrodes will be the site of electrochemical reactions and the total set of these reactions (at both electrodes) is called of galvanic cell reactions.

In the case of the *Daniell cell*, schematically presented in Fig. 2, a container is divided into two compartments by means of a porous wall, each compartment being an electrode.



FIGURE 1.I.2 - Schematic (a) and symbolic (b) representation of a galvanic cell.

In compartment I the metal is copper and the liquid is an aqueous solution of copper sulfate. In compartment II the metal is zinc and the liquid is an aqueous solution of zinc sulfate. The electrodes make electrical contact across the porous membrane.

The overall reaction in the cell is obtained by adding the two electrochemical reactions taking place one at each electrode. These results:

| $Cu \rightarrow Cu^{2+} + 2e^{-}$                | : on the electrode of copper; | (1.I.51) |
|--------------------------------------------------|-------------------------------|----------|
| $\operatorname{Zn}^{2+} + 2e^{-} \rightarrow Zn$ | : in the zinc electrode;      | (1.I.52) |
| $Cu + Zn^{2+} \rightarrow Cu^{2+} + Zn$          | : in cell;                    | (1.I.53) |
| $Cu + ZnSO_4 \rightarrow CuSO_4 + Zn$            | : neutral reaction;           | (1.I.54) |

When the terminals are open the reaction activity in the cell tends to cease (macroscopically), thermodynamic equilibrium is reached and an equilibrium voltage,  $E_0$ , is reached and remains.  $E_0$  is, therefore, a thermodynamic property of the composite system (galvanic cell) and its relationship with other properties of the system can be given, for example, by Eq. 1.I.28. The use of Eq. 1.I.28 can be exemplified in the *Daniell cell*.

It is convenient to schematize the system in the form given by Fig. 1.I.3.

| 1                | 2                             | 3                             | 4                | 5                |
|------------------|-------------------------------|-------------------------------|------------------|------------------|
| Cu <sup>2+</sup> | Cu <sup>2+</sup>              | Zn <sup>2+</sup>              | Zn <sup>2+</sup> | Cu <sup>2+</sup> |
| 2e               | SO <sub>4</sub> <sup>2-</sup> | SO <sub>4</sub> <sup>2-</sup> | 2e <sup>-</sup>  | 2e <sup>-</sup>  |

FIGURE 1.I.3 - Schematic form of the galvanic cell showing the phases and ions in equilibrium.

So, by Eqs. 1.I.28 and 1.I.11 will have:

$$\mu_{Cu^{2+}}^{(1)} + 2F\Phi^{(1)} = \mu_{Cu^{2+}}^{(2)} + 2F\Phi^{(2)} \rightarrow 2F\Phi_{12} = \mu_{Cu^{2+}}^{(2)} - \mu_{Cu^{2+}}^{(1)}$$

$$\mu_{SO_4^{2-},2} - 2F\Phi_2 = \mu_{SO_4^{2-},3} - 2F\Phi_3 \rightarrow -2F\Phi_{23} = \mu_{SO_4^{2-},3} - \mu_{SO_4^{2-},2}$$

$$\mu_{Zn^{2+}}^{(3)} + 2F\Phi^{(3)} = \mu_{Zn^{2+}}^{(4)} + 2F\Phi^{(4)} \rightarrow 2F\Phi_{34} = \mu_{Zn^{2+}}^{(4)} - \mu_{Zn^{2+}}^{(3)}$$

$$\mu_{e^-}^{(4)} - F\Phi^{(4)} = \mu_{e^-}^{(5)} - F\Phi^{(5)} \rightarrow -F\Phi_{45} = \mu_{e^-}^{(5)} - \mu_{e^-}^{(4)}$$

Adding up all the electrical potential drops in the cell gives:

$$E_{0} = \Phi_{15} = \frac{1}{2F} \left[ -\mu_{Cu^{2+}}^{(1)} + \left( \mu_{Cu^{2+}}^{(2)} + \mu_{SO_{4}^{-}}^{(2)} \right) + \left( -\mu_{SO_{2}^{-}}^{(3)} - \mu_{Zn^{2+}}^{(3)} \right) + \left( \mu_{Zn^{2+}}^{(4)} + 2\mu_{e^{-}}^{(4)} \right) - 2\mu_{e^{-}}^{(5)} \right]$$
(1.I.55)

and since:

$$\mu_{Cu^{2+}}^{(1)} + 2\mu_{e^-}^{(5)} = \mu_{Cu}$$
(1.I.56)

then

$$E_0 = (\Phi_1 - \Phi_5) = \frac{1}{2F} (\mu_{Zn} + \mu_{CuSO_4} - \mu_{Cu} - \mu_{ZnSO_4})$$
(1.I.57)

perfectly compatible with the neutral reaction of the Daniell cell, Eq. 1.I.54.

If, in Eq. 1.I.55, the potential drop is considered negligible,  $\Phi_{\rm 23}$  , at the net junction, then results:

$$E_0 = \frac{1}{2F} \left( \mu_{Zn} + \mu_{Cu^{2+}} - \mu_{Cu} - \mu_{Zn^{2+}} \right)$$
(1.I.58)

perfectly compatible with the complete reaction of the Daniell cell, Eq. 1.I.53.

Eq. 1.I.58 can also be written in the form:

$$E_{0} = \frac{1}{2F} \left( \mu_{Cu^{2+}} - \mu_{Cu} \right) - \frac{1}{2F} \left( \mu_{Zn^{2+}} - \mu_{Zn} \right)$$
(1.I.59)

When Eq. 1.I.59 is compared with Eq. 1.I.50 results:

$$E_0 = E_{0,Cu} - E_{0,Zn} \tag{1.1.60}$$

$$E_{0,Cu} = \frac{1}{2F} \left( \mu_{Cu^{2+}} - \mu_{Cu} \right)$$
(1.I.61)

$$E_{0,Z_n} = \frac{1}{2F} \left( \mu_{Z_n^{2+}} - \mu_{Z_n} \right)$$
(1.I.62)

Equations perfectly compatible with the *Daniell cell* half-reactions, Eqs. 1.I.51 and 1.I.52.

On the other hand, for reaction j given by:

$$v_{j1}A_1 + v_{j2}A_2 + \dots + v_{jm}A_m^{\pm ne^-} 0$$
; j=1,2,...,r (1.I.63)

a molar Gibbs free energy of reaction is defined by the relation:

$$\Delta g_r^{\,j} = \sum_{k=1}^m v_{jk} \mu_k^{(\alpha)} \; ; \; \; j = 1, 2, ..., r \tag{1.I.64}$$

Observing Eqs. 1.I.57 to 1.I.60, it is verified, in any case, that:

$$E_0 = \frac{1}{nF} \Delta g_r = \frac{1}{nF} \sum_{j=1}^r \sum_{k=1}^m v_{jk} \mu_k^{(\alpha)}$$
(1.I.65)

Thus, the cell potential (voltage) or electrode potentials are proportional to the change in molar Gibbs free energy of the reaction. Obtaining the energy, in the form of heat, involved with the reactions can be found by the Gibbs-Helmholtz relation Eq. 1.I.22, which becomes:

$$\left[\frac{\partial}{\partial T}\left(\frac{\Delta g_r}{T^{(\alpha)}}\right)\right]_{P^{(\alpha)},N_k^{(\alpha)}} = -\frac{\Delta h_r}{(T^{(\alpha)})^2}$$
(1.I.66)

Where  $\Delta h_r$  is the molar enthalpy of reaction. Based on Eq. 1.I.65 results:

$$\left[\frac{\partial}{\partial T}\left(\frac{E_0}{T^{(\alpha)}}\right)\right]_{P_{\alpha},N_{\kappa,\alpha}} = -\frac{\Delta h_r}{nF(T^{(\alpha)})^2}$$
(1.I.67)

Eqs. 1.I.64, 1.I.65 and 1.I.66 are very useful in the thermodynamics of electrochemical systems. Using Eqs 1.I.40 and 1.I.40b in Eq. 1.I.65 can be written.

$$E_0 = \frac{1}{nF} \Delta g_r = \frac{1}{nF} \sum_{j=1}^r \sum_{k=1}^m v_{jk} (\mu_k^0 + \ln \hat{a}_{k,\alpha})$$
(1.I.68)

whence it results:

$$E_0 = E^0 + \frac{RT}{nF} \sum_{j=1}^r \sum_{k=1}^m v_{jk} \ln \hat{a}_{k,\alpha}$$
(1.I.69)

on what:

$$\mathbf{E}^{0} = \frac{1}{nF} \Delta g_{r}^{0} \quad ; \qquad \Delta g_{r}^{0} = \sum_{j=1}^{r} \sum_{k=1}^{m} v_{jk} \mu_{k}^{0} \tag{1.I.70}$$

In these equations  $E^0 e \Delta g_r^0$  are, respectively, the standard cell voltage and the standard molar Gibbs free energy of the reaction:

When Eq. 1.I.69 is applied to an electrode where only the reaction occurs,  $O \stackrel{\pm ne^-}{=} R$ , then the Nernst equation results:

$$E_{0,m} = E_m^0 + \frac{RT}{nF} \ln(\frac{\hat{a}_o}{\hat{a}_R}) \quad \text{e} \quad E_m^0 = \frac{1}{nF} (\mu_o^0 - \mu_R^0)$$
(1.I.71)
In this equation  $E_{0,m} e E_m^0$  are, respectively, the *electrode potential* equilibrium and the *standard electrode potential* equilibrium.

## 1.I.2. ion exchange adsorption.

in electrochemical equilibrium:

$$\mathbf{T}^{(1)} = \mathbf{T}^{(2)} = T ; \qquad (1.I.72)$$

$$P^{(1)}; constant (1.I.73)$$

 $P^{(2)}; constant (1.I.74)$ 

$$\eta_k^{(1)} = \eta_k^{(2)} \tag{1.1.75}$$

and by Eq. 1.I.41 we have:

$$\frac{\mu_k^{0(\alpha)}}{RT^{(\alpha)}} + \ln(\frac{\hat{f}_k^{(\alpha)}}{\hat{f}_k^{0(\alpha)}}) + \frac{z_k F}{RT^{(\alpha)}} \Phi^{(\alpha)} = \frac{\eta_k^{(\alpha)}}{RT^{(\alpha)}}$$
(1.I.76)

then Eqs. 1.I.75 and 1.I.72 stay:

$$\frac{\mu_k^{0(1)}}{RT^{(1)}} + \ln(\frac{\hat{f}_k^{(1)}}{\hat{f}_k^{0(1)}}) + \frac{z_k F}{RT^{(1)}} \Phi^{(1)} = \frac{\mu_k^{0(2)}}{RT^{(2)}} + \ln(\frac{\hat{f}_k^{(2)}}{\hat{f}_k^{0(2)}}) + \frac{z_k F}{RT^{(2)}} \Phi^{(2)}$$
(1.I.77)

Rearrangement of the equilibrium condition Eq. 1.I.77:

$$\frac{1}{z_k} \ln(\frac{K_k^0 \hat{a}_k^{(2)}}{\hat{a}_k^{(1)}}) = \frac{F}{RT} (\Phi^{(1)} - \Phi^{(2)}); \quad \forall \ k$$
(1.I.78)

where:

$$K_k^0 = \exp\left(\frac{\mu_k^{0(2)}}{RT} - \frac{\mu_k^{0(1)}}{RT}\right)$$
(1.I.79)

and so,

$$\frac{1}{z_i} \ln(\frac{K_i^0 \hat{a}_i^{(2)}}{\hat{a}_i^{(1)}}) = \frac{1}{z_j} \ln(\frac{K_j^0 \hat{a}_j^{(2)} i}{\hat{a}_j^{(1)}}); \quad \forall i, j$$
(1.I.80)

resulting:

$$\left[\left(\frac{K_{i}^{0}\hat{a}_{i}^{(2)}}{\hat{a}_{i}^{(1)}}\right)^{\frac{1}{z_{i}}} = \left[\left(\frac{K_{j}^{0}\hat{a}_{j}^{(2)}}{\hat{a}_{j}^{(1)}}\right)^{\frac{1}{z_{j}}}; \quad \forall \text{ i, j}$$

$$(1.I.81)$$

or,

$$\left[\left(\frac{K_{i}^{0}\hat{a}_{i}^{(2)}}{\hat{a}_{i}^{(1)}}\right)\right]^{z_{j}} = \left[\left(\frac{K_{j}^{0}\hat{a}_{j}^{(2)}}{\hat{a}_{j}^{(1)}}\right)\right]^{z_{i}}; \quad \forall \text{ i, j}$$
(1.I.82)

with:

$$\hat{a}_i^{(1)} = \gamma_i^{(1)} m_i^{(1)} \text{ such that } : \quad \gamma_i^{(1)} \to 1 \quad \text{when} \quad m_i^{(1)} \to 0 \tag{1.I.83}$$

$$\hat{a}_{i}^{(2)} = \gamma_{i}^{(2)} c_{i}^{(2)} \text{ such that } : \quad \gamma_{i}^{(2)} \to 1 \quad \text{when} \quad c_{i}^{(2)} \to 0$$
 (1.I.84)

with  $m_i^{(1)}$  in (mol/kg<sub>sol</sub>) e  $c_i^{(2)}$  in (mol/kg<sub>ads</sub>)

In this treatment, the activity coefficients of the ions in the solution,  $\gamma_k^{(1)}$ , and in the solid phase,  $\gamma_k^{(2)}$ , are represented *in molal concentration* (molality) in *Henri's law convention*, and thus Eq. 1.I.82 can be conveniently written in the form:

$$\frac{\left[\left(\frac{\gamma_i^{(2)}c_i^{(2)}}{\gamma_i^{(1)}m_i^{(1)}}\right)\right]^{z_i}}{\left[\left(\frac{\gamma_j^{(2)}c_j^{(2)}}{\gamma_j^{(1)}m_j^{(1)}}\right)\right]^{z_i}} = \frac{(K_j^0)^{z_i}}{(K_i^0)^{z_j}} \equiv K_{ij}; \quad \forall i, j$$
(1.I.85)

or,

$$K_{ij} = \frac{(\gamma_i^{(2)} c_i^{(2)})^{z_j}}{(\gamma_j^{(2)} c_j^{(2)})^{z_i}} \frac{(\gamma_j^{(1)} m_j^{(1)})^{z_i}}{(\gamma_i^{(1)} m_i^{(1)})^{z_j}}; \quad \forall i, j$$
(1.I.86)

or alternatively:

$$\frac{\left[\left(\frac{\gamma_{i}^{(1)}m_{i}^{(1)}}{\gamma_{i}^{(2)}c_{i}^{(2)}}\right)\right]^{\frac{1}{z_{i}}}}{\left[\left(\frac{\gamma_{j}^{(1)}m_{j}^{(1)}}{\gamma_{j}^{(2)}c_{j}^{(2)}}\right)\right]^{\frac{1}{z_{j}}}} = \frac{(K_{i}^{0})^{z_{i}}}{(K_{j}^{0})^{z_{j}}} \equiv K_{j}^{i}; \quad \forall \text{ i, j}$$

$$(1.I.87)$$

$$K_{j}^{i} = \left(\frac{\gamma_{i}^{(1)}m_{i}^{(1)}}{\gamma_{i}^{(2)}c_{i}^{(2)}}\right)^{\frac{1}{z_{i}}} \left(\frac{\gamma_{j}^{(2)}c_{j}^{(2)}}{\gamma_{j}^{(1)}m_{j}^{(1)}}\right)^{\frac{1}{z_{j}}}; \quad \forall i, j$$
(1.I.88)

Although the equations 1.I.85 and 1.I.88 are thermodynamically equivalent there is a preference in the literature for the form 1.I.88. Thus, aiming at comparing data without the need for readjustments, we will adopt Eq. 1.I.88.

Defining a corrected selectivity coefficient (Vancelow) for the solution phase as:

$$\widetilde{K}_{j}^{i} = \left(\frac{\gamma_{i}^{(1)}m_{i}^{(1)}}{c_{i}^{(2)}}\right)^{\frac{1}{z_{i}}} \left(\frac{c_{j}^{(2)}}{\gamma_{j}^{(1)}m_{j}^{(1)}}\right)^{\frac{1}{z_{j}}}; \quad \forall \text{ i, j}$$
(1.I.89)

Eq. 1.I.89 simplifies to:

$$K_{j}^{i} = \tilde{K}_{j}^{i} \left(\frac{1}{\gamma_{i}^{(2)}}\right)^{\frac{1}{z_{i}}} \left(\frac{\gamma_{j}^{(2)}}{1}\right)^{\frac{1}{z_{j}}}; \quad \forall i, j$$
(1.I.90)

whence,

$$\ln(\tilde{K}_{i}^{j}) = \ln(K_{i}^{j}) - \frac{1}{z_{i}} \ln \gamma_{i}^{(2)} - \frac{1}{z_{j}} \ln \gamma_{j}^{(2)}$$
(1.I.91)

and still for n components.

$$K_k^i = K_j^i K_k^j; \quad \forall \ i, j, k$$
(1.I.92)

$$K_{j}^{i} = \frac{1}{K_{i}^{j}} K_{j}^{i} \text{ if } i \neq j \text{ and } K_{j}^{i} = 1 \text{ if } i = j$$

$$(1.I.93)$$

with,

$$\widetilde{K} = \prod_{k=1}^{n} \widetilde{K}_{k}^{1} \quad \mathbf{e} \qquad K = \prod_{k=1}^{n} K_{k}^{1} \tag{1.I.94}$$

Consequently, for n exchangeable ions we write:

$$\ln(\tilde{K}) = \ln(K) + \frac{n}{z_1} \ln \gamma_1^{(2)} - \sum_{k=1}^n \frac{1}{z_k} \ln \gamma_k^{(2)}$$
(1.I.95)

It should be noted that only (n-1) equations in the form of Eq. 1.I.88 are independent in a system containing n exchangeable ions. On the other hand, in the form of Eqs. 1.I.85 and 1.I.86, the corrected selectivity coefficient is in the form:

$$\widetilde{K}_{ij} = \frac{(c_i^{(2)})^{z_j}}{(c_j^{(2)})^{z_i}} \frac{(\gamma_j^{(1)} m_j^{(1)})^{z_i}}{(\gamma_i^{(1)} m_i^{(1)})^{z_j}}; \quad \forall i, j$$
(1.I.96)

and then

$$\ln(\tilde{K}_{ij}) = \ln(K_{ij}) + z_i \ln \gamma_j^{(2)} - z_j \ln \gamma_i^{(2)}$$
(1.I.97)

#### complementary equations

To obtain *complementary equations* it will be necessary to invoke the electroneutrality condition in each individual system and in the composite system.

The amount of charge of the k chemical species in the  $\alpha$  phase is given by the equation 1.I.6.

$$Q_k^{(\alpha)} = z_\kappa F N_k^{(\alpha)}$$

For the *liquid phase*  $\alpha$ =L, select as a basis 1 kg of solvent(water)

resulting:

$$q_k^{(L)} = z_{\kappa} F m_k^{(L)}$$
(1.I.98a)

and, consequently, the selection of *molality* as arbitrated concentration.

For the *solid phase*  $\alpha$ =S, select as a basis 1 kg of adsorbent(ads)

resulting:

$$q_k^{(S)} = z_\kappa F c_k^{(S)}$$
 (1.I.98b)

and, consequently, the selection of *molal concentration* as arbitrated concentration.

so, for the liquid phase to meet the electroneutrality criterion the sum of the *nc* cations must be exactly equal to the sum of the *na* anions and remain constant in any process, and then:

$$F\sum_{c=1}^{nc} z_c m_c^{(L)} = F\sum_{a=1}^{na} z_a m_a^{(L)} = ct1$$
(1.I.99)

where **ct1** is a constant. A more appropriate and characteristic constant of the *ionic solution* can be defined by:

$$TN = \frac{ct1}{F}$$
; total normality (1.I.100)

producing more easily usable expressions:

$$\sum_{c=1}^{nc} z_c m_c^{(L)} = TN \quad \text{; for cations} \tag{1.I.101a}$$
$$\sum_{a=1}^{na} z_a m_a^{(L)} = TN \quad \text{; for anions} \tag{1.I.101b}$$

The exchange matrix has a finite number of charges that can be exchanged and this limit must be respected by cations and anions in solution. In this sense, if the matrix is a *cation exchanger*, this limit is given by the cation exchange capacity, CEC (equivalent weight) and thus:

$$\sum_{c=1}^{n_c} z_c F c_c^{(S)} = ct2$$
(1.I.102)

where **ct2** is a constant. A more appropriate and characteristic constant of the *ionic solid solution* can be defined by:

 $CEC = \frac{ct2}{F}$ ; cation exchange capacity

producing more easily usable expression

$$\sum_{c=1}^{nc} z_c c_c^{(S)} = CEC$$

where  $c_c^{(S)}$  is the cation concentration in the cation exchange matrix (mol/m<sub>ads</sub>). From these complementary equations, normalized variables can be defined by:

$$y_c^L = \frac{z_c m_c^{(L)}}{TN}$$
; equivalent fraction in the liquid phase (1.I.103a)

$$x_c^s = \frac{z_c c_c^{(s)}}{CEC}$$
; equivalent fraction in the solid phase (1.I.103b)

these new variables meet the following conditions:

$$\sum_{c=1}^{n_c} y_c^{(L)} = 1; (1.I.104a)$$

$$\sum_{c=1}^{nc} x_c^{(S)} = 1 \tag{1.I.104b}$$

On the other hand, the natural variable for phases in the thermodynamic equilibrium equations is the molar fraction  $X_k^{(\alpha)}$  and it becomes necessary to recover this information. *molar fraction and equivalent fraction*.

It should be noted that ion exchange adsorption is not exactly an *ion exchange*, but a *charge exchange*. In this sense, two important properties need to be differentiated: the molar fraction and the equivalent fraction.

The ion, whether formed by a single chemical element (single ions) or formed by two or more chemical elements (composite ions) are the k individuals of interest in an  $\alpha$  phase. Its natural quantification is the number of k individuals in an  $\alpha$  phase, usually the number of mols,  $N_{K}^{(\alpha)}$  however when the charge is of greater interest the ratio: number of k individuals in an  $\alpha$  phase per electrical charge carried:

$$N_{eq(k)}^{(\alpha)} = \frac{N_K^{(\alpha)}}{z_k}; number of equivalents$$
(1.I.105)

denominated number of equivalents is more useful and more used. Normalized variables are even more useful and interesting, such as the *molar fraction* and the *equivalent fraction*, defined by:

$$X_{K}^{(\alpha)} = \frac{N_{K}^{(\alpha)}}{\sum_{j=1}^{n^{c}} N_{j}^{(\alpha)}}; molar fraction$$
(1.I.106a)

$$x_{K}^{(\alpha)} = \frac{N_{eq(k)}^{(\alpha)}}{\sum_{j=1}^{nc} N_{eq(j)}^{(\alpha)}}; equivalent fraction$$
(1.I.106b)

which are identical only when the k cations of  $\alpha$  phase have unit charges (z<sub>c</sub>=1)

Selecting the mass of adsorbent as the basis for the equation 1.I.105 results:

$$c_{eq(k)}^{(S)} = \frac{c_k^{(S)}}{z_k}; equivalent \ concentration \tag{1.I.107}$$

and so

and

$$c_k^{(S)} = z_k c_{eq(k)}^{(S)}; (1.I.108)$$

comparing with Eq. 1.I.103b results:

$$c_c^s = \frac{(CEC)x_c^s}{z_c};$$
 (1.I.109)

with  $c_k^{(s)}$  in (mol/kg<sub>ads</sub>) and  $c_{eq(k)}^{(s)}$  in (eq/kg<sub>ads</sub>)

It should be noted, at this point in the formulation, that the parameter that actually interests the adsorptive process is the concentration of the k component in the adsorbent, preferably in the form:

$$c_k^{(2)} = f(c_k^{(1)})$$
; with  $\left(\frac{mol_k}{g_{ads}}\right)$  in the adsorbent and  $\left(\frac{mol_k}{liter}\right)$  in the solution

In the sequence, the methodology for obtaining data by computational method will be proposed.

The thermodynamic conditions required at equilibrium, as already shown, are:

$$\mathbf{T}^{(1)} = \mathbf{T}^{(2)} = T ; \qquad (1.I.110)$$

Constant  $P^{(1)}$  and  $P^{(2)}$ 

$$K_{j}^{i} = \left(\frac{\gamma_{i}^{(1)}m_{i}^{(1)}}{\gamma_{i}^{(2)}c_{i}^{(2)}}\right)^{\frac{1}{z_{i}}} \left(\frac{\gamma_{j}^{(2)}c_{j}^{(2)}}{\gamma_{j}^{(1)}m_{j}^{(1)}}\right)^{\frac{1}{z_{j}}}; \quad \forall i, j$$
(1.I.111)

$$\sum_{k=1}^{m} z_k m_k^{(1)} = TN$$
(1.I.112)

$$\sum_{k=1}^{m} z_k c_k^{(2)} = CEC \tag{1.I.113}$$

The thermodynamic equilibrium conditions were obtained at constant temperature and pressure, clearly imposing a relationship between the temperatures in the phases, equation 1.I.110, not happening the same with the pressure. In fact, we don't even know if there is any relationship between the pressures in the phases, being necessary to answer the question first: *what would be the pressure in the solid ionic solution*? In this sense, it is only important to conduct the experiments at a fixed and constant pressure for fidelity to the fundamentals, although its influence is not experimentally perceived, which can be disregarded in the characterization of the phases.

Characterizing phase (1) we have the following variables  $T^{(1)}, m_1^{(1)}, ..., m_k^{(1)}, ..., m_m^{(1)}$  and characterizing phase (2) we have  $T^{(2)}, c_1^{(2)}, ..., c_m^{(2)}$ , for the complete characterization of

the equilibrium state. Thus totaling 2(m+1) intensive properties completely specifying the equilibrium. The relationships between them are given by the above equilibrium conditions and so we have (1) Eq. 1.I.110; (*m*-1) equations of the type 1.I.111; and the (1) Eq. 1.I.112 and (1) Eq. 1.I.113, totaling (*m*+2) available, the problem looks like this with F = 2(m+1) - (m+2) = m, degrees of freedom.

In Table 1.I.1 we propose the routine for obtaining data referring to equilibrium in ion exchange adsorption in a system with  $\mathbf{m}$  exchangeable ions, a subroutine for the complete specification of the equilibrium state, described in **3** operational **blocks**:

In **block 1**, in addition to the system parameter data, the **m** information needed to eliminate the degrees of freedom, represented by temperature and liquid phase composition, is sufficient to deal with the equilibrium problem in the case of ideal solutions. If idealization does not occur, correlations must be provided for the calculation of  $\gamma_k^{(1)}$  and  $\gamma_k^{(2)}$ .

In **Block 2**, an iterative calculation determines  $(m_m^{(1)} \text{ and } c_1^{(2)}, \dots, c_k^{(2)}, \dots, c_m^{(2)})$ :

In **Block 3**, other properties of interest are computed, including those effectively sought, the *isotherm* of the k component of interest, and the *k*-*fractional coverage*.



### 1.I.3. specific applications.

#### 1.I.3.1 Binary systems

**Example 1.I.1 Binary Cation Solutions** 

For binaries in which the index 1 refers to the ion that prevails in the adsorbent (the one who saturate the adsorbent, sometimes called the *resident ion* in contrast to the ion that replaces it called the *interchangeable ion*) this experimental and numerical example we will consider a cation exchange from aqueous solution onto homoionic clinoptilolite, (Na-clinoptilolite) which after activation treatment is saturated with Na. For this equilibrium study an aqueous solution of chlorides, NaCl and KCl was used. Figure 1.I.4 shows experimental data in their usual forms. Both show the partition of constituents between phases: in form **a**) the constituent of the ordinate is the same as that of the abscissa while in form **b**) the abscissa is always the interchangeable constituent the use is a matter of preference and form **b**) is ours favorite.



FIGURE 1.I.4- Phases diagram ion exchange system (Na-K)

For the numerical treatment of the proposed model, the routine suggested in table 1.I.1 will be used. Figure 1.I.5 shows experimental and simulated results:



FIGURE 1.I.5- Experimental and model results

In Fig 1.I.5.(a) the system is *ideal* in the solid phase and *ideal* in the liquid phase. In Fig 1.I.5.(b) the system is *ideal* in the solid phase and *not ideal* in the liquid phase. In Fig 1.I.5.(c) the system is *not ideal* in the solid phase and *not ideal* in the liquid phase.

The first observation is that a totally ideal (a) or partially ideal (b) system, although they adequately describe the phenomenon, that is, a decay in the cation present initially in the adsorbent, (Na), and an increase in the exchanged cation, (K), there is no accuracy in the representation of laboratory data. This corroborates frequent observations that electrically charged systems are strongly not ideal.

To complete the example, the isotherm of interest related to the results presented in Fig. 1.I.6. also showing an adjustment of our data by the Langmuir and Sips correlations.



FIGURE 1.I.6.- Potassium experimental and simulated isotherm results.

It seems to us, didactically interesting, to present part of the methodology used to obtain these results. A more complete set of data can be found on the research work of Torres Fernández  $(2004)^5$ 

### **1.I.3.1.1.** Methodology for obtaining data in the study of ion exchange.

It is worth mentioning that it is not possible to conduct adsorption studies without a complete knowledge of the adsorbent:

for synthetic materials the characterization is, in general, given by the manufacturer, but in the case of natural materials, this must be provided by the researcher in his laboratory, being this the most laborious task and perhaps the one with the highest financial cost.

<sup>&</sup>lt;sup>5</sup> Torres Fernández, J.C (2004), Seletividade da Clinoptilolita natural por metais tóxicos em sistemas aquosos. Tese de Doutorado, Universidade Federal de São Carlos, São Carlos - SP, 152p.

### **Adsorbent: Na-clinoptilolite**

The mineral of size between 125-75  $\mu$ m was treated with 1N sodium acetate buffer solution (pH equal to 5) to dissolve the carbonates. Other impurities were separated from the clinoptilolite by density separation using mixtures of tetrabromoethane and N,N-dimethylformamide. The solid part was washed three times with acetone and portions of deionized water five times. The solid was mixed with sodium dithionate-citrate-bicarbonate solution to dissolve the iron oxides.

Homoionic clinoptilolite was prepared by treating batches of 40g of the mineral with 400mL of 3M NaCl solution in a 2 L flask, refluxing at the solution's boiling temperature and autogenous agitation for two weeks. The NaCl solutions were replaced after two days of contact. The clinoptilolite samples thus treated were washed several times with deionized water at 90 °C, dried in an oven at 65 °C and equilibrated with vapors of saturated NaCl solution in a desiccator for 10 days.

*X-ray diffraction*: X-ray diffraction patterns of samples prepared from clinoptilolite mineral were obtained using a Siemens model D-5005 diffractometer, using CuK $\alpha_1$ ,  $\lambda = 1,54056$  Å, Ni filter, 40 kV and 40 mA. The clinoptilolite diffractogram does not show secondary phases formed during the treatment of the samples.

*Chemical analysis*: Standard procedures followed rigorously presented the data shown in Table 1.I.2.(a) and Table 1.I.2.(b).

| Component                      | % Weight      |                 |               |                 |            |  |
|--------------------------------|---------------|-----------------|---------------|-----------------|------------|--|
|                                | NC            | NaC             | NaCTT         | NaCC            | NaC**      |  |
| Na <sub>2</sub> O              | 1,36±0,03     | 5,75±0,07       | 2,09±0,04     | 0,56±0,02       | 6,36±0,04  |  |
| K <sub>2</sub> O               | $1,32\pm0,02$ | $0,75\pm0,02$   | $0,56\pm0,01$ | 0,11±0,02       | 0,66±0,05  |  |
| MgO                            | 0,51±0,03     | $0,17\pm0,02$   | $0,12\pm0,01$ | $0,08\pm0,01$   | 0,16±0,03  |  |
| CaO                            | 3,94±0,17     | $0,84{\pm}0,02$ | 0,37±0,02     | 0,47±0,02       | 0,02±0,01  |  |
| TiO <sub>2</sub>               | $0,27\pm0,02$ | 0,29±0,01       | $0,12\pm0,01$ | 0,16±0,01       | 0,04±0,03  |  |
| Fe <sub>2</sub> O <sub>3</sub> | $1,38\pm0,03$ | 1,35±0,03       | $0,42\pm0,01$ | 0,30±0,01       | 0,04±0,02  |  |
| $Al_2O_3$                      | 11,27±0,09    | 11,23±0,17      | 6,93±0,04     | $5,74{\pm}0,08$ | 11,28±0,09 |  |
| $SiO_2$                        | 67,96±0,30    | 67,25±0,12      | 77,59±0,04    | 81,79±0,04      | 68,28±0,57 |  |
| $H_2O$                         | 12,00         | 12,38           | 11,80         | 10,80           | -          |  |
| Total*                         | 88,00         | 87,62           | 88,20         | 89,20           | 87,20      |  |

Table 1.I.2.(a) Chemical analysis of samples.

\*Total based on dry matter; standard deviations are based on the analysis of a sequence of three samples for each sample type.

NC, natural clinoptilolite;

NaC, sodium clinoptilolite;

NaCTT, a heat-treated sodium form;

NaCC, calcined sodium form; \*\*Na-clinoptilolite (Pabalan, 1994);

| Sample  | CEC*  | CEC** | Si/Al |
|---------|-------|-------|-------|
| NC      | 2,08  | 2,08  | 5,12  |
| NaC     | 1,86  | 1,83  | 5,08  |
| NaCTT   | 0,68  | 1,10  | 9,50  |
| NaCC    | 0,18  | 0,94  | 12,08 |
| $NaC^*$ | 2,05* | 2,04* | 5,14  |
|         |       |       |       |

Table 1.I.2.(b) Ion exchange capacity and Si/Al molar ratio of samples

\*Exchange capacity ( $\times 10^{-3}$  eq/g) from total exchangeable metal equivalents;

\*\*Capacity calculated from the content of metals that contribute to the exchange sites: [moles (Al + Fe)-

equivalents (K + Mg + Ca)] or difference between moles of total and inaccessible sites, in the sodium mineral;

\*Moles (Al + Fe), in the purified mineral;

NaC\* (Pabalan, 1994).

#### Ion exchange experiments

The experiments were carried out at 30°C for binary systems ( $Na^+ - Cu^{2+}$ ),

 $(Na^+ - Zn^{2+})$  and  $(Na^+ - Pb^{2+})$ . By thermodynamic equilibrium: amounts of Naclinoptilolite with solutions containing the two competing cations in different equivalent ratios, but with constant normality (0.005 eq L<sup>-1</sup>). The aqueous solutions of the cations were prepared from the nitrates (reactant grade) of the corresponding cations. The normality of 0.5 N solutions of cations were checked using AAS (atomic absorption spectrophotometer, Varian: model SpectrAA-200).

The masses of clinoptilolite used for the experiments were in the range between 0.02-2.0 g, mixed with solution volumes of 50 ml. The clinoptilolite and the solutions were mixed in 50 ml polyethylene bottles and placed in a thermostated temperature shaker, Tecnal: model TE-420 and shaking for one week. Kinetic studies indicated that equilibrium is reached within three days. Once equilibrium was reached, aliquots of the initial and in equilibrium solutions were taken and analyzed for cations using AAS.

#### Thermodynamic models.

#### Model for ions in the aqueous phase

The activity coefficients  $\gamma_i^{(L)}$ , which represent the non-ideal behavior of the liquid solution, can be calculated from well-established electrolyte solution theories (Brønsted, 1922; Guggenheim, 1935). Due to its usefulness for multicomponent systems over a wide range of concentrations and temperatures, the ionic interaction model developed by Pitzer (1991) was used in this study to calculate the activity coefficients of species in the electrolyte solution.

#### Models for ions in the zeolite phase

The thermodynamic treatment of ion exchange equilibrium has been discussed in a significant number of publications (Barrer and Klinowski, 1972; Fletcher, Franklin and Townsend, 1984). For the binary exchange involving the cations  $A^{z_A+}$  and  $B^{z_B+}$ , the reaction, at equilibrium, can be written as:

$$z_B A^{z_A+}{}_{(L)} + z_A B L_{z_B} \rightleftharpoons z_A B^{z_B+}{}_{(L)} + z_B A L_{z_A}$$
(1.I.114)

Where  $z_A$  + and  $z_B$  + are the valences of the respective cations and L is defined as a portion of the zeolite lattice that bears a unit negative charge.

By equation 1.I.88 we have:

$$K_{j}^{i} = \left(\frac{\gamma_{i}^{(1)}m_{i}^{(1)}}{\gamma_{i}^{(2)}c_{i}^{(2)}}\right)^{\frac{1}{z_{i}}} \left(\frac{\gamma_{j}^{(2)}c_{j}^{(2)}}{\gamma_{j}^{(1)}m_{j}^{(1)}}\right)^{\frac{1}{z_{j}}}; \quad \forall \text{ i, j}$$
(1.I.115)

Removing, for convenience only, the non-ideality of the *solid mixture* from the equation, it is possible to define a corrected selectivity coefficient as:

$$\widetilde{K}_{j}^{i} = \left(\frac{\gamma_{i}^{(1)}m_{i}^{(1)}}{c_{i}^{(2)}}\right)^{\frac{1}{z_{i}}} \left(\frac{c_{j}^{(2)}}{\gamma_{j}^{(1)}m_{j}^{(1)}}\right)^{\frac{1}{z_{j}}}; \quad \forall i, j$$
(1.I.116)

Consequently, for n exchangeable ions we write:

$$\ln \tilde{K} = \ln K + \frac{n}{z_1} \ln \gamma_1^{(S)} - \sum_{k=1}^n \frac{1}{z_k} \ln \gamma_k^{(S)}$$
(1.I.117)

being

$$\tilde{K} = \prod_{k=1}^{n} \tilde{K}_{k}^{1}$$
 and  $K = \prod_{k=1}^{n} K_{k}^{1}$  (1.I.118)

It is worth noting that only (n-1) equations in the form of Eq. 1.I.115. are independent in a system containing n exchangeable ions.

In Eq. 1.I.116.  $\tilde{K}$  is *Vanselow's* (1932) corrected selectivity coefficient. In this treatment, the activity coefficients of the ions in the solution  $\gamma_i^{(L)}$  and in the solid phase  $\gamma_i^{(S)}$  are represented in the molal convention, respectively, the non-ideality of the solid phase is reflected in the activity coefficients  $\gamma_A^{(S)}$  and  $\gamma_B^{(S)}$ . Commonly, the models used for this representation are based on general equations for the excess Gibbs free energy per mole of mixture,  $g^E$ .

A useful thermodynamic formulation, due to the relative simplicity and suitability is that of *Margules*. For a binary system, the corresponding expressions for the activity coefficients in the *solid mixture* are:

$$\ln \gamma_A^{(S)} = (x_B^{(S)})^2 \Big[ A_{AB} + 2x_A^{(S)} (A_{AB} - A_{BA}) \Big]$$
(1.I.119)

and

$$\ln \gamma_B^{(S)} = (x_A^{(S)})^2 \Big[ A_{BA} + 2x_B^{(S)} \left( A_{BA} - A_{AB} \right) \Big]$$
(1.I.120)

in which the parameters  $A_{BA}$  and  $A_{AB}$  suggest not only the magnitudes of the activity coefficients, but also the asymmetry of  $g^{E}(T, x)$ . An alternative formulation is that of *Van Laar*, in which the activity coefficients of ions in the solid solution are given by:

$$\ln \gamma_A^{(S)} = \frac{A_{AB}^{'} (A_{BA}^{'})^2 (x_B^{(S)})^2}{\left(A_{AB}^{'} x_A^{(S)} + A_{BA}^{'} x_B^{(S)}\right)^2}$$
(1.I.121)

and

$$\ln \gamma_B^{(S)} = \frac{A_{BA}^{'} (A_{AB}^{'})^2 (x_A^{(S)})^2}{\left(A_{BA}^{'} x_B^{(S)} + A_{AB}^{'} x_A^{(S)}\right)^2}$$
(1.I.122)

where the parameters  $A_{BA}$  and  $A_{AB}$  are interpreted similarly to  $A_{BA}$  and  $A_{AB}$  in the Margules model.

Isotherms are usually shown graphically as *equivalent cationic fractions* of the ion in *solid solution* against these quantities in the *liquid solution*. The values of  $E_i^{(S)}$  and  $E_i^{(L)}$  were calculated from the mass of zeolite ( $m_z$  in grams), the volume of solution (V, liter), and the initial (i) and final (f) molar concentrations (M<sub>A,i</sub>, mol/L of solution) of the cations (i), using the equations:

$$E_{A}^{(S)} = z_{A} \frac{\left(M_{A,i} - M_{A,f}\right)V}{m_{z}CEC}; \qquad (1.I.123)$$

and

$$E_{A}^{(L)} = z_{A} M_{A,f} / TN$$
(1.I.124)

where TN is the total normality of the aqueous phase.

$$\Delta G^{\circ} = -RT \ln K, \tag{1.I.125}$$

where K, by definition, is the equilibrium constant of the exchange reaction.

The exchange isotherms of the systems  $(Na^+ - Cu^{2+}), (Na^+ - Zn^{2+})$  and  $(Na^+ - Pb^{2+})$ are represented in Figures (1.I.7 - 1.I.9), according to the Margules model, **MM**, and the Van Laar model, VLM. In these graphs, the circles represent the equivalent fractions of the counter-ion or incoming ion(interchangeable) and the crosses the equivalent fractions of the *resident* ion  $(Na^+)$ . The isotherms in Figure 1.I.7. showed a sigmoid behavior, which shows a reversibility of the zeolite selectivity as a function of the amounts of the ion  $Cu^{2+}$  in the solution  $(E_{Cu}^{(L)})$ . The system exchange isotherms  $Zn^{2+} - Na^+$  (Figure 1.I.8) are similar to those observed for the system  $Cu^{2+} - Na^+$ . The inflections shown by the isotherms of these two systems may be due to the existence of more than two types of energetically different cationic sites in the structure of clinoptilolite (Yang and Armbruster, 1996), for divalent cations and for sodium. The concave shape of the isotherm of the  $Zn^{2+}$  in the system  $Zn^{2+} - Na^{+}$ , in the range of composition  $0.49 < E_{Zn}^{(L)} < 0.96$  indicates the preference of clinoptilolite for Na<sup>+</sup> ions with increasing concentration of the divalent metal in the aqueous solution. This result may be due to the fact that, in this range of compositions, the Na<sup>+</sup> cation occupies less stable exchange sites for the  $Zn^{2+}$  or sites of lower energy of interaction with the divalent cation. The rectangular hyperbola shape of the isotherm of  $Pb^{2+}$  confirms a typical phenomenology of cases where one of the phases shows a strong preference for one cation over the other, as shown in Figure 1.I.9. This type of profile indicates that the interactions between the transition metal and most of the crystal lattice sites of the zeolite have low and very close stabilization energies. The experimental points of the isotherm of the  $Pb^{2+}$  above the diagonal to  $0 < E_{Pb}^{(L)} < 1$  indicate the preference of clinoptilolite for the cation  $Pb^{2+}$ , with respect to  $Na^+$ in the total normality and temperature of the study. The greater preference of clinoptilolite for cations  $Pb^{2+}$  can be interpreted from the low hydration energy of this cation (associated with the large crystallographic radius), in relation to the rest of the studied divalent transition metals. Thus, despite its higher charge, this cation occupies all types of sites in the HEU structure (Gunter et al., 1994). The isotherm traces for the different exchange systems, obtained through the use of Margules (MM) and Van Laar (VLM) models are represented by continuous curves in the isotherms graphs, as shown in Figures (1.1.7 - 1.1.9). In general, the data obtained for the three systems are able to adequately fit the models. However, when clinoptilolite shows a strong preference for one of the cations, in a range of compositions, and this preference is inverted in another range, the model deviates from the experimental points in the parts of this with a strong change of slope. From the graphs (Figures 1.I.7 – 1.I.9) it was observed that the Van Laar model adjusted itself more adequately to the data of the isotherms of the system  $(Cu^{2+} - Na^{+})$  while the Margules model was better suited to the data of the  $(Zn^{2+} - Na^+)$  and  $(Pb^{2+} - Na^+)$ . The selectivity of zeolite by cations was calculated

through the values of the adjustment parameters  $(\ln K; A_{BA} \text{ or } A_{BA}; A_{AB} \text{ or } A_{AB})$ , and the standard Gibbs free energy of the reaction  $(\Delta G^0)$ , as shown in Table 1.I.3.

Table 1.I.3. Model results. System Model  $\Delta G^0$ K (J/mol)  $2Na^+ \rightleftharpoons Cu^{2+}$  MM 0,124 5170 VLM 0,117 5301  $2Na^+ \rightleftharpoons Zn^{2+}$ MM 0,070 6595 VLM 0,067 6717  $2Na^+ \rightleftharpoons Pb^{2+}$ MM 0,543 1512 VLM 1447 0,558



FIGURE 1.I.7. Isotherms for the ion exchange system  $Na^+ - Cu^{2+}$ 



FIGURE 1.18. Isotherms for the ion exchange system  $Na^+ - Zn^{2+}$ 



FIGURE 1.I.9. Isotherms for the ion exchange system  $Na^+ - Pb^{2+}$ 

From the tabulated and K values, the selectivity series was observed:  $Na^+ > Pb^{2+} >> Cu^{2+} > Zn^{2+}$ .

The values of the parameters calculated using these models, as a function of the relationship between the hydration energies of the exchange cations (  $\Delta G_{h,M_1}^0 / \Delta G_{h,M_2}^0$ ), revealed the following results:

(1) The parameter ( $A_{BA}$  (or  $A_{BA}$ ) was more negative as the relationship increased between hydration energies (for ratio values < 1) or with increasing counter-ion size;

(2) The parameter  $(A_{AB} \text{ (or } A_{AB}) \text{ becomes less negative in the sense of increasing the relationship between these energies. Interpreting the values of the parameters as measures of the stabilization energies of the zeolite lattice when one type of cation is replaced by another, it is observed that the greatest stabilization of the lattice occurs in the process of replacement of the ion by the ion and, the greater destabilization, the contrary process. This interpretation can be made based on the values of for each exchange reaction, listed in Table 1.I.3.$ 

(3) Function  $g^{E}/RT$ : the adsorbent shows greater selectivity for the counter-ion when the asymmetry (in this case) of this function is negative, or curve shifted to the right of the center of compositions in the zeolite.

The variations of the  $\gamma_i^{(S)}$  and  $g^E / RT$  with  $x_i^{(S)}$  (with i counter-ion), obtained using the Van Laar model, are shown in Figure 1.I.7. One aspect observed in the behavior of the graphs was the symmetry (or asymmetry) shown by this function, for each system. In the case of exchange, this function showed asymmetry with respect to the center of compositions in the zeolite (Figure 1.I.10).

The asymmetry of this function is a direct consequence of the difference between the values of the interaction parameters calculated from the models. The distance of the intercept between the function, for both cations, with respect to the composition center decreases in the direction This series can be confirmed from the difference between the parameter values calculated using each model. On the other hand, the distance from the intersection between the functions  $\gamma_i^{(S)}$  for both cations decrease following the series:

 $Na^{+}-Cu^{2+} > Na^{+}-Zn^{2+} > Na^{+}-Pb^{2+}.$ 



FIGURE 1.I.10. Functions, F: ( $g^E / RT$ , red;  $\gamma_{Cu}^{(S)}$ , green,  $\gamma_{Na}^{(S)}$ , blue).

The differences between the parameters showed that the asymmetry of the function  $\gamma_i^{(S)}$  can be positive or negative, depending on the sign of this difference. So,  $\gamma_i^{(S)}$  moves left or right with respect to the center of compositions. The system that showed the greatest asymmetry was the  $Na^+ - Cu^{2+}$  (+), adopting an arbitrary convention. The sign that represents the direction of the asymmetry will depend on the homoionic form of the zeolite (or the counterion) and on its relative selectivity for the cations. When the difference sign  $A_{BA} - A_{AB}$  is negative (shift to the right of the composition center), it means that the zeolite "prefers" the counter-ion and vice versa. The graphs of the change in excess free energy of the solution,  $g^{E}/RT$ , with the composition of the counter-ion in the zeolite phase, for each system, calculated from the models, reflect the asymmetry observed for the functions  $\gamma_i^{(S)}$ . Thus, there was a coincidence between the minimum of the function  $g^{E}/RT$  and the intersection of functions  $\gamma^{(S)}$  for both cations. The value of composition in the solid phase  $(x_A^{(S)}, x_B^{(S)})$ that minimizes the function  $g^{E}/RT$ , corresponds to the most stable composition value for the solid mixture in question. On the other hand, where this function showed greater asymmetry, the value of its minimum was also more negative. This result is a direct consequence of the difference between the selectivity of zeolite for aqueous cations, which is reflected in a deformation of the function  $g^{E}/RT$ , due to stabilization of the solid mixture, for extreme composition values. Taking into account the convention adopted above, the analysis of the function  $g^{E}/RT$  can be done as follows: the adsorbent shows greater selectivity for the counterion when the asymmetry of the curve  $g^{E}/RT$  is negative, or curve shifted to the right of the center of compositions.

#### other considerations

- The most stable electrical arrangements that result from the interaction of cations with the zeolite lattice at the exchange sites, in a given solution composition, are responsible for the relative distributions of cations between the two phases; these are, the points of the isotherms; -System  $Cu^{2+} - Na^+ - clinoptilolita$  shows a sigmoid isotherm, indicating reversible selectivity of zeolite. It means: (a) existence of two or more types of cationic sites, energetically different, occupied by the  $Cu^{2+}$  in the structure of clinoptilolite; (b) o  $Na^+$  can occupy other types of clinoptilolite sites not occupied by ions  $Cu^{2+}$ . Selectivity:  $Na^+ > Cu^{2+}$ -System  $Zn^{2+} - Na^+ - clinoptilolita$  shows a sigmoid isotherm, indicating the presence of more than two groups of energetically differentiated sites, occupied by the cations  $Zn^{2+}$  in the structure of clinoptilolite. Selectivity:  $Na^+ > Zn^{2+}$ ;

-System  $Pb^{2+} - Na^+ - clinoptilolita$  shows a rectangular hyperbola-like isotherm, indicating phenomenology of greater preference of the exchanger for one of the ions in almost the entire range of solution compositions. Selectivity (in the *TN* and *T* of the study):  $Pb^{2+} > Na^+$ ; - When  $x_A^{(S)} \rightarrow 1$ : (1) the  $Cu^{2+}$  more easily replaces the  $Na^+$ , than the  $Zn^{2+}$  to  $Na^+$ ; (2) the  $Pb^{2+}$  more easily replaces the  $Na^+$ , than the  $Cu^{2+}$ ; (3) the  $Pb^{2+}$  more easily replaces the  $Zn^{2+}$ , than the  $Cu^{2+}$ . indicates that: (1) the ion  $Cu^{2+}$  may offer greater stabilization to the zeolite lattice than the rest of the cations at high-energy interaction sites, although the occurrence of a lower population of this cation at the rest of the zeolite lattice exchange positions; (2) the cations  $Pb^{2+}$  and  $Na^+$ , of low lattice interaction, are more likely to occupy all types of clinoptilolite (HEU) lattice sites.

- The model of Van Laar more appropriately adjusts system data  $Cu^{2+} - Na^+$ , being the model of Margules more suitable in the case of the system  $Zn^{2+} - Na^+$ .

- Of the values of K and  $\Delta G^0$  obtained: Selectivity:  $Na^+ > Pb^{2+} \gg Cu^{2+} > Zn^{2+}$ .

- The parameter  $A_{BA}$  (and  $\dot{A_{BA}}$ ) is more negative as the ratio between the hydration energies of the cations increases (ratio less than 1);

-The parameter  $A_{AB}$  (and  $\dot{A_{AB}}$ ) it has become less negative in the sense of increasing the relationship between these energies.

-Function  $g^E / RT$ : the adsorbent shows greater selectivity for the counterion when the asymmetry (in this case) of this function is negative, or curve shifted to the right of the center of compositions in the zeolite.

## 1.I.3.2 Ternary systems

### Experimental points: selectivity

In the table 1.I.4. the thermodynamic equilibrium data of the ternary system (Na; Zn; Cu) are shown in the form of the natural variables of the model a *molality* of the cation in the solution, **mc** and the *equivalent fractions* of the cation in the adsorbent,  $\mathbf{x}_c$ . sometimes denoted by **Ec**.

| mc[Na](mol/kg) | mc[Zn](mol/kg) | mc[Cu](mol/kg) | xc[Na] | xc[Zn] | xc[Cu] |
|----------------|----------------|----------------|--------|--------|--------|
| .00452         | .00000413      | .000167        | .689   | .019   | .296   |
| .00439         | .0000265       | .000211        | .671   | .0554  | .272   |
| .00421         | .0000599       | .000236        | .660   | .0918  | .253   |
| .00403         | .000115        | .000261        | .649   | .123   | .233   |
| .00401         | .000138        | .000272        | .606   | .170   | .216   |
| .00376         | .000234        | .000283        | .602   | .191   | .197   |
| .00355         | .000347        | .000271        | .595   | .209   | .185   |
| .00331         | .000463        | .000255        | .592   | .224   | .173   |
| .00300         | .000606        | .000236        | .602   | .234   | .164   |
| .00270         | .000757        | .000233        | .612   | .234   | .143   |
| .00257         | .000855        | .000203        | .580   | .268   | .134   |
| .00231         | .00100         | .000170        | .582   | .273   | .125   |
| .00193         | .00118         | .000155        | .620   | .269   | .105   |
| .00167         | .00137         | .000116        | .623   | .245   | .0995  |
| .00131         | .00153         | .0000879       | .666   | .236   | .0793  |
| .00113         | .00165         | .0000441       | .640   | .272   | .0717  |
| .000770        | .00182         | .0000328       | .694   | .268   | .0301  |

Table 1.I.4. ion-exchange equilibrium data of the ternary system (Na; Zn; Cu)

When the amount of data makes a graphic representation difficult, the almost mandatory form is the data table as shown in Table 1.I.4. However, we prefer to "see" the results rather than "read". In this sense, a graphic representation gives us a quick idea of what we want to appreciate.

So far, no really adequate way has been found to represent the isothermal chemical equilibrium of ion exchange with three ions. The difficulty in graphically representing this type of systems comes from the fact that each experimental point represents only one composition in a phase. Therefore, the task in this sense is to visualize the connection or correspondence between the equilibrium points (or compositions) in the two phases. In the case of ternaries, we believe that it is still possible if we use the *Gibbs ternary diagram*, whose usual layout is shown in figure 1.I.11. In this sense, data resulting from experimental data or simulation of the system under study will be made available. Immediately, it is not possible, as usual, to draw conodal lines (tie lines) or to delimit regions where phases exist. It is only the visualization of the correspondence between the equilibrium states relative to the values of the compositions in each phase, being only a resource for analysis, deserving an adequate adaptation. The data to be used in this diagram must necessarily be in *molar fractions* or *equivalent fractions*.



FIGURE 1.I.11. Gibbs Triangular Diagram, for representation of ternaries.

We will exemplify with our experimental data, Torres Fernández (2004) and presented in Table 1.I.4. The isothermal chemical equilibrium of ion exchange, corresponding to one of the ternary systems studied by us. The experimental data in the ternary diagrams will be presented in figure 1.I.12 in equivalent fractions. Without the grid lines for a better visualization and with some auxiliary lines to favor the discussion.



FIGURE 1.I.12. Ternary ion exchange diagrams,  $Zn^{2+} - Cu^{2+} - Na^+$  crosses in red dots: *aqueous solution*; circles in blue dots: *zeolite phase*. green lines: correspondence of states

What can we "see" in this representation, which would be a little "hidden" in table 1.I.4 of the data?

**1**-The complete description of the concentration in each phase and the correspondence between them;

**2-**Three auxiliary lines were inserted in the presentation. The blue dots moving away from **a** line indicate that the solid phase is exchanging Na with Zn and Cu. The figure can be interpreted as a process that leaves a Na-Cu binary and moves towards a Na-Zn binary. Although there is availability of Zn and Cu ions in the solution, the CEC, once reached, does not allow exchange and the points accumulate around this value. It is also verified, in this process, that the preference is initially for Cu and then an inversion of selectivity of the preference for Zn. It is also observed that in the vicinity of saturation, the zeolite phase is more selective to Cu and that an energetic rearrangement imposes an inversion of selectivity, resorbing almost all of the Na, in order to readsorb Cu in the following states; This phenomenon deserves a particular microscopic study.

3- A first aspect of this representation is that, although the initial amount of the cation covers almost the entire composition range of the solution, the equivalent fractions of this ion in the zeolite are in the range (0.019-0.027) corresponding to a maximum amount of 56% of the cation in the zeolite phase. When the cation  $Pb^{2+}$  replaces the  $Zn^{2+}$  in this system, the maximum amount adsorbed by the zeolite was ~98% in the diagram  $Pb^{2+} - Cu^{2+} - Na^+$ . On the other hand, the input of ions  $Cu^{2+}$  in clinoptilolite was a consequence of the decrease in the initial content of  $Zn^{2+}$  in the solution. Comparing Diagrams  $Pb^{2+} - Cu^{2+} - Na^+$ , a greater selectivity of clinoptilolite for ions was also verified  $Cu^{2+}$  in the presence of  $Zn^{2+}$ , in relation to  $Pb^{2+}$ .

From the experimental data in Table 1.I.4, it is possible to construct individual isotherms showing the partition of k constituents between phases, as for example in figure 1.I.13 the partition of Zn.



FIGURE 1.I.13. Zinc isotherm in the ternary system  $Zn^{2+} - Cu^{2+} - Na^+$ : the curve is a fit of the Langmuir equation.

When a simulation of ternaries is desired, some simplification is adopted. In many cases, due to the complexity of the description of the non-ideality in the solid phase, only the non-ideality of the *liquid solution* is taken into account. simplifying the relationship to:

$$\widetilde{K}_{j}^{i} = \left(\frac{\gamma_{i}^{(1)}m_{i}^{(1)}}{c_{i}^{(2)}}\right)^{\frac{1}{z_{i}}} \left(\frac{c_{j}^{(2)}}{\gamma_{j}^{(1)}m_{j}^{(1)}}\right)^{\frac{1}{z_{j}}}; \quad \forall \text{ i, j}$$

whereas for the liquid *solution* a simpler equation (classic model) is also used for the activity coefficient:

$$\ln(\gamma_k) = -\frac{1}{2} \frac{z_k}{1 + \sqrt{In}}$$
; *Debye–Hückel* equation

in which *In* is the molar ionic strength, given by:

$$In = \sum_{k=1}^{m} m_k z_k^2 \quad \text{therefore:}$$

$$\left( -\frac{1/2}{\frac{z_k}{1 + \sqrt{\sum_{k=1}^{n} m_k z_k^2}}} \right)$$

Under these conditions table 1.I.1 is modified to:

 Table 1.I.5 Routine to determine equilibrium in ion exchange adsorption in ternary system.

 Block 1:

Input data

$$K_2^1; K_3^1;$$
  
 $z_k; k=1, 2, 3.$   
TN;  
CEC.

 $m_1^{(1)}, m_2^{(1)}, T;$  (m=3) necessary information concerning the degrees of freedom

*Debye–Hückel* equation was selected for the non-ideality of the *liquid ionic solution* The non-ideality of the adsorbent (*zeolite phase*) was not considered.



Below we present the results of applying the algorithm of table 1.I.5 to a non-ideal system in the *liquid ionic solution*, figure 1.I.14 and totally ideal in figure 1.I.15.



FIGURE 1.I.14 Diagrams of ternary ion exchange  $Zn^{2+} - Cu^{2+} - Na^+$ . crosses in red dots: *aqueous solution*; circles in blue dots: *zeolite phase*. green lines: *correspondence of states*.



FIGURE 1.I.15 Diagrams of ternary ion exchange  $Zn^{2+} - Cu^{2+} - Na^+$ . crosses in red dots: *aqueous solution*; circles in blue dots: *zeolite phase*. green lines: *correspondence of states*.

The visual comparison of figures 1.I.14 and 1.I.15 provided by the proposed model with the figure 1.I.12 obtained by experimentation, although they show the probable behavior of the thermodynamic equilibrium, does not present data accuracy, forcing the description of the non-ideality of the adsorbed phase through appropriate correlations to ternary systems. It should be noted, however, that the mean relative deviations 0.288(Na); 0.677(Zn); 0.295(Cu) are small even for the ideal case. Our studies aimed at predicting ternary data from correlations obtained for non-ideality of binaries has been frustrated so far, although we are convinced that it can be done.

## CHAPTER 1 part II. thermodynamics of surfaces

In part II we will deal with systems with phenomena of boundaries (adsorptive systems) not taking into account, momentarily, the electrical charge already dealt with in part 1.I. Thus, based on what has already been presented, we can start by postulating a fundamental relationship of thermodynamics in the energetic form as:

## **1.II.1.** The fundamental equation and thermodynamic potentials

$$U^{(\alpha)} = U^{(\alpha)} \Big( S^{(\alpha)}, V^{(\alpha)}, A^{(\alpha)}, N^{(\alpha)}_k, ... \Big); \alpha = 1, 2, ..., \pi. \text{ And } \kappa = 1, 2, ..., m.$$
(1.II.1)

and your total differential like:

$$dU^{(\alpha)} = \left(\frac{\partial U^{(\alpha)}}{\partial S^{(\alpha)}}\right)_{V^{(\alpha)}, A^{(\alpha)}, N^{(\alpha)}_{k}} dS^{(\alpha)} + \left(\frac{\partial U^{(\alpha)}}{\partial V^{(\alpha)}}\right)_{S^{(\alpha)}, A^{(\alpha)}, N^{(\alpha)}_{k}} dV^{(\alpha)} + \left(\frac{\partial U^{(\alpha)}}{\partial A^{(\alpha)}}\right)_{S^{(\alpha)}, V^{(\alpha)}, N^{(\alpha)}_{k}} dA^{(\alpha)} + \sum_{\kappa=1}^{m} \left(\frac{\partial U^{(\alpha)}}{\partial N^{(\alpha)}_{k}}\right)_{S^{(\alpha)}, V^{(\alpha)}, A^{(\alpha)}, N^{(\alpha)}_{j\neq k}} dN^{(\alpha)}_{k}$$

$$(1.II.2)$$

and potentials like:

$$\begin{pmatrix} \frac{\partial U^{(\alpha)}}{\partial S^{(\alpha)}} \end{pmatrix}_{V^{(\alpha)}, A^{(\alpha)}, N_{k}^{(\alpha)}} = T^{(\alpha)} \quad \text{; Thermal potential (absolute temperature)} \\ - \begin{pmatrix} \frac{\partial U^{(\alpha)}}{\partial V^{(\alpha)}} \end{pmatrix}_{S^{(\alpha)}, A^{(\alpha)}, N_{k}^{(\alpha)}} = P^{(\alpha)} \quad \text{; Mechanical potential (absolute pressure)}$$

$$-\left(\frac{\partial U^{(\alpha)}}{\partial A^{(\alpha)}}\right)_{S^{(\alpha)},V^{(\alpha)},N_{k}^{(\alpha)}} = \Pi^{(\alpha)}; \text{ Interfacial potential}$$

$$\left(\frac{\partial U^{(\alpha)}}{\partial N_{k}^{(\alpha)}}\right)_{S^{(\alpha)},V^{(\alpha)},A^{(\alpha)},N_{j\neq k}^{(\alpha)}} = \mu_{k}^{(\alpha)}; \text{ chemical potential}$$
(1.II.3)

whose functional relations (equations of state) are:

$$T^{(\alpha)} = T^{(\alpha)} \Big( S^{(\alpha)}, V^{(\alpha)}, A^{(\alpha)}, \dots, N^{(\alpha)}_K, \dots \Big)$$
$$P^{(\alpha)} = P^{(\alpha)} \Big( S^{(\alpha)}, V^{(\alpha)}, A^{(\alpha)}, \dots, N^{(\alpha)}_K, \dots \Big)$$

$$\Pi^{(\alpha)} = \Pi^{(\alpha)} \Big( S^{(\alpha)}, V^{(\alpha)}, A^{(\alpha)}, \dots, N^{(\alpha)}_{K}, \dots \Big)$$

$$\mu^{(\alpha)}_{k} = \mu^{(\alpha)}_{k} \Big( S^{(\alpha)}, V^{(\alpha)}, A^{(\alpha)}, \dots, N^{(\alpha)}_{K}, \dots \Big)$$
(1.II.4)

In terms of the equations of state the relationship of Eq. 1.II.2 takes the form:

$$dU^{(\alpha)} = T^{(\alpha)} dS^{(\alpha)} - P^{(\alpha)} dV^{(\alpha)} - \Pi^{(\alpha)} dA^{(\alpha)} + \sum_{\kappa=1}^{m} \mu_{k}^{(\alpha)} dN_{k}^{(\alpha)}$$
(1.II.5)

Eq. 1.II.5 can also be expressed in entropic form by:

$$dS^{(\alpha)} = \frac{dU^{(\alpha)}}{T^{(\alpha)}} + \frac{P^{(\alpha)}}{T^{(\alpha)}} dV^{(\alpha)} + \frac{\Pi^{(\alpha)}}{T^{(\alpha)}} dA^{(\alpha)} - \sum_{k=1}^{m} \frac{\mu_{k}^{(\alpha)}}{T^{(\alpha)}} dN_{k}^{(\alpha)}$$
(1.II.6)

### **1.II.1.1. Integration of the Fundamental Equation of Thermodynamics**

Using Euler's theorem of homogeneous functions (Callen, 1985) for the integration of Eq. 1.II.5 results:

$$U^{(\alpha)} = T^{(\alpha)} S^{(\alpha)} - P^{(\alpha)} V^{(\alpha)} - \Pi^{(\alpha)} A^{(\alpha)} + \sum_{\kappa=1}^{m} \mu_k^{(\alpha)} N_k^{(\alpha)}$$
(1.II.7)

## **1.II.1.2. the free energies**

It is important to note that the products  $T^{(\alpha)}S^{(\alpha)}$ ,  $P^{(\alpha)}V^{(\alpha)}e \ \Pi^{(\alpha)}A^{(\alpha)}$  are energies similar in nature to U<sub>\alpha</sub>. Thus, through these energies it is possible to define others such as:

$$H^{(\alpha)} = U^{(\alpha)} + P^{(\alpha)}V^{(\alpha)} + \Pi^{(\alpha)}A^{(\alpha)}; \text{ enthalpy}$$

$$F^{(\alpha)} = U^{(\alpha)} - T^{(\alpha)}S^{(\alpha)} + \Pi^{(\alpha)}A^{(\alpha)}; \text{Helmholtz free energy}$$

$$G^{(\alpha)} = U^{(\alpha)} - T^{(\alpha)}S^{(\alpha)} + P^{(\alpha)}V^{(\alpha)} + \Pi^{(\alpha)}A^{(\alpha)}; \text{Gibbs free energy}$$
(1.II.8)

In adsorption, some authors call energy,  $(\Pi^{(\alpha)}A^{(\alpha)})$  as free energy of immersion,  $\phi^{(\alpha)}$ 

Note that these functions defined by Eqs. 1.II.8 were slightly modified from their usual definitions due to the introduction of the new variable,  $A^{(\alpha)}$ .

These definitions allow us to rewrite Eq.1.II.8 in more convenient ways, such as:

$$dH^{(\alpha)} = T^{(\alpha)} dS^{(\alpha)} + P^{(\alpha)} dV^{(\alpha)} - Ad\Pi^{(\alpha)} \sum_{k=1}^{m} \left( \frac{\partial H^{(\alpha)}}{\partial N_{k}^{(\alpha)}} \right)_{S^{(\alpha)}, V^{(\alpha)}, \Pi^{(\alpha)}, N_{j \neq k}^{(\alpha)}} dN_{k}^{(\alpha)}$$

$$dF^{(\alpha)} = S^{(\alpha)} d\Gamma^{(\alpha)} - P^{(\alpha)} dV^{(\alpha)} - Ad\Pi^{(\alpha)} \sum_{k=1}^{m} \left( \frac{\partial F^{(\alpha)}}{\partial N_{k}^{(\alpha)}} \right)_{T^{(\alpha)}, V^{(\alpha)}, \Pi^{(\alpha)}, N_{j \neq k}^{(\alpha)}} dN_{k}^{(\alpha)}$$

$$(1.II.9)$$

$$dG^{(\alpha)} = S^{(\alpha)} d\Gamma^{(\alpha)} - V^{(\alpha)} dP^{(\alpha)} - Ad\Pi^{(\alpha)} \sum_{k=1}^{m} \left( \frac{\partial G^{(\alpha)}}{\partial N_{k}^{(\alpha)}} \right)_{T^{(\alpha)}, P^{(\alpha)}, \Pi^{(\alpha)}, N_{j \neq k}^{(\alpha)}} dN_{k}^{(\alpha)}$$

## 1.II.1.3. Gibbs-Helmholtz and Gibbs-Duhen relationships

In a similar way to the one developed in part I, we arrive at the Gibbs-Helmholtz relationship.

$$\left[\frac{\partial}{\partial T^{(\alpha)}} \left(\frac{G^{(\alpha)}}{T^{(\alpha)}}\right)\right]_{P^{(\alpha)},\Pi^{(\alpha)},N^{(\alpha)}_{k}} = -\frac{H^{(\alpha)}}{(T^{(\alpha)})^{2}}$$
(1.II.10)

It is important to note that the equation 1.II.9c is fully characterized by a state to  $(T^{(\alpha)}, P^{(\alpha)}, \Pi^{(\alpha)}, ..., N_k^{(\alpha)}, ...)$  that is, only intensive parameters that are obviously easier to quantify and control, hence the relevant importance of Gibbs free energy for equilibrium processes.

$$G^{(\alpha)} = G^{(\alpha)} \left( T^{(\alpha)}, P^{(\alpha)}, \Pi^{(\alpha)}, \dots, N^{(\alpha)}_{k}, \dots \right)$$
(1.II.11)

although the function  $G(\alpha)$  is a natural function of these state variables, all the others can be reformulated in terms of these state variables as a function of the relationship between them.

### 1.II.1.3.1. partial molar properties

The partial molar quantities also show a slight change in definition including a constancy of the Interfacial potential in the act of partially deriving and thus if:

$$M^{(\alpha)} = M^{(\alpha)} \left( T^{(\alpha)}, P^{(\alpha)}, \Pi^{(\alpha)}, \dots, N^{(\alpha)}_{k}, \dots \right)$$
(1.II.12)

is any extensive property of the individual system  $\alpha$  then its total differential will be:

$$dM^{(\alpha)} = \left(\frac{\partial \mathbf{M}^{(\alpha)}}{\partial \mathbf{T}^{(\alpha)}}\right)_{P^{(\alpha)}, \Pi^{(\alpha)}, N^{(\alpha)}_{k}, M} d\mathbf{T}^{(\alpha)} + \left(\frac{\partial \mathbf{M}^{(\alpha)}}{\partial \mathbf{P}^{(\alpha)}}\right)_{T^{(\alpha)}, \Pi^{(\alpha)}, N^{(\alpha)}_{k}, M} dP^{(\alpha)} + \left(\frac{\partial \mathbf{M}^{(\alpha)}}{\partial \mathbf{M}^{(\alpha)}}\right)_{T^{(\alpha)}, P^{(\alpha)}, \Pi^{(\alpha)}, N^{(\alpha)}_{j \neq k}, M} dN^{(\alpha)}_{k}$$

$$(1.II.13)$$

The partial molar property corresponding to  $M^{(\alpha)}$  is defined by:

$$\overline{m}_{k}^{(\alpha)} = \left(\frac{\partial \mathbf{M}^{(\alpha)}}{\partial \mathbf{N}_{k}^{(\alpha)}}\right)_{T^{(\alpha)}, P^{(\alpha)}, \Pi^{(\alpha)}, N^{(\alpha)}_{j \neq k}}$$
(1.II.14)

the integration of Eq. 1.II.13 becoming constants  $T^{(\alpha)}$ ,  $P^{(\alpha)}$ ,  $\pi^{(\alpha)}$ ,  $N_k^{(\alpha)}$  results in:

$$\mathbf{M}^{(\alpha)} = \sum_{k=1}^{m} \mathbf{N}_{k}^{(\alpha)} \left( \frac{\partial \mathbf{M}^{(\alpha)}}{\partial \mathbf{N}_{k}^{(\alpha)}} \right)_{T^{(\alpha)}, P^{(\alpha)}, \Pi^{(\alpha)}, N_{j \neq k}^{(\alpha)}} = \sum_{k=1}^{m} \mathbf{N}_{k}^{(\alpha)} \overline{m}_{k}^{(\alpha)}$$
(1.II.15)

On the other hand, the differential of Eq. 1.II.15 compared with Eq. 1.II.13 leads to:

$$\left(\frac{\partial \mathbf{M}^{(\alpha)}}{\partial \mathbf{T}^{(\alpha)}}\right)_{P^{(\alpha)},\Pi^{(\alpha)},\Phi^{(\alpha)},N^{(\alpha)}_{k},}d\mathbf{T}^{(\alpha)} + \left(\frac{\partial \mathbf{M}^{(\alpha)}}{\partial \mathbf{P}^{(\alpha)}}\right)_{T^{(\alpha)},\Pi^{(\alpha)},\Phi^{(\alpha)},N^{(\alpha)}_{k},}dP^{(\alpha)} + \left(\frac{\partial \mathbf{M}^{(\alpha)}}{\partial \Pi^{(\alpha)}}\right)_{T^{(\alpha)},P^{(\alpha)},\Phi^{(\alpha)},N^{(\alpha)}_{k},}d\Pi^{(\alpha)} - \sum_{k=1}^{m} \mathbf{N}_{k}^{(\alpha)}d\overline{m}_{k}^{(\alpha)} = 0$$
(1.II.16)

which is the generalized form of the Gibbs-Duhen equation.

Under process conditions at constant  $T^{(\alpha)}$ ,  $P^{(\alpha)} e \Pi^{(\alpha)}$  results for Eq. 1.II.16

$$\sum_{k=1}^{m} N_k^{(\alpha)} d\overline{m}_k^{(\alpha)} = 0; \text{ at constant } T^{(\alpha)}, P^{(\alpha)} e \Pi^{(\alpha)}$$
(1.II.17)

Introducing molar quantities for the phase,  $\alpha$ , by the definitions:

$$\mathbf{m}^{(\alpha)} \equiv \frac{\mathbf{M}^{(\alpha)}}{\mathbf{N}^{(\alpha)}}$$
;  $x_k^{(\alpha)} \equiv \frac{N_k^{(\alpha)}}{\mathbf{N}^{(\alpha)}}$  with  $\mathbf{N}^{(\alpha)} = \sum_{k=1}^m \mathbf{N}_k^{(\alpha)}$ 

results:

$$\left(\frac{\partial \mathbf{m}^{(\alpha)}}{\partial \mathbf{T}^{(\alpha)}}\right)_{P^{(\alpha)},\Pi^{(\alpha)},\Phi^{(\alpha)},N_{k}^{(\alpha)},} d\mathbf{T}^{(\alpha)} + \left(\frac{\partial \mathbf{m}^{(\alpha)}}{\partial \mathbf{P}^{(\alpha)}}\right)_{T^{(\alpha)},\Pi^{(\alpha)},\Phi^{(\alpha)},N_{k}^{(\alpha)},} dP^{(\alpha)} + \left(\frac{\partial \mathbf{m}^{(\alpha)}}{\partial \mathbf{\Pi}^{(\alpha)}}\right)_{T^{(\alpha)},P^{(\alpha)},\Phi^{(\alpha)},N_{k}^{(\alpha)},} d\Pi^{(\alpha)} - \sum_{k=1}^{m} \mathbf{x}_{k}^{(\alpha)} d\overline{m}_{k}^{(\alpha)} = 0$$
(1.II.18)

When in equations 1.II.16 and 1.II.18 one takes (  $M^{(\alpha)} \equiv G^{(\alpha)}$  ) results:

$$-S^{(\alpha)}dT^{(\alpha)} + V^{(\alpha)}dP^{(\alpha)} +$$

$$+A^{(\alpha)}d\Pi^{(\alpha)} - \sum_{k=1}^{m} N_{k}^{(\alpha)}d\mu_{k}^{(\alpha)} = 0$$
and
$$-S^{(\alpha)}dT^{(\alpha)} + V^{(\alpha)}dP^{(\alpha)} +$$

$$+a^{(\alpha)}d\Pi^{(\alpha)} - \sum_{k=1}^{m} x_{k}^{(\alpha)}d\mu_{k}^{(\alpha)} = 0$$
(1.II.19)

# 1.II.1.3.2. Gibbs isotherm

The first of Eqs. 1.II.19 at constant  $T^{(\alpha)}$  and  $P^{(\alpha)}$  retrieve a result widely used in surface thermodynamics.

$$\sum_{k=1}^{m} N_{k}^{(\alpha)} d\mu_{k}^{(\alpha)} = A^{(\alpha)} d\Pi^{(\alpha)} \qquad Gibbs \ isotherm$$
(1.II.19b)

returning to Eq. 1.II.18 we have:

$$dG^{(\alpha)} = -\mathbf{S}^{(\alpha)}d\mathbf{T}^{(\alpha)} + \mathbf{V}^{(\alpha)}dP^{(\alpha)} - \Pi^{(\alpha)}dA^{(\alpha)} + \sum_{k=1}^{m}\mu_{k}^{(\alpha)}dN_{k}^{(\alpha)} = 0$$
(1.II.20)

defining a partial molar quantity for area A gives:

$$\frac{\overline{a}_{k}^{(\alpha)}}{\partial N_{k}^{(\alpha)}} = \left(\frac{\partial A^{(\alpha)}}{\partial N_{k}^{(\alpha)}}\right)_{T^{(\alpha)}, P^{(\alpha)}, N_{j \neq k}^{(\alpha)}} 
dA^{(\alpha)} = \sum_{k=1}^{m} \overline{a}_{k}^{-(\alpha)} dN_{k}^{(\alpha)}$$
(1.II.21)

with Eq. 1.II.21 in Eq. 1.II.20 shall result:

$$dG^{(\alpha)} = -\mathbf{S}^{(\alpha)}d\mathbf{T}^{(\alpha)} + \mathbf{V}^{(\alpha)}dP^{(\alpha)} - \Pi^{(\alpha)}\sum_{k=1}^{m} \overline{a}_{k}^{(\alpha)}dN_{k}^{(\alpha)} + \sum_{k=1}^{m} \mu_{k}^{(\alpha)}dN_{k}^{(\alpha)} = 0$$

$$dG^{(\alpha)} = -\mathbf{S}^{(\alpha)}d\mathbf{T}^{(\alpha)} + \mathbf{V}^{(\alpha)}dP^{(\alpha)} + \sum_{k=1}^{m} (\mu_{k}^{(\alpha)} - \Pi^{(\alpha)}\overline{a}_{k}^{(\alpha)})dN_{k}^{(\alpha)} = 0$$
(1.II.22)

and defining a new partial molar property by:

$$\xi_{k}^{(\alpha)} \equiv (\mu_{k}^{(\alpha)} - \Pi^{(\alpha)} \overline{a}_{k}^{(\alpha)})$$
(1.II.23)

comes to:

$$dG^{(\alpha)} = -S^{(\alpha)}dT^{(\alpha)} + V^{(\alpha)}dP^{(\alpha)} + \sum_{k=1}^{m} (\xi_k^{(\alpha)})dN_k^{(\alpha)} = 0$$
(1.II.24)

and consequently:

$$\begin{aligned} \boldsymbol{\xi}_{k}^{(\alpha)} &\equiv \left(\frac{\partial G^{(\alpha)}}{\partial N_{k}^{(\alpha)}}\right)_{T^{(\alpha)}, P^{(\alpha)}, N_{j \neq k}}^{(\alpha)} \equiv \overline{g}_{k}^{(\alpha)} \\ and \\ d\boldsymbol{\xi}_{k}^{(\alpha)} &= d\overline{g}_{k}^{(\alpha)} \end{aligned} \tag{1.II.25}$$

and the Gibbs-Duren equation becomes:

$$-S^{(\alpha)}dT^{(\alpha)} + V^{(\alpha)}dP^{(\alpha)} - \sum_{k=1}^{m} (N_{k}^{(\alpha)}d\xi_{k}^{(\alpha)}) = 0$$
  
and  
$$-S^{(\alpha)}dT^{(\alpha)} + v^{(\alpha)}dP^{(\alpha)} - \sum_{k=1}^{m} (x_{k}^{(\alpha)}d\xi_{k}^{(\alpha)}) = 0$$
(1.II.26)

by the Eq.1.II.23

$$d\xi_{k}^{(\alpha)} = d\mu_{k}^{(\alpha)} - d(\Pi^{(\alpha)} \bar{a}_{k}^{(\alpha)}) = d\bar{g}_{k}^{(\alpha)}$$
(1.II.27)

but,

$$d\mu_k^{(\alpha)} = RTd\ln\left(\hat{f}_k^{(\alpha)}\right) \tag{1.II.28}$$

$$d\xi_{k}^{(\alpha)} = RTd \ln\left(\hat{f}_{k}^{(\alpha)}\right) - d(\Pi^{(\alpha)}\overline{a}_{k}^{(\alpha)}) = d\overline{g}_{k}^{(\alpha)}$$
(1.II.29)

but by Eq. 1.II.26a (Gibbs-Duren) at constant  $T^{(\alpha)}$  and  $P^{(\alpha)}$ 

$$\sum_{k=1}^{m} N_{k}^{(\alpha)} d\xi_{k}^{(\alpha)} = 0; \quad \text{at constant} \ T^{(\alpha)} and \ P^{(\alpha)}$$
(1.II.30)

$$\sum_{k=1}^{m} N_{k}^{(\alpha)} d\xi_{k}^{(\alpha)} = \sum_{k=1}^{m} N_{k}^{(\alpha)} \Big( RT^{(\alpha)} d \ln(\hat{f}_{k}^{(\alpha)}) - d(\Pi^{(\alpha)} \bar{a}_{k}^{(\alpha)}) \Big) = 0$$
(1.II.31)

$$\sum_{k=1}^{m} N_{k}^{(\alpha)} \left( RT^{(\alpha)} d \ln(\hat{f}_{k}^{(\alpha)}) \right) = d(\Pi^{(\alpha)} \sum_{k=1}^{m} N_{k}^{(\alpha)} \bar{a}_{k}^{(\alpha)}) = d(\Pi^{(\alpha)} A^{(\alpha)})$$

$$\sum_{k=1}^{m} N_{k}^{(\alpha)} \left( d \ln(\hat{f}_{k}^{(\alpha)}) \right) = d(\frac{\Pi^{(\alpha)}}{RT^{(\alpha)}} \sum_{k=1}^{m} N_{k}^{(\alpha)} \bar{a}_{k}^{(\alpha)}) = d(\frac{\Pi^{(\alpha)}}{RT^{(\alpha)}} A^{(\alpha)})$$
(1.II.32)

$$\sum_{k=1}^{m} N_{k}^{(\alpha)} \left( d \ln(\hat{f}_{k}^{(\alpha)}) \right) = d\left( \frac{\Pi^{(\alpha)}}{RT^{(\alpha)}} A^{(\alpha)} \right)$$
(1.II.33)

### **1.II.2.** The thermodynamic equilibrium problem

Although one is denoting the individual system generically by the symbol,  $\alpha$ , the symbol,  $\beta$ , will be adopted to denote another one forming part of the composite system. Eq. 1.II.6 (**FET**) in entropic form, for the system,  $\alpha$ , and for the system,  $\beta$ , is given by:

$$dS^{(\alpha)} = \frac{dU^{(\alpha)}}{T^{(\alpha)}} + \frac{P^{(\alpha)}}{T^{(\alpha)}} dV^{(\alpha)} + \frac{\Pi^{(\alpha)}}{T^{(\alpha)}} dA^{(\alpha)} - \sum_{\kappa=1}^{m} \frac{\mu_{k}^{(\alpha)}}{T^{(\alpha)}} dN_{k}^{(\alpha)}$$
(1.II.34)

$$dS^{(\beta)} = \frac{dU^{(\beta)}}{T^{(\beta)}} + \frac{P^{(\beta)}}{T^{(\beta)}} dV^{(\alpha)} + \frac{\Pi^{(\beta)}}{T^{(\beta)}} dA^{(\beta)} - \sum_{k=1}^{m} \frac{\mu_{k}^{(\beta)}}{T^{(\beta)}} dN_{k}^{(\beta)}$$
(1.II.35)

$$dU^{(\beta)} = -dU^{(\alpha)} \qquad a)$$

$$dV^{(\beta)} = -dV^{(\alpha)} \qquad b)$$

$$dN_k^{(\beta)} = -dN_k^{(\alpha)} \qquad c) \qquad (1.II.36)$$
and
$$dS_t^S = dS^{(\beta)} + dS^{(\alpha)} \qquad d)$$

in which  $S_t^{S}$ ,  $S^{(\beta)}$ ,  $S^{(\alpha)}$  are, respectively, the total entropy of the composite (isolated) system and the entropies of the individual systems that constitute it.

So based on Eq.1.II.36(d) Eq. 1.II.34 and Eq. 1.II.35 it is possible to build:

$$dS_{t}^{S} = \left(\frac{dU^{(\beta)}}{T^{(\beta)}} + \frac{P^{(\beta)}}{T^{(\beta)}}dV^{(\alpha)} + \frac{\Pi^{(\beta)}}{T^{(\beta)}}dA^{(\beta)} - \sum_{\kappa=1}^{m}\frac{\mu_{k}^{(\beta)}}{T^{(\beta)}}dN_{k}^{(\beta)}\right) + \left(\frac{dU^{(\alpha)}}{T^{(\alpha)}} + \frac{P^{(\alpha)}}{T^{(\alpha)}}dV^{(\alpha)} + \frac{\Pi^{(\alpha)}}{T^{(\alpha)}}dA^{(\alpha)} - \sum_{\kappa=1}^{m}\frac{\mu_{k}^{(\alpha)}}{T^{(\alpha)}}dN_{k}^{(\alpha)}\right)$$
(1.II.37)

For the purpose of simplifying the treatment of the resulting equation, a relationship between the volume, V and the area, A, will be defined, given by:

$$dA^{(i)} = \left(\frac{\partial A^{(i)}}{\partial V^{(i)}}\right) dV^{(i)} \quad i = \alpha \text{ or } \beta$$

$$a_{(\nu,i)} \equiv \left(\frac{\partial A^{(i)}}{\partial V^{(i)}}\right) \qquad (1.II.38)$$

replacing Eqs. 1.II.36(a, b, c and d) in Eq. 1.II.37 results:

$$dS_{t}^{S} = \left(\frac{1}{T^{(\alpha)}} - \frac{1}{T^{(\beta)}}\right) dU^{(\alpha)} + \left[\frac{P^{(\alpha)}}{T^{(\alpha)}} - \frac{P^{(\beta)}}{T^{(\beta)}} + \frac{\Pi^{(\alpha)} \left(\frac{\partial A^{(\alpha)}}{\partial V^{(\alpha)}}\right)}{T^{(\alpha)}} - \frac{\Pi^{(\beta)} \left(\frac{\partial A^{(\beta)}}{\partial V^{(\beta)}}\right)}{T^{(\beta)}}\right] dV^{(\alpha)} + \left(\frac{\mu_{k}^{(\alpha)}}{T^{(\alpha)}} - \frac{\mu_{k}^{(\beta)}}{T^{(\beta)}}\right) dN_{k}^{(\alpha)}\right)$$
(1.II.39)

In the equilibrium of a composite system isolated, the parameters assume values that maximize entropy and so by the equilibrium criterion:

$$dS_t^S = 0$$

Remembering that  $dU^{(\alpha)}$ ,  $dV^{(\alpha)}$ ,  $dN_k^{(\alpha)}$ , are increments as small as you like, but they are not zero, since they are variables of the composite system, so that Eq. 1.II.39 is null, it is necessary and sufficient that its coefficients are null, thus resulting in equivalent conditions of equilibrium criterion, namely:

$$\left(\frac{1}{T^{(\alpha)}} - \frac{1}{T^{(\beta)}}\right) = 0$$

$$\left[\frac{P^{(\alpha)}}{T^{(\alpha)}} - \frac{P^{(\beta)}}{T^{(\beta)}} + \frac{\Pi^{(\alpha)}\left(\frac{\partial A^{(\alpha)}}{\partial V^{(\alpha)}}\right)}{T^{(\alpha)}} - \frac{\Pi^{(\beta)}\left(\frac{\partial A^{(\beta)}}{\partial V^{(\beta)}}\right)}{T^{(\beta)}}\right] = 0$$
(1.II.40)
$$\frac{\mu_{k}^{(\alpha)}}{T^{(\alpha)}} - \frac{\mu_{k}^{(\beta)}}{T^{(\beta)}}\right) = 0$$

Therefore, in equilibrium:

$$T^{(\alpha)} = T^{(\beta)}$$

$$P^{(\alpha)} - P^{(\beta)} = \Pi^{(\alpha)} \left( \frac{\partial A^{(\alpha)}}{\partial V^{(\alpha)}} \right) - \Pi^{(\beta)} \left( \frac{\partial A^{(\beta)}}{\partial V^{(\beta)}} \right) = \Pi^{(\alpha)} \mathbf{a}_{(\nu,\alpha)} - \Pi^{(\beta)} \mathbf{a}_{(\nu,\beta)}$$
(1.II.41)
$$\mu_k^{(\alpha)} = \mu_k^{(\beta)}$$

defining:

$$\zeta_{(\nu,\alpha,\beta)} = [\Pi^{(\alpha)} \mathbf{a}_{(\nu,\alpha)} - \Pi^{(\beta)} \mathbf{a}_{(\nu,\beta)}]$$
(1.II.42)

it is written

$$T^{(\alpha)} = T^{(\beta)}$$

$$P^{(\alpha)} - P^{(\beta)} = \zeta_{(\nu,\alpha,\beta)}$$

$$\mu_k^{(\alpha)} = \mu_k^{(\beta)}$$
(1.II.43)

## 1.II.2.1. Jurin's law and capillary pressure

It should be noted that the thermal and chemical equilibrium are how we usually write them, but the mechanical equilibrium is affected by the Interfacial potential of both phases, allowing the thermodynamic treatment of surfaces. It is worth noting that the relationship proposed by Eq. 1.II.41 is not necessarily satisfied for any pair of phases,  $\alpha$  and  $\beta$ , but it is quite naturally abundant in problems where the dispersed phase is fragmented into small parts.

It is interesting to note that one of the classic laboratory experiments in elementary school is one that shows the magic of a fluid rising through the interior of a capillary tube (Jurin's law). Appearing, of course, in this formulation not as a law but as a consequence of the second law of thermodynamics and represented by this remarkable equation. Jurin's law was stated as follows: "The height, **h** reached by the water from the level of its surface, is inversely proportional to the radius, **r** of the capillary tube": that is,  $h = (\frac{constant}{r})$ ; which is

deduced from a mechanical balance between the weight of the column of liquid and the force resulting from the action of the interfacial tension and given by:

$$h = \frac{2\sigma}{\rho_f g r}$$

The mechanical equilibrium calculations in this particular system: the water-air interface: are correctly described by the Young-Laplace law given by:

$$\Delta P = \sigma \frac{dA}{dV} \tag{1.II.44}$$

Where  $\Delta P = P^{(\alpha)} - P^{(\beta)}$  is the pressure difference between the phases and called *capillary pressure*, widely used in soil physics, with particular interest in two-phase flow in porous media, and,  $\sigma$ , the interfacial tension called surface tension when water is in equilibrium with the air of the local atmosphere, in the conditions of temperature and pressure of this.

For the mechanical equilibrium of a bubble in the *liquid-vapor* system or a drop in the *liquid-liquid* system and considering a spherical shape for a particle of the dispersed phase, it is obtained:

$$A = 4\pi r^{2} \text{ e } dA = 8\pi r$$

$$V = \frac{4}{3}\pi r^{3} \text{ e } dV = 4\pi r^{2}$$

$$\frac{dA}{dV} = \frac{2}{r}$$
(1.II.45)

with these data in Eq. 1.II.44 the best-known form for the *Young-Laplace* equation results:

$$\Delta P = P^{(\alpha)} - P^{(\beta)} = \frac{2\sigma}{r} \tag{1.II.46}$$

and, in this particular case, to recognize the scattering tension as an interfacial tension and not a scattering pressure as can be understood from several authors.

When part of the system is not composed in a fragmented form, that is, the systems are extensive and the interface is flat, in this case in the limit it is as if the radius of curvature tends to infinity, and thus:

$$\lim_{r \to \infty} \left(\frac{2\sigma}{r}\right) = 0; \text{ and } \Delta P = 0 \quad \Rightarrow P^{(\alpha)} = P^{(\beta)} \tag{1.II.47}$$

recovering the most common result of the study of phase equilibrium.
$$T^{(\alpha)} = T^{(\beta)}$$

$$P^{(\alpha)} = P^{(\beta)}$$

$$\mu_k^{(\alpha)} = \mu_k^{(\beta)}$$
(1.II.48)

In *multiphase multicomponent equilibrium*, the vast majority of problems of interest are almost always biphasic. In this sense, the relevant simplification will be:

k=1.2, 3, ..., m; and  $\alpha$ =1 and  $\beta$ =2;

$$T^{(1)} = T^{(2)}$$

$$P^{(1)} - P^{(2)} = \Pi^{(1)} \left( \frac{\partial A^{(1)}}{\partial V^{(1)}} \right) - \Pi^{(2)} \left( \frac{\partial A^{(2)}}{\partial V^{(2)}} \right) = \Pi^{(1)} \mathbf{a}_{(\nu,1)} - \Pi^{(2)} \mathbf{a}_{(\nu,2)}$$
(1.II.49)
$$\mu_k^{(1)} = \mu_k^{(2)}$$

or, in a more condensed form:

$$T^{(1)} = T^{(2)}$$

$$P^{(1)} - P^{(2)} = \zeta_{(v,1,2)}$$

$$\mu_k^{(1)} = \mu_k^{(2)}$$
(1.II.50)

The most recurrent two-phase systems are related to an extensive fluid as a continuous phase, called simply by, "bulk", and a dispersed phase in the form of an immiscible fluid, a gel or a microporous solid, which for the purposes of applications will be denoted by two-phase systems of type I (fluid-fluid), II (fluid-gel) and III (fluid-solid), with the continuous phase always denoted by  $\alpha$ =1 and the fragmented phase by  $\alpha$ =2.

The consideration of an extensive individual system for the bulk phase is equivalent to admitting that  $dA^{(1)} \ll dV^{(1)}$  and so:

$$\left(\frac{\partial A^{(1)}}{\partial V^{(1)}}\right) \cong 0$$

resulting, for mechanical equilibrium, the relation:

$$P^{(1)} - P^{(2)} = -\Pi^{(2)} \left( \frac{\partial A^{(2)}}{\partial V^{(2)}} \right) = -\Pi^{(2)} a_{(\nu,2)}$$
(1.II.51)

Regarding type I (fluid-fluid) systems in biphasic equilibrium,  $P^{(1)}$  and  $P^{(2)}$  are the thermodynamic pressures as already understood, but when the system is of type III (fluid-solid) the pressure  $P^{(2)}$ , individually, lacks meaning and can, until the meaning is understood, be understood by an effective pressure given by:

$$P^{(2)} = \Pi^{(2)} a_{(v,2)} + P^{(1)} = P^{(2)}_{effective}$$
(1.II.52)

It is imperative to remember that the solid is not a solution in the thermodynamic sense, and the term *solid solution* is just an ingenious device for inclusion in the formulation. The direct experimental determination of any macroscopic property within it is difficult to perform and, if performed, will be taken as a local average of a supposedly continuous and homogeneous system. In many thermodynamic systems, the area appears as a natural boundary and can almost always be accurately determined. In the case of porous solids, objects of study of various segments of processes of interest; adsorption, for example, the area appears intrinsically in its natural formation (zeolites) or assisted formation (active carbon), that is, it is distributed in the solid volume, being itself a volumetric or mass concentration.

$$\mathbf{a}_{(v,i)} \equiv \left(\frac{\partial A^{(i)}}{\partial V^{(i)}}\right) \text{specific volumetric area}$$
(1.II.53)

$$a_{(m,i)} \equiv \left(\frac{\partial A^{(i)}}{\partial m^{(i)}}\right) \text{specific mass area}$$
(1.II.54)

the relationship between them is the actual density of the solid,  $\rho_s$ 

$$\mathbf{a}_{(v,i)} \equiv \rho_s a_{(m,i)} \tag{1.11.55}$$

since mass measurements are simpler and more accurate than volumes, specific mass areas are more common and so,

$$a_{(m,\alpha)} = \frac{A^{(\alpha)}}{m_{ads}}$$
(1.II.56)

given the uniformity shown by the vast majority of porous solids, this property is practically constant, regardless of the particle size.

## 1.II.2.2. Kelvin's equation.

Interfacial tension is more common in the form of surface tension, which is the equilibrium between liquid water and atmospheric air, which in addition to water vapor has other gases in its composition and even water is not always pure. In this sense we will consider a water vapor in condensation forming small uniform drops of radius r, and we will consider this equilibrium state at temperature T and analyze the effect of pressure. The extended phase, the vapor, will be denoted by  $\alpha$  and the liquid phase by  $\beta$ .

The equilibrium conditions are:

$$T^{(\alpha)} = T^{(\beta)} = T$$
$$f^{(\alpha)}(P^{\alpha}, T) = f^{(\beta)}(P^{\beta}, T)$$

The effect of pressure on the fugacity of the pure component in the drop (curved surface) can be related to the pressure on a flat surface which is its saturation pressure,  $P^{sat}(T)$  by Poynting correction:

$$f^{(\beta)}(P^{\beta},T) = f^{(\beta)}(P^{sat},T) \exp\left[\frac{1}{RT} \int_{P^{sat}}^{P^{\beta}} v^{\beta} dP\right]$$

and the fugacity in the gas phase in terms of the fugacity coefficient,

$$f^{(\alpha)}(P^{\alpha},T) = \phi^{(\alpha)}(P^{\alpha},T)P^{\alpha}$$

and

$$f^{(\beta)}(P^{sat},T) = \phi^{(\beta)}(P^{sat},T)Psat$$

and we get

$$\phi^{(\alpha)}(P^{\alpha},T)P^{\alpha} = \phi^{(\beta)}(P^{sat},T)P^{sat} \exp\left[\frac{1}{RT}\int_{P^{sat}}^{P^{\beta}} v^{\beta}dP\right]$$

equation that relates  $P^{\alpha}$  and  $P^{\beta}$  with  $P^{sat}$  and other system properties such as the molar volume of the liquid,  $v^{\beta}$ , and the fugacity coefficients.

At low and moderate pressures, the fugacity coefficients differ more from unity than between themselves and we have:

$$\phi^{(\alpha)}(P^{\alpha},T) \approx \phi^{(\beta)}(P^{sat},T)$$

on the other hand, the molar volume of liquids has little dependence on pressure simplifying the integration and thus,

$$P^{\alpha} = P^{sat} \exp\left[\frac{v^{\beta}(P^{\beta} - P^{sat})}{RT}\right]$$

by the Young-Laplace equation Eq. 1.II.46 we have:

$$P^{\beta} = P^{\alpha} + \frac{2\sigma}{r} \tag{1.II.55}$$

$$P^{\alpha} = P^{sat} \exp\left[\frac{v^{\beta}(P^{\alpha} - P^{sat} + \frac{2\sigma}{r})}{RT}\right]$$
(1.II.55b)

In so many cases  $P^{\alpha}$  it's not much bigger than  $P^{sat}$  prevailing the interfacial tension term resulting in one of the forms of the *Kelvin equation*:

$$P^{\alpha} = P^{sat} \exp\left[\frac{2\sigma v^{\beta}}{rRT}\right]$$
(1.II.56)

showing that the pressure in the liquid phase exceeds that of saturation on a planar surface and will be much more accentuated the smaller the droplet radius.

Closing this section involving pressures on non-planar surfaces, we will present the illustrations:

illustration il.1.II.1. Direct application of the Kelvin equation

Estimative the radius of a water droplet and the pressure inside it at P=1.1bar and T=373 K in liquid-vapor equilibrium.

The necessary data at 1.1bar and 373K, are:

Saturating vapor pressure = 1.013 bar; Surface tension= 0.0589 N/m; Molar volume=  $1.87 \times 10^{-5} \text{ m}^3/\text{mol}$ Ideal gas constant=  $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ 

direct substitution in Eq. 1.II.56 gives us the radius, r

 $\mathbf{r} = 8.6 \text{x} 10^{-9} \text{m} = 8.6 \text{nm}$ 

and for the pressure inside the drop the use of Eq.1.II.55, Young-Laplace equation

$$P^{\beta} = P^{\alpha} + \frac{2\sigma}{r} = 1.1 \times 10^5 + 1.37 \times 10^7 = 1.38 \times 10^7 \text{ Pa} = 138 \text{ bar}$$

Within such drops the *calculated* pressure is very large. It is this *high pressure* that *increases* the fugacity of the liquid water so that a higher vapor phase fugacity results at equilibrium.

We will illustrate below with an example in *medicine* in the field of *hemodynamics*: part of physiology that studies the *laws of flow of blood* in the vessels (pressure, velocity, etc...). The specialty is one of the most advanced in recent decades and has reduced morbidity and mortality rates.

#### illustration il.1.II.2. Blood circulation blocked by a thrombus

The formation of a clot is a complex process regulated by different mechanical and biochemical mechanisms. Disorders that affect the blood clotting system can cause various abnormalities such as thrombosis (excessive clotting) or bleeding (insufficient clotting). In this context, the low shear rate flow stimulates the clot to grow, which when it senses a narrowing of the artery, it cannot pass through it and dire consequences are imminent. This report from the medical field has its origin in the action of *capillary pressure*, which we intend to explain.

Consider, based on the figure il.II.1,  $\mathbf{R}$  is the radius of the artery and  $\mathbf{r}$  the radius of the stenosis or throat, common use of the term in the study of flow with restricted area of passage.



Figure iI.II.1. blood flow blocked by a thrombus

For the analysis we will consider 3 regions as shown in the figure and locally the pressure  $P_1$ ,  $P_2$  and  $P_3$  at the time of blocking.

For analysis, equation 1.II.44 will be used

$$\Delta P = \sigma \frac{dA}{dV}$$
 Where  $\Delta P = P^{(\alpha)} - P^{(\beta)}$ 

In interface 1 with 2 we have:

$$P_2 = P_1 + \frac{\sigma_{1,2} \, dA_{1,2}}{dv}$$

and in interface 3 with 2 we have:  $\overline{a}$ 

$$P_2 = P_3 + \frac{\sigma_{2,3} \, dA_{2,3}}{dv}$$

then:

$$P_1 + \frac{\sigma_{1,2} \, dA_{1,2}}{dv} = P_3 + \frac{\sigma_{2,3} \, dA_{2,3}}{dv}$$

but by the equation 1.II.45,

$$dA_{1,2} \coloneqq 2 \frac{dv}{R}$$

and

$$dA_{2,3} \coloneqq 2 \frac{dv}{r}$$

resulting,

$$P_1 - P_3 = 2 \sigma \left(\frac{1}{r} - \frac{1}{R}\right)$$

or in the usual form of capillary pressure:

$$\Delta_p = 2 \sigma \left( \frac{1}{r} - \frac{1}{R} \right)$$

which is the general form of the Young-Laplace equation.

One of the biggest causes of death or disability is carotid obstruction. The common carotid has diameters between 3.7 to 11 mm for men. Considering for the purpose of numerical application  $\mathbf{r} = f$ . **R**, where f is the obstruction factor:

f=1 artery without any restriction;f=0 artery totally occluded.resulting in the Young-Laplace equation parameterized in f:

$$\Delta_p = 2 \sigma \left( \frac{1}{fR} - \frac{1}{R} \right)$$

Adopting the value of 63 mN/m for the interfacial tension and R=5mm results for the pressure difference of the pressure in the thrombus in mmHg:



Figure II.II.2. Pressure difference in the thrombus depending on the obstruction factor.

Increase of approximately 1 mmHg per degree of obstruction, flow almost ceasing at f = 20%. Taking into account that the length of the thrombus is on the order of the radius of the artery, the gradient reaches a value of 605 mmHg. The system responds by increasing pressure and may rupture the artery in a hemorrhagic event.

A large clot can block a large amount of blood flowing through the blocked artery, causing the brain cells supplied by that artery to die.

If the patient is stable, urgent intervention is required. It is important to understand that the artery-clot system is in equilibrium and will remain so if this equilibrium is not reversed. This is done by introducing mechanical or chemical work.

Mechanical work is not only a therapeutic instrument (coronary angioplasty), it can also be pharmacological. Vasodilators are drugs that dilate blood vessels - veins and arteries - by relaxing the smooth muscles in their walls, increasing the diameter of the artery and releasing the clot. However, we do not recommend this procedure as a first action, because the clot released may block a smaller artery further up. The ideal drug in our opinion is the one that destroys the interfacial tension and consequently the clot, these are called surfactants, which fix at the interface and are able to reduce the value of the interface tension from 100 to 0.01 dyne/cm. enough to perform the desired action.

In petroleum engineering, this procedure refers to a tertiary recovery of retained oil by capillary pressure. The observation of this phenomenon in transparent micromodels is to be contemplated with admiration and interest.

The illustration developed is obviously dramatic, but the capillarity mechanism is widely used by nature, soil and vegetation confirm it.

#### 1.II.3. adsorption

From here, attention will be given specifically to adsorptive processes where;  $\alpha=1$  is the extended or "bulk" phase and  $\alpha=2$  the *solid solution* or simply adsorbent.

The thermodynamic conditions required at equilibrium are:

$$T^{(1)} = T^{(2)} \tag{1.II.57}$$

$$P^{(1)} = P^{(2)} - \Pi^{(2)} \mathbf{a}_{(\nu,2)}$$
(1.II.58)

$$\hat{f}_{k}^{(1)} = \hat{f}_{k}^{(2)}$$
 k=1,2,....,m (1.II.59)

From the conservation of mass it still results for each individual system:

$$\sum_{k=1}^{m} x_k^{(1)} = 1 \tag{1.II.60}$$

$$\sum_{k=1}^{m} x_k^{(2)} = 1$$
(1.II.61)

Characterizing phase (1) we have the following variables  $T^{(1)}$ ,  $P^{(1)}$ ,  $x_1^{(1)}$ ,... $x_k^{(1)}$ ,... $x_m^{(1)}$  and characterizing phase (2) we have  $T^{(2)}$ ,  $\Pi^{(2)}$ ,  $x_1^{(2)}$ ,... $x_k^{(2)}$ ,... $x_m^{(2)}$  and, as already discussed, pressure,  $P^{(2)}$ , in the adsorbent, because it lacks sense, it is replaced by the interfacial tension,  $\Pi^{(2)}$ , for the complete characterization of the equilibrium state. Thus totaling 2(m+2) intensive properties completely specifying the equilibrium. With the abandonment of the property,  $P^{(2)}$ , we are also neglecting Eq. 1.II.58 and thus getting an Eq. 1.II.57, m equations of type 1.II.59 and the two 1.II.60 and 1.II.61, totaling (m+3) available, the problem looks like this with  $\mathbf{F} = 2(m+2) - (m+3) = m+1$ , degrees of freedom.

The *standard state* adopted will be that of the k *pure component*, such that:

$$\lim_{x_{k}^{(\alpha)} \to 1} (\gamma_{k}^{(\alpha)}) \to 1$$
(1.II.62)

# 1.II.3.1. Complementary equations for the phases

In terms of fugacity it results:

-in phase 1:

$$\sum_{k=1}^{m} N_{k}^{(1)} (RT^{(1)} d \ln(\hat{f}_{k}^{(1)})) = 0$$
 at constant  $T^{(1)}, P^{(1)}, x_{k}^{(1)}$  (1.II.63)

-in phase 2:

$$\sum_{k=1}^{m} N_{k}^{(2)} \left( d \ln(\hat{f}_{k}^{(2)}) \right) = d\left( \frac{\Pi^{(2)}}{RT^{(2)}} A^{(2)} \right) \quad \text{at constant } T^{(2)}, \mathbb{P}^{(2)}, \ \mathbf{x}_{k}^{(2)} \tag{1.II.64}$$

This last equation, applied to the system containing only the k pure component, under the same conditions as the original solution gives:

$$\frac{\mathbf{N}_{k}^{0(2)}}{m_{ads}} \left[ d\ln(\hat{f}_{k}^{0(2)}) \right] = d(\frac{\Pi^{(2)}a_{(m,2)}}{RT}) = dz^{(2)}$$
(1.II.65)

where by definition:

$$C_k^{(2)} \equiv \frac{N_k^{(2)}}{m_{ads}}$$
 e  $C_t^{(2)} \equiv \frac{1}{m_{ads}} \sum_{k=1}^m N_k^{(2)}$  and  $x_k^{(2)} = \frac{C_k^{(2)}}{C_t^{(2)}}$  (1.II.66)

and still:

$$z^{(2)} \equiv \left(\frac{\Pi^{(2)}}{RT} \frac{A^{(2)}}{m_{ads}}\right) = \frac{\Pi^{(2)} a_{(m,2)}}{RT}$$
(1.II.67)

which is most useful in the form:

$$\left[\frac{d\hat{f}_{k}^{0(2)}}{\hat{f}_{k}^{0(2)}}\right] = \frac{1}{C_{k}^{0(2)}} dz^{(2)} \text{ or } \left[\frac{d\hat{f}_{k}^{0(2)}}{dz}\right] = \frac{\hat{f}_{k}^{0(2)}}{C_{k}^{0(2)}}$$
(1.II.68)

The fugacity of the k component in solution, can be written in terms of parameters associated with non-idealities, such as fugacity coefficients or activity coefficients, and thus:

$$\hat{f}_{k}^{(\alpha)} = x_{k}^{(\alpha)} \hat{\phi}_{k}^{(\alpha)} P^{(\alpha)} \text{ or } \hat{f}_{k}^{(\alpha)} = x_{k}^{(\alpha)} \gamma_{k}^{(\alpha)} f_{k}^{0(\alpha)}$$
(1.II.69)

At this point it is necessary to understand that it will not be possible to determine the concentrations,  $C_k^{(2)}$ , because in the formulation of the equilibrium problem, important information was not provided as discussed in item 1.3. We lack information on the value of the total number of moles in the adsorbed phase, N<sup>(2)</sup>. However, it is possible to infer this value assuming the relationship is valid:

$$\frac{1}{N_t^{(2)}} = \sum_{k=1}^m \frac{x_k^{(2)}}{N_k^{0(2)}}$$
(1.II.70)

which sets as a limit for the k component its pure component capacity at a given Interfacial potential at the system temperature, and, consequently,

$$\frac{1}{C_t^{(2)}} = \sum_{k=1}^m \frac{x_k^{(2)}}{C_k^{0(2)}}$$
(1.II.71)

and still:

$$C_{k}^{(\alpha)} = x_{k}^{(\alpha)} C_{t}^{(2)}$$
(1.II.72)

The relationship presented is thermodynamically acceptable, but it may be physically incorrect, given the mechanisms of accommodation of chemical compounds in the adsorption sites. This is a working hypothesis and its usefulness is evident.

When phase 1 is gaseous, it is convenient to lighten the notation by denoting, in the bulk phase  $x_k^{(1)}$  simply  $y_k$ , and in the adsorbent phase  $x_k^{(2)}$  simply  $x_k$ , at equilibrium, and so Eq.1.II.56c results as usual:

$$y_k \hat{\phi}_k P = x_k \gamma_k f_k^0 \tag{1.II.73}$$

At this point in development, a consideration of the equilibrium of the pure component at constant temperature (adsorption isotherm) deserves attention.

The gas phase is characterized completely by the pressure P and the solid solution by the number of mols of the k component,  $N_k^{(2)}$  and the adsorbent mass,  $m_{ads}$  since the temperature is constant.

The data are, from the beginning of the adsorption studies, presented in the form:

$$\frac{N_k^{(2)}}{m_{ads}} = C_k^{(2)} = f(P)$$
(1.II.74)

The most famous form of this equation is also called *adsorption isotherm* it is undoubtedly that due to *Langmuir* deduced, initially, by kinetic mechanisms (1918). Its universally known mathematical form is:

$$C_{k}^{(2)} = C_{k,s}^{(2)} \frac{(b_{k}P)}{\left[1 + (b_{k}P)\right]}$$
(1.II.75)

in this equation  $C_{k,s}^{(2)}$  and  $b_k$  are the Langmuir constants and, respectively, the *maximum* adsorption capacity (saturation) and the *affinity coefficient*.

# 1.II.3.2. Usual forms:

$$\theta_k = \frac{(b_k P)}{\left[1 + (b_k P)\right]} \text{ or } \frac{\theta_k}{1 - \theta_k} = b_k P; \qquad (1.\text{II.76})$$

where,  $\theta_k = \frac{C_k}{C_{k,s}}$  (fractional coverage)

the Eq. 1.II.73 for the pure component results:

$$\hat{\phi}_k P = f_k^0 \tag{1.II.77}$$

At pressures on the order of the local atmosphere pressure or lower, the fugacity coefficient tends to unity, and Eq. 1.II.77 presents a remarkable result:

$$P = f_k^0 \tag{1.II.78}$$

that is, the fugacity of the k component in the adsorbent, that of the standard state, is numerically equal to the pressure of the gas phase and equivalent to it, and that applied to a particular isotherm result, for the standard state:

$$C_{k}^{0(2)} = C_{k,s}^{0(2)} \frac{(b_{k}f_{k}^{0})}{\left[1 + (b_{k}f_{k}^{0})\right]}$$
(1.II.79)

allowing to obtain the fugacity in the adopted standard state, and, consequently, to obtain the Interfacial potential by Eq. 1.II.68 below rewritten.

$$\left[\frac{d\hat{f}_{k}^{0(2)}}{dz}\right] = \frac{\hat{f}_{k}^{0(2)}}{C_{k}^{0(2)}} \quad \text{with initial condition } \hat{f}_{k}^{0(2)}(0) = 0$$
(1.II.80)

whose exact solution for the Langmuir isotherm is:

$$f_k^{0(2)} = \frac{1}{b_k} \left[ \exp(\frac{z}{C_{k,s}^{0(2)}}) - 1 \right]$$
(1.II.81)

and still:

$$z = C_{k,s}^{0(2)} \ln(1 + b_k f_k^{0(2)}) = \frac{\Pi^{(2)} a_{m,2}}{RT}$$
(1.II.82)

Thus, a robust link between the *Interfacial potential* and parameters of the pure component isotherm was produced. A few isotherms can provide an analytical solution to Eq. 1.II.80 Almost always a numerical solution must be undertaken. It will be seen later, in the applications section, that the Langmuir equation is incapable of reproducing, with the desired accuracy, a large part of the available experimental data. However, for an equation with only two adjustable parameters it is an extraordinary equation. It is reasonably established, and it is almost evident, that relationships with more adjustable parameters are more powerful. The immediate proposals are modifications of the Langmuir equation, falling back on it, in the case of insignificance of the added parameter.

The *Sips* and *Toth* equations with just one more parameter are suitable:

$$C_{k}^{0(2)} = C_{k,s}^{(2)} \frac{(b_{k} f_{k}^{0(2)})^{\frac{1}{t_{k}}}}{\left[1 + (b_{k} f^{0(2)})^{\frac{1}{t_{k}}}\right]}; \quad (Sips)$$

$$C_{k}^{0(2)} = C_{k,s}^{(2)} \frac{(b_{k} f_{k}^{0(2)})}{\left[1 + (b_{k} f^{0(2)})^{t_{k}}\right]^{\frac{1}{t_{k}}}}; \quad (Toth)$$

$$(1.II.84)$$

It is evident the addition of a parameter,  $t_k$ , which, surprisingly, makes a substantial difference. The Langmuir equation is suitable if  $t_k = 1$ .

Although almost equivalent, it seems to us that Toth's is superior.

The preference for the Sips equation is that it allows an analytical solution to Eq. 1.II.80., representing in consequence an enormous convenience, as can be seen below:

$$f_k^{0(2)} = \frac{1}{b_k} \left[ \exp(\frac{z}{C_{k,s}^{0(2)}}) - 1 \right]^{t_k}$$
(1.II.85)

and still:

$$z = t_k C_{k,s}^{0(2)} \ln[(1 + b_k f_k^{0(2)})^{\frac{1}{t_k}}] = \frac{\Pi^{(2)} a_{m,2}}{RT}$$
(1.II.86)

In the sequence, a routine for the complete specification of the *equilibrium state* is presented, schematized in **3** operational **blocks**.

At the **block 1**, in addition to the parameter data of the pure isotherms, the (m+1) information necessary to eliminate the degrees of freedom, represented by the temperature, pressure and composition of the gas phase, and sufficient to deal with the problem of equilibrium in the case of ideal solutions. If the idealization is not verified, correlations must be provided for the calculation of  $\hat{\phi}_k^{(1)}$  and  $\gamma_k^{(2)}$ .

At the **Block 2**, an iterative calculation determines  $\begin{pmatrix} z, & f_k^{0(2)} & e & x_k^{(2)} \end{pmatrix}$  respectively, the *Interfacial potential*, the *fugacity of the pure component* in the standard state and the *composition* of the solid solution.

At the **Block 3**, other properties of interest are calculated, among them those that are actually sought, the total adsorbed concentration,  $C_t^{(2)}$  and the *fractional coverage* of the k-component of interest,  $C_k^{(2)}$ .

Table 1 summarizes the routine:

Table 1. Routine for determining equilibrium in gas phase adsorption

| Block 1:Input data $C_{k,s}^{(2)}, \mathbf{b}_k, \mathbf{t}_k; \ \kappa=1, 2,, m.$ (pure isotherm) $y_1^{(1)},, y_{m-1}^{(1)}, T, P; \ (m+1)$ necessary informationParameters for the correlations of fugacity<br>coefficients, $\hat{\phi}_k^{(1)}$ and activity $\gamma_k^{(2)}$ .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                                                                                                                                                                                                                                                                                      |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Block 2:<br>equations for equilibrium                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | <b>Block 3:</b><br>supplementary calculations:                                                                                                                                                                                                                                       |
| $\sum_{k=1}^{m-1} \frac{(q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_{k})^{(1)}(1-q_$ | $calculation of C_{k}^{0(2)}:$ $C_{k}^{0(2)} = C_{k,s}^{(2)} \frac{(b_{k}f_{k}^{0(2)})^{\frac{1}{t_{k}}}}{\left[1 + (b_{k}f^{0(2)})^{\frac{1}{t_{k}}}\right]} \text{(Sips)}$ $calculation of C_{t}^{(2)}:$ $\frac{1}{C_{t}^{(2)}} = \sum_{k=1}^{m} \frac{x_{k}^{(2)}}{C_{k}^{0(2)}}$ |
| $\gamma_{k}^{(2)} = \gamma_{k}^{(2)} (T, \dots, x_{k}^{(2)}, \dots); \kappa = 1, 2, \dots, m.$ $y_{k}^{(1)} \hat{\phi}_{k}^{(1)} P = x_{k}^{(2)} \gamma_{k}^{(2)} f_{k}^{0(2)}; \kappa = 1, 2, \dots, m$ <i>calculation of</i> $F = 1 - \sum_{k=1}^{n} x_{k}^{(2)}; \text{ (until convergence, at F=0)}$ $<<<$                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | $C_{k}^{(2)} = x_{k}^{(2)}C_{t}^{(2)}$                                                                                                                                                                                                                                               |

In the case of equilibrium, in liquid phase adsorption, the routine is the same, replacing in **block 2** the chemical equilibrium equation by:

$$x_k^{(1)} \gamma_k^{(1)} P_k^{sat} = x_k^{(2)} \gamma_k^{(2)} f_k^{0(2)}$$
(1.II.87)

and compatible changes in **block 1**.

The routine suggested in Table 1. it only illustrates the practical use of the formulation and a didactic approach to conduct, reminding the reader of the difficulty of producing these results with first-generation personal computers and primitive languages for mathematical calculations. At the moment with the available computing power, elaborate languages, the results are just waiting for the execution key to be pressed.

# **1.II.3.3.** specific applications

Example e.1.II.1. Binary solutions governed by the Langmuir equation in an ideal solid/gas system.

| Table e.1.II.1. Routine for binaries (solid/gaseous) Langmuir-ideal |                                                                                                                                                                  |                                                                                                |  |  |  |
|---------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------|--|--|--|
| Block 1:                                                            | Block 2:                                                                                                                                                         | Block 3:                                                                                       |  |  |  |
|                                                                     | $\frac{equilibrium equalions}{v = 1 - v}$                                                                                                                        | $\frac{supplementary\ calculations}{(\frac{z}{2})}$                                            |  |  |  |
| <i>pure isotherm</i><br>$C_{s_1, b_1}$ :for component 1             | $y_2 - 1  y_1$                                                                                                                                                   | $fo_1 = \frac{\mathbf{e}^{\left(\overline{cs_1}\right)} - 1}{b_1};$                            |  |  |  |
| $Cs_2, b_2$ : for component 2;                                      | $\mathbf{v}, P = \frac{x_1 \left( \mathbf{e}^{\left( \frac{\overline{c}}{cs_1} \right)} - 1 \right)}{\mathbf{e}^{\left( \frac{\overline{c}}{cs_1} \right)} - 1}$ | $fo_2 = \frac{\mathbf{e}^{\left(\frac{z}{Cs_2}\right)} - 1}{\frac{z}{Cs_2} + \frac{z}{Cs_2}};$ |  |  |  |
| $y_1$ , T and P;                                                    | $\begin{pmatrix} & b_1 \\ & & \begin{pmatrix} \frac{z}{Cs_2} \end{pmatrix} \end{pmatrix}$                                                                        | $Co_1 = \frac{Cs_1 b_1 fo_1}{1 + b_1 fo_2};$                                                   |  |  |  |
|                                                                     | $(1 - y_1) P = \frac{x_2(\mathbf{e}^{(1-y_1)} - 1)}{b_2}$                                                                                                        | $Co_2 = \frac{Cs_2 b_2 fo_2}{Cs_2 b_2 fo_2};$                                                  |  |  |  |
|                                                                     | $x_1 + x_2 = 1$                                                                                                                                                  | $Ct = \frac{1}{1 + b_2 f o_2}$                                                                 |  |  |  |
|                                                                     | obtaining: $y_2, z, x_1, x_2$                                                                                                                                    | $\frac{x_1}{Co_1} + \frac{x_2}{Co_2}$                                                          |  |  |  |

For systems satisfying these conditions the calculation procedure is simply given by:

can be solved even with "Microsoft Excel" with the solver add-in.

In the sequence we will present an equilibrium problem (solid-gas) for the system: Ethane (1) and Ethylene (2) in activated carbon at T=333K and P=101kPa, using the routine in Table e.1.II.1:

- 1- with the Langmuir isotherm and ideal system;
- 2- with the Thoth isotherm and ideal system.

Entering the necessary data and calculating results:



Figure e.1. Ideal solutions and formulation by Langmuir



Figure e.2. Ideal solutions and formulation by Toth

Figures (a) and (b), of the respective cases, show that there is not a substantial difference between the two models and this can also be observed with other isotherm models. They are not very relevant to the calculation of these parameters at equilibrium. Figure (c) shows the relevance of a more accurate model, since the equilibrium data, although almost identical, will feed different isotherm models (Block 3), there they will make an important difference, since the most relevant equilibrium parameter is precisely the amount adsorbed per mass of adsorbent, that is, figure (c) is the true isotherm. At this point, a criticism that is made in the sense of orientation, as we ourselves have already stumbled on this, is in order. We built isotherm models and only tested for equilibrium data of the type shown in figure (a), but when we applied it to data of the type of figure (c) we were surprised by the failure of the result.

Example e.1.II.2. Binary solutions governed by the Langmuir equation in an ideal solid/*liquid* system.

For systems satisfying these conditions the calculation procedure is practically the same as for the solid/gas situation; using  $P_i^{sat}$  in place of P and keeping,  $y_1$  in place of  $x_1^{(1)}$ , to ease the notation, being simply given by:

| Table e.1.II.2. routine for binaries (solid/liquid) Langmuir-ideal |                                                                                                                                     |                                                                    |  |  |
|--------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------|--|--|
| Block 1: <i>Input data</i> Block 2:                                |                                                                                                                                     | Block 3:                                                           |  |  |
|                                                                    | equilibrium equations                                                                                                               | supplementary calculations                                         |  |  |
| pure isotherm                                                      |                                                                                                                                     |                                                                    |  |  |
| $C_{s_1, b_1}$ : for component 1                                   | $y^2 = 1 - y_1$                                                                                                                     | $\left(\frac{z}{Cs_1}\right)$                                      |  |  |
| $Cs_2, b_2$ : for component 2;                                     | $x_{i} = x_{i} \left( \mathbf{e}^{\left(\frac{z}{Cs_{i}}\right)} - 1 \right)$                                                       | $fo_1 = \frac{e^{(1)} - 1}{b_1};$                                  |  |  |
| $y_1$ , T and P;                                                   | $y_1 Fsat_1 = \frac{b_1}{b_1}$ $(1 - y_1) Psat_2 = \frac{x_2 \left(\mathbf{e}^{\left(\frac{z}{Cs_2}\right)} - 1\right)}{c_1 - c_2}$ | $fo_2 = \frac{\mathbf{e}^{\left(\frac{z}{Cs_2}\right)} - 1}{b_2};$ |  |  |
|                                                                    | $x_1 + x_2 = 1$ $b_2$                                                                                                               | $Co_1 = \frac{Cs_1 b_1 fo_1}{1 + b_1 fo_1};$                       |  |  |
|                                                                    | <i>obtaining</i> : $y_2, z, x_1, x_2$                                                                                               | $Co_2 = \frac{Cs_2 b_2 fo_2}{1 + b_2 fo_2};$                       |  |  |
|                                                                    |                                                                                                                                     | $Ct = \frac{1}{\frac{x_1}{Co_1} + \frac{x_2}{Co_2}}$               |  |  |

In the sequence we will present an equilibrium problem (solid/liquid) for the system: Benzene (1) and Cyclohexane (2) in activated carbon at T=303K.



Figure e.3. Ideal solutions and formulation by ideal Langmuir

Phenomenologically, there is an acceptable description, but a poor representation of the isotherm with high deviations at concentrations below 60% in the external phase. It is possible to show that a non-ideality assumption to the *solid solution* and/or *liquid solution*, with an appropriate correlation, greatly improves the accuracy of the prediction. This is

shown in figure e.4.



Figure e.4. Non-ideal solutions and formulation by Langmuir.

The correction was made assuming only non-ideality of the *liquid phase* and the correlation was used;

$$\frac{G^{E(1)}}{RT^{(1)}} = B(T^{(1)})x_1^{(1)}x_2^{(1)} \quad \text{implying in} \quad \ln(\gamma_k^{(1)}) = B(1-x_k^{(1)})^2 \tag{1.II.88}$$

remembering that, in simplified notation, we have:  $y_1$  in place of  $x_1^{(1)}$ .

and so,

$$\ln(\gamma_1^{(1)}) = B(1 - y_1)^2$$
 and  $\ln(\gamma_2^{(1)}) = B(y_1)^2$  (1.II.89)

### **1.II.3.4.** Adsorption Theory in Ideal Solutions

The assumption of ideality in the phases gives them a connotation of ideal solution and, thus, a particular case of the formulation presented here is the *Ideal Adsorption Solution Theory* (**IAST**). In which one works only with isotherms of k pure component without any appeal to ideality corrections. For the initial estimation of the design of an adsorption system, it is possible to use an IAST, relieving the technical and computational work, allowing a quick preliminary analysis, recommending or not a more elaborate form. However, frequent cases of inversion of selectivity, also called *azeotropy*, require a more elaborate formulation. Later in this text, we intend to present possible criteria for the identification of systems likely to present such an inversion of selectivity. In the sequence, we present cases with this characteristic. In figure e.5. (d) we have literature data<sup>6</sup> and in (a), (b) and (c) data, calculated by us, using correlations for the activity coefficient for the *solid solution*.

<sup>&</sup>lt;sup>6</sup>Hyun, SH; Danner, RP; J. Chem. Eng. Date 1982, 27,196-200.



Figure e.5. non-ideal solutions

Interestingly, Hyun and Danner (1982) claim that none of the models they tested predicted the slight azeotropic behavior found experimentally at 298K for  $C_2H_4$ -CO<sub>2</sub>. In figure e.5.(a) it is clear that this can be predicted, providing solid phase non-ideality information based on the Wilson correlation shown in figure e.5.(e).

Multicomponent cases can of course be handled by the formulation developed here. However multicomponent systems are not as plentiful as binaries. A few do not always present all the necessary data as they follow the specific purpose and planning of the researchers and cannot be fully used. In this sense, many difficulties appear and, so that it does not seem just an ambitious proposal, we intend to appreciate at least ternary systems.

## 1.II.3.5. Ternary Systems in Ideal Solutions

The first difficulty is that, as seen, a multi-constituent system has (m+1) degrees of freedom. In the case of ternaries, we have m=3 and there will be 4 degrees of freedom. The bulk phase is when variables can be more easily fixed and controlled. If temperature and pressure are set as is of interest two compositions should be set out of 3 and so experimentation is very limited. We found difficulties even in simulations, let alone in experimental planning and execution, which may be one of the reasons why we do not have so many multicomponent experimental results. Since the formulation basically needs isotherms of pure components, the simulation only depends on the search for these data. For the illustration that we will do next, we will use binary studies in which various components were used in the compositions of binary pairs even though ternary data are not there. In this sense we will use data already studied in the previous section, as they fully meet. In figure A1, are shown the experimental data of Hyun and Danner (1982) which we fit by the Sips isotherm. Similar results will be found there for other temperatures: figure A2.



Figure A1. Pure component isotherms in 13X molecular sieve at 298 K



Figure A2. Pure component isotherms in 13X molecular sieve at 323 K

From these data we will treat the ternary system  $CO_2 C_2H_4$  and  $C_2H_6$  among other combinations. First, however, we want to share some observations we made on this dataset. Note that isobutane (i-C<sub>4</sub>H<sub>10</sub>) cuts all other isotherms; This may be the reason why it

presents inversion of selectivity with the other components or, at least, strong non-ideality in the adsorbed phase. At low pressures  $CO_2$  also cuts  $C_2H_4$ , that is, we are saying that the isotherms of pure components can perhaps give more information than the usual ones. Based on these data, we developed a mathematical criterion for the analysis of pure isotherms, using only the adjusted parameters, which would indicate the existence of strong non-ideality in the adsorbed phase and even the existence of azeotropy. It was tested only with these data, not being scientifically sufficient, however a search for systems showing azeotropy could confirm the proposition. That said, here's an illustration with the proposed system: $1(CO_2)$ ,  $2(C_2H_4)$  and  $3(C_2H_6)$  in13X molecular sieve at 298 K, in line with pure component isotherms as shown in Figure A1.

Even understanding that the system is most likely not ideal in the adsorbed phase as discussed above, it will be considered ideal in both phases for simulation purposes and in terms of adjustments by the Sips isotherm as in figure A1. The algorithm for performing the calculations is shown in table A.1.

| Table A.1. Routine for ternaries (solid/gaseous) Sips-ideal |                                                                                            |                                                                                        |  |  |  |
|-------------------------------------------------------------|--------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------|--|--|--|
| Block 1: Input data:                                        | Block 2:                                                                                   | Block 3:                                                                               |  |  |  |
| -                                                           | <u>equilibrium equations:</u>                                                              | supplementary calculations:                                                            |  |  |  |
| pure isotherm                                               |                                                                                            |                                                                                        |  |  |  |
| $Cs_1, b_1, t_1$ : for component 1                          | $y_3 = 1 - y_1 - y_2$                                                                      | $\mathbf{e}^{\left(\frac{z}{Cs_1}\right)} - 1$ :                                       |  |  |  |
| $Cs_2, b_2, t_2$ : for component 2                          | $\left( \left( \frac{z}{z} \right) \right)$                                                | $fo_1 = \frac{b_1}{b_1}$                                                               |  |  |  |
| $Cs_3, b_3, t_3$ : for component 3;                         | $y_1 P = \frac{x_1 \left( \mathbf{e}^{(C_1)} - 1 \right)}{b_1};$                           | $fo_2 = \frac{\mathbf{e}^{\left(\frac{z}{c_2}\right)} - 1}{b_2};$                      |  |  |  |
| $y_1, y_2$ , T and P.                                       | $(1-y_1) P = \frac{x_2 \left( \mathbf{e}^{\left(\frac{z}{Cs_2}\right)} - 1 \right)}{b_2};$ | $fo_3 = \frac{\mathbf{e}^{\left(\frac{z}{Cs_3}\right)} - 1}{b_3};$                     |  |  |  |
|                                                             | $(1 - y_1 - y_2) P = -\frac{b_3}{b_3}$<br>$x_1 + x_2 + x_3 = 1$                            | $Co_1 = \frac{Cs_1 b_1 fo_1}{1 + \_b_1 fo_1};$                                         |  |  |  |
|                                                             | obtaining:                                                                                 | $Co_2 = \frac{Cs_2 b_2 fo_2}{1 + b_2 fo_2};$                                           |  |  |  |
|                                                             | $y_3, z, x_1, x_2, x_3$                                                                    | $Co_3 = \frac{Cs_3 b_3 fo_3}{1. + b_3 fo_3};$                                          |  |  |  |
|                                                             |                                                                                            | $C_{t} = \frac{1}{\frac{x_{1}}{Co_{1}} + \frac{x_{2}}{Co_{2}} + \frac{x_{3}}{Co_{3}}}$ |  |  |  |

$$C_k^{(2)} = C_{k,s}^{(2)} \frac{(b_k P)^{\frac{1}{t_k}}}{\left[1 + (b_k P)^{\frac{1}{t_k}}\right]}$$
; **Sips** isotherm

| Table A.2. parameter values adjusted by the Sips isotherm |                  |                      |        |  |
|-----------------------------------------------------------|------------------|----------------------|--------|--|
| k                                                         | Ck,s (mmol/gads) | b <sub>k</sub> (kPa) | $t_k$  |  |
| CO <sub>2</sub>                                           | 5.0578           | 0.0763               | 1.6395 |  |
| C <sub>2</sub> H <sub>4</sub>                             | 3.1229           | 0.1937               | 1.4286 |  |
| i-C <sub>4</sub> H <sub>10</sub>                          | 2.0563           | 2.2377               | 2.5279 |  |
| C <sub>2</sub> H <sub>6</sub>                             | 2.5224           | 0.0469               | 0.7865 |  |

Another difficulty in multicomponent systems is the presentation of equilibrium data in a pictorial form as we often do. In the case of ternaries, we believe, as discussed earlier in the text, that it is still possible if we use the *Gibbs ternary diagram*. In this sense, the data resulting from the simulation of the system under study will be made available as follows:



Figure A3. Representation of equilibrium states in ternary systems: (+) gas phase; (0) adsorbed phase.

It should be immediately noted that they are not equilibrium diagrams in the usual sense and thus the lines are not real conodal lines (tie lines) but only indicative of the correspondence between the equilibrium states relative to the values of the compositions in each phase, being only a resource for analysis. It is easy to see in Figure A3 the nature of the arbitrary composition of the gas phase. In a) the composition of the gas phase is high in component  $3(C_2H_6)$  in b) c) and d) median values. Graphic representations like these were very useful in analyzing our results for ternaries in ion exchange. It is evident that individual component-by-component analyzes are interesting and appropriate as shown by the  $CO_2$  partition in the traditional xy diagram in figure A4.

Figure A4. (b) immediately shows the imperfection of this type of representation because due to the limitation of the variation range of component  $1(CO_2)$  so that the other components can be accommodated, it ends up showing only the arbitrated compositions and is only acceptable depending on the particular choice we made of the composition of the gas

phase as shown in Figure A4. (a). In order to better understand the problem posed, we will present the result for another choice of gas phase composition, figure A5.



Figure A4. (a) Equilibrium in the ternary adsorption of  $CO_2 C_2H_4$  and  $C_2H_6$ (b) Prediction of  $CO_2$  partition.



Figure A5. (a) Equilibrium in the ternary adsorption of CO<sub>2</sub> C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> (b) Prediction of CO<sub>2</sub> partition.

7 states of the gas phase were chosen, keeping the concentration of  $CO_2$  constant. There are, therefore, 7 different states for the adsorbed phase, resulting in the partition of  $CO_2$  the figure at the side (b) which, even if correct, will have very little use. We believe that in the ternary case the Gibbs diagram will be the best graphical representation to show the equilibrium states completely. Exploring the information from the visualization in this diagram will be the task to be undertaken from now on. In the particular case of this ternary system, it is instructive to observe some characteristics. Considering the results shown in figures A4 and A5 and specifically figure A6(a) it is possible to affirm that the states in the adsorbed phase are presented preferentially in the upper part of the figure, moving to the left. Indicative that it is efficient in the removal of  $CO_2$  and partially in the removal of  $C_2H_4$ , justifying the search for experimental data that confirm the prediction.

Since it is interesting to think about a PSA process for the removal of  $CO_2$ , it is opportune to appreciate the effect of pressure on equilibrium, this simulation is shown in figure A6.



Figure A6. Equilibrium in the ternary adsorption of  $CO_2 C_2H_4$  and  $C_2H_6$ : pressure effect.

As the pressure of 20 atm most likely affects the ideality of the gas phase, more rigorous results demand correction through the fugacity coefficient.

In table A.2 we have data available for 4 components and thus a quaternary simulation can be undertaken and the data presented in pseudo ternary diagrams. like what we use<sup>7</sup> in the study of the phase equilibrium of the system: microemulsion-water-oil.

It will not be possible to close this chapter without referring to the great advance provided by the electronic microprocessing of our computers. And consequently, the tools of statistical thermodynamics and molecular simulation. In this sense, aiming at a junction between what is being proposed here and this admirable electronic laboratory in which our computer was constituted, we suggest:

1-Make use of molecular simulation to obtain the isotherms of pure components, which is practically the only laboratory effort we need to evaluate the multicomponent equilibrium as we have just exemplified;

2- Adopt the classic correlations to represent non-idealities, such as those used here: Margules and Wilson and predict their parameters for direct application in the formulation;

3- Elaborate along the lines of the theory of *regular solutions* (Scatchard-Hildebrand), adopting states of the pure gaseous or liquid components as *hypothetical solids* and provision *molar volumes* and *solubility parameters* of the pure components in this hypothetical state to describe non-ideality of the adsorbed phase.

<sup>&</sup>lt;sup>7</sup>Gubulin, JC (1980) Contribution à l'analyse transitoire du transfert de matière dans un système microémulsion eau-huile. Thèse de Docteur Ingénieur, IGC de L'INPT (Toulouse-France)

# CHAPTER 2 MASS TRANSFER KINETICS

## **2.1. Introduction**

As we warned in the preface regarding the interdependence between Kinetics and Transport Phenomena, we will have to inform the reader that he should go to Chapter 3 and read until item 3.2-*The transport equations* from which we will pinch the following extract:

Mass balance of k component in  $\alpha$  phase

$$\frac{\partial}{\partial t} \left[ \upsilon_{\alpha} C_{k,\alpha} \right] + \operatorname{div} \left[ \vec{\varphi}_{k,\alpha} \right] = \upsilon_{\alpha} R_{k,\alpha}$$
(2.1)

with,

$$\vec{\varphi}_{k,\alpha} = C_{k,\alpha} \vec{v}_{k,\alpha}$$

where,  $\vec{v}_{k,\alpha} = \vec{\varphi}_{k,\alpha}$  are, respectively, the local velocity vector of the k chemical species inside the  $\alpha$  phase, and, the local mass flux density vector of the k chemical species inside the  $\alpha$  phase.

It is not intended to go beyond what is already well formulated. In this sense, it is important to remember the system that most recovers results from well-established and tested formulations.

1- model at the level of a Particle; model 1.

2- model at the level of a set of particles, model 2.

A particle should be understood as a representative individual of the dispersed phase and characterized by: a *size*, a *shape* and a *chemical composition*; it can be a bubble, a drop, or a solid fragment. Some authors, not many, call model 1 the microscopic model and model 2 the macroscopic model. We do not appreciate this terminology, as it conflicts with these concepts defined in thermodynamics, where microscopic concerns atomic coordinates and, macroscopic, a statistical process of averaging myriads of atomic coordinates, which generate macroscopic parameters. In a notation that still makes mention of these references we will simply adopt a *micro model* for **model 1** and a *macro model* for **model 2**.

As in Chapter 1, the subject will be treated in two parts, as specific cases of the formulation:

- Part I- Electrolytic systems;
- Part II- Non-electrolytic systems.

The main objective of this methodology *micro-macro* is obtaining model parameters through simple independent experiments, as shown in the literature. The *micro model* usually names the kinetic mechanism and the *macro model* the equipment or installation. In adsorption, for example, we have the *pore diffusion model* for the micro system and the *fixed bed adsorption column* for the macro system, among many.

# CHAPTER 2 Part I. Electrolytic Systems, Electrochemical Kinetics

## 2.I.1.-Preliminary considerations

The practical use of electrochemical systems is always associated with some electrochemical reaction proceeding in one direction at a finite rate. Natural electrochemical processes such as the corrosion of metals under the influence of the environment also evolve in one direction and at a finite rate. In both cases the electrochemical systems are not in equilibrium and their properties are completely different from those corresponding to systems in equilibrium. Since the overall reaction in the electrochemical system is composed of the reactions at the electrodes, the behavior of each of the electrodes under irreversibility conditions must differ from their behavior under equilibrium conditions. Under equilibrium conditions the rate at which a reaction progresses, at the electrode, in the anodic direction and in the cathodic direction is the same. Since an electrochemical reaction involves the transfer of charged particles, the frequency of transfer of the particles in both directions must be equivalent to a certain amount of current. At equilibrium you will have:  $I_a = I_c = I_0$ , where the currents  $I_a$  e  $I_c$  correspond, respectively, to the anodic and cathodic processes.

 $I_0$  is called the exchange current. The exchange current characterizes the kinetics of ion exchange under equilibrium conditions. The fact that the two reaction rates are identical and in opposite directions, on the same electrode, implies that there are no qualitative and quantitative changes in the composition of the system. Since the partial currents,  $I_a \in I_c$  are equal, then, under kinetic equilibrium conditions the electrode potential is independent of time and determined only by the temperature, pressure, composition and electrical state of the system. The electrode potential  $E_{0,m}$  under these conditions is called the reversible electrode potential or equilibrium electrode potential and can be calculated via thermodynamics.  $E_0$ , likewise, through thermodynamics, can be determined by the Gibbs free energy of reaction.

Under non-equilibrium conditions the electrochemical reaction progresses in a given direction at a finite rate and it turns out that:  $I_a \neq I_c \neq I_0$  and, thus, neither of the two partial currents is identical to the exchange current and one of the two conditions is being verified:  $I_a > I_c$  ou  $I_a < I_c$ . In the first condition, the reaction at the electrode evolves predominantly in the anodic direction. In the second condition it will evolve predominantly

in the cathodic direction. Thus, because the reaction progresses predominantly in one direction or the other, the mass and compositions of the metal and the solution in the vicinity of the interface change with time. The electrode potential  $E_m(I)$  is generally not equal to the equilibrium potential  $E_{0,m}$  and cannot be calculated thermodynamically; its value depends not only on the conditions of composition, temperature and pressure, but mainly on the value of the current intensity. E(I), likewise, will be different from that of the equilibrium state,  $E_0$ , and cannot be calculated thermodynamically. Thus, for irreversible electrochemical processes, or cells,

## 2.I.2.- Faraday's laws

Since the passage of electric current through electrochemical systems, or cells, promotes chemical reactions, there must be a relationship between the amount of electric charge and the amount of mass reacted. For any electrochemical reaction to occur in a cell, electrons must pass through a circuit connecting the two electrodes. For this reason, the current I is a convenient measure of the rate of reaction in the cell while the charge Q=I $\Delta$ t, which passes over a period of time  $\Delta$ t, indicates the total amount of reaction that has taken place. The results of these investigations can be summarized, according to Faraday, in the following laws.

1 - The quantity, that is, the mass of the electrolyzed substance is directly proportional to the charge that crosses the solution;

2 - Using the same charge, the mass of the electrolyzed substance is directly proportional to the respective equivalent weight, Eg, of substance.

The following equations result from these laws:  $m = K_1 Q$  and  $m = K_2 E_g$  whence:

$$m = \frac{M_k}{Fz_k} I\Delta t$$
(2.I.1)

where  $M_k$  is the molecular weight of the metal,  $z_k$  is the oxidation number and F=96485Coulombs/(mol) is Faraday's constant.

Eq. 2.I.1 is fundamental in electrochemistry and is generally used as a limiting condition for efficiency calculations.

#### **2.I.3.-** Electrode Overpotential

When a current of electrons flows through an electrode, which was previously at an equilibrium potential  $E_{0.m}$ , in which no current was flowing, there is a potential displacement given by:

$$\eta = E_{m}(I) - E_{0,m}$$
(2.I.2)

When the referred overpotential,  $\eta$ , originates from the deposition process, it is called the deposition overpotential. In general, even at low current densities, an equilibrium potential shift occurs and its magnitude depends on the working conditions and the nature of the ion reduction process. The presence of an overpotential makes the cathode deposition potential more negative.

The total overpotential observed at the electrode is basically composed of three factors:

-concentration overpotential -ohmic overpotential -activation overpotential

## concentration overpotential, nc

If chemical reactions occur in the electrolyte, which are independent of the potential, there will be a decrease in the concentration of active species, generating a reaction overpotential, $\eta_r$ . This chemical reaction can proceed either homogeneously or heterogeneously on the electrode surface. If the mass transport (of the active species) to or from the electrode surface is the slowest step, a diffusion overpotential will arise,  $\eta_d$ . It is the sum of the diffusion and reaction overpotentials which is called the concentration overpotential,  $\eta_c$ 

## <u>ohmic overpotential</u>, ηΩ

When the electrode is coated with a poorly conductive film, such as a layer of oxide, sulfate, insoluble salt, grease, gas or other insulating material, or a layer of poorly conductive liquid, the resistance of these layers differs from that of the electrolyte. In practice, this is indicated by an increase in the potential required for the deposition process. During the deposition process there is also a certain distance between the positioning of the cathode and the anode so that there will always be an additional resistance due to the resistivity of the electrolyte.

# activation overpotential, na

As discussed, the overall reaction at an electrode is composed of a series of partial reactions, at least one of which is a reaction in which charge carriers (electrons or ions) are transferred through the electrical double layer; such reactions are therefore called charge transfer reactions. The rate of these charge transfer reactions is determined by the potential

difference across the electrical double layer and is of fundamental importance in electrochemical kinetics, since it is the only reaction directly affected by the electrode potential. These charge transfer reactions generate an overpotential known as charge transfer overpotential or, simply, Activation Overpotential,  $\eta_a$ .

## 2.I.4.-Kinetics and controlling factors

There are several steps involved in an electrodeposition process, starting with the hydrated ion within the solution and ending with the metal atom incorporated into the metallic structure at the cathode. The slowest step will decide the overall rate of reaction and is called the "determining step". The slowness of a step is equivalent to a "resistance" offered to the deposition process and is observed through an overpotential.

Consider the electrode reaction of the type  $O + ne \leftrightarrow R$ , where O is the species that is reduced to R and R is the species that is oxidized to O. This reaction will therefore be governed by the rate of the following mechanisms:

- Mass transport of the species O from inside the solution to the surface of the electrode or of the species R from the surface of the electrode to the interior of the solution.

- Transfer of electrons on the electrode surface causing the reduction of the O species to R or the oxidation of R to O.

These mechanisms are shown schematically in Fig. 2.I.1:



FIGURE 2.I.1 - Schematic representation of the processes involved during the reduction of an O to R species.

In this way, the rate of the reaction will be controlled by whichever step is slower and the reaction will be controlled by either *Transport* (mass transport) or by *activation* (electron transfer).

#### Activation control

Consider again the electrochemical reaction at the electrode  $O + ne \leftrightarrow R$  that takes place in a cell, as shown schematically in Fig. 2.I.2. below.



FIGURE 2.I.2. - Schematic representation of a cell.

This cell contains two electrodes, one for working,  $E_w$ , with a smaller area and made of inert material (Platinum) and another for reference of the Normal Hydrogen Electrode type (NHE). The solution in the  $E_w$  compartment is deoxygenated and contains low concentrations of  $C_O$  and  $C_R$  of electroactive species O and R. In this way, the cell characteristics are determined only by the variations of the properties on the  $E_w$  surface. If the two electrodes are connected and the cell potential is monitored, it will be verified that after some time the potential of the working electrode will reach a stationary value, indicating that the cell is in equilibrium. At this time the  $E_w$  potential will be in agreement with the *Nernst equation*.

$$E_{eq} = E_{o,m} = E_m^0 + \frac{RT}{nF} \ln\left(\frac{C_o}{C_R}\right)$$
(2.I.3)

where the equilibrium potential,  $E_{eq}$ , is related to the standard potential,  $E_m^0$ , of the O/R pair and the surface concentrations, C<sub>0</sub> and C<sub>R</sub>, of O and R.

It is clearly observed that the equilibrium potential assumes the value of the standard potential when  $C_0$  and  $C_R$  are equal. It is also observed that when equilibrium is reached, the current indicated on the ammeter is zero. However, this equilibrium is dynamic, that is, in reality, an oxidation and a reduction reaction continue to occur, however, with the same intensity and opposite directions. If the  $E_w$  potential is shifted to values more negative than the equilibrium potential, according to the Nernst Equation, in order for equilibrium to be reestablished, there must be an increase in the concentration of R, which is obtained by the conversion of O into R, generating a cathodic current. On the contrary, if the  $E_w$  potential is shifted to values more positive than the equilibrium one, an anodic current will be generated, due to the conversion of R to O.

The rate of reduction of O, written in terms of *current densities*, depends on a constant rate, k, and on the surface concentration  $C_0$ . The reduction current density, therefore, can be given by:

$$i_a = \frac{I}{A} = nFkC_o$$
 where  $k = k_o \exp\left[-\left(\frac{\alpha nF}{RT}E_m\right)\right]$  (2.I.4)

In these equations A is the area of the electrode, k is a parameter that depends on the electric field near the electrode surface, and, consequently, on the electrode potential,  $E_m(I)$ , and  $\alpha$  is the *charge transfer coefficient*.

The reduction current density equation then takes the form

$$i_{a} = nFk_{o}C_{o} \exp\left[-\frac{\alpha nF}{RT}E_{m}\right]$$
(2.I.5)

For the oxidation reaction, following the same procedure, we arrive at the equation

$$\dot{i}_{c} = nFk_{R}C_{R} \exp\left[\frac{(1-\alpha)nF}{RT}E_{m}\right]$$
(2.I.6)

so that the resulting current density i will be given by the difference between the reduction and oxidation current density. One can write:

$$i = nF \left\{ k_o C_o \exp \left[ -\frac{\alpha nF}{RT} E_m \right] - k_R C_R \exp \left[ \frac{(1-\alpha)nF}{RT} E_m \right] \right\}$$
(2.I.7)

The graphical representation of these functions is shown in Fig. 2.I.3., in order to visualize the behavior of the anodic and cathodic currents and the resulting curve of the total current density. The exchange current density and the equilibrium potential are also shown,  $E_{0,m} = E_{eq}$ .



FIGURE 2.I.3. - Graphic representation of current variation with potential Since at equilibrium the resulting current is zero, we have:

$$i_{0} = nFk_{o}C_{o} \exp\left[-\frac{\alpha nF}{RT}E_{eq}\right] = nFk_{R}C_{R} \exp\left[\frac{(1-\alpha)nF}{RT}E_{eq}\right]$$
(2.I.8)

so that if an overpotential is defined  $\eta = E - E_{eq}$ , which can be considered as the  $E_w$  potential using the equilibrium potential of the O/R pair as a reference, a simpler and fundamentally more important equation can be obtained.

$$\mathbf{i} = \mathbf{i}_0 \left\{ \exp\left[-\frac{\alpha nF}{RT}\eta\right] - \exp\left[\frac{(1-\alpha)nF}{RT}\eta\right] \right\}, \quad \mathbf{i}_0 = nFk_0C_0 \quad (2.I.9)$$

which is known as the *Butler-Volmer equation* and which presents an IE relationship as long as the standard potential of the O/R pair, the exchange current density and the charge transfer coefficient,  $\alpha$ , are known.

For the case in which clearly a process of electrodeposition, the Butler-Volmer equation boils down to:

$$i = i_0 \exp\left[-\frac{\alpha nF}{RT}\eta\right]$$
(2.I.10)

so that, changing to logarithmic form and explaining  $\eta$ , we get:

$$\eta = a + b \log i \tag{2.I.11}$$

expression, known as the Tafel equation, where:

$$a = \frac{2.3RT}{\alpha nF} \log(i_0) \text{ and } b = \frac{2.3RT}{\alpha nF}$$
(2.I.12)

making it possible, as shown in Fig. 2.I.4., the calculation of the value of the *charge transfer coefficient*, from the angular coefficient of the linear region of the curve obtained, and the *exchange current density*, by extrapolation of the linear region on the log (i) axis for zero overpotential.



#### FIGURE 2.I.4. - Representation of the Tafel curve.

#### Control by mass transport

In general, in an electrochemical system, it is necessary to consider three modes of mass transport;

- Diffusion: when the movement of species occurs due to a concentration gradient;

- Migration: when the movement of charged species occurs due to an electrical potential gradient;

- Convection: when the movement of species occurs due to a gradient of mechanical forces.

Thus, relative to a fixed coordinate system, the total mass flux density of k species within a  $\alpha$  phase, the *Nernst-Planck* equation is given:

$$C_{k,\alpha}\vec{v}_{k,\alpha} = -D_{k,\alpha}\operatorname{grad}C_{k,\alpha} - Fz_k\mu_{k,\alpha}C_{k,\alpha}\operatorname{grad}\Phi_{\alpha} + C_{k,\alpha}\vec{v}_{\alpha} \qquad (2.I.13)$$

In this equation,  $C_{k,\alpha}$ ,  $\vec{v}_{k,\alpha}$ ,  $D_{k,\alpha}$ ,  $\mu_{k,\alpha}$  e  $\vec{v}_{\alpha}$  are, respectively, the mass concentration of the k component inside the  $\alpha$  phase, the velocity of the k component inside the  $\alpha$  phase, the diffusion coefficient of the k component inside the  $\alpha$  phase, the mobility of the k component inside the  $\alpha$  phase, and the  $\alpha$  phase velocity. The first term on the right represents the contribution due to phase diffusion, the second term represents the contribution due to ionic migration and the third term due to convective mass transfer.

If a given chemical species is an ion, with a charge number  $z_k$  and a molecular mass  $M_{k}$ , then due to the movement of this chemical species there will be associated with this movement an ionic current inside the  $\alpha$  phase, given by:

$$\vec{i}_{k,\alpha} = F \frac{Z_k}{M_k} C_{k,\alpha} \vec{v}_{k,\alpha}$$
(2.I.14)

Eqs. 2.I.13. and 2.I.14. apply correctly to the core of the solution. However, in the immediate vicinity of the electrode, in the inner layer, the potential gradient is zero and, therefore, the second term can be disregarded. The fluid (electrolyte) velocity at the electrode surface is zero, so the third term can also be neglected. So you will have:

$$\vec{i}_{k,\alpha} = F \frac{Z_k}{M_k} \left( -D_{k,\alpha} \operatorname{grad} C_{k,\alpha} \right)$$
(2.I.15)

Assuming that the diffusion process occurs only in the hydrodynamic boundary layer of thickness  $\delta$ , that the concentration profile of species k within this layer is approximately linear where  $C_{k,\alpha} \in C_{k,\alpha}^*$  are, respectively, the concentrations; at the edge of the boundary layer (both of the solution) and the immediate vicinity of the electrode and that, in this layer,

the mass flow has a direction normal to the electrode surface so that a local average charge transfer density can be defined,  $i_{k,\alpha}^*$ , then:

$$\dot{i}_{k,\alpha}^{*} = -F \frac{Z_{k}}{M_{k}} D_{k,\alpha} \left[ \frac{(C_{k,\alpha} - C_{k,\alpha}^{*})}{\delta} \right]$$
(2.I.16)

It is observed in this equation that, when  $C_{k,\alpha}^*$  tends to zero, either as a function of the slowness of the mass transfer process or the speed of the intrinsic kinetics on the surface, the current density reaches a threshold value defined as *limit current Density* given by the expression:

$$i_{\lim} = -F \frac{z_k}{M_k} D_{k,\alpha} \frac{C_{k,\alpha}}{\delta}$$
(2.I.17)

It is therefore possible to better understand an IE curve, such as the one represented by the Butler-Volmer in Fig. 2.I.3., when the potential variation range is extended, reaching the *limit current density*. This result is best represented in Fig. 2.I.5.



FIGURE 2.I.5. - Representation of the IE curve indicating the region in which the limit current is reached.

It is also interesting to represent the kinetics of the reaction in terms of the local rate of mass production of the k chemical species, per unit area of reaction,  $r_{k,\alpha}$ . It is easy to verify that:

$$\mathbf{r}_{\mathbf{k},\alpha} = \mathbf{i}_{\mathbf{k},\alpha}^* \frac{\mathbf{M}_{\mathbf{k}}}{\mathbf{z}_{\mathbf{k}} \mathbf{F}}$$
(2.I.18)

mixed control

When one of the mechanisms does not clearly prevail, either intrinsic kinetics or mass transport, the control will be mixed. Thus, both intrinsic kinetics and mass transport must be taken into account. Under these conditions, kinetic and transport expressions must be provided in order to complete the problem formulation.

The kinetic expression can be given, for example, by the Butler-Volmer equation:

$$i_{k,\alpha}^{*} = -nFk_{k0}C_{k,\alpha}^{*}\left\{exp\left[-\frac{\alpha nF}{RT}\eta\right] - exp\left[\frac{(1-\alpha)nF}{RT}\eta\right]\right\}$$
(2.I.19)

The transport expression can be given, for example, by Eq. 2.I.16.

Equating Eqs. 2.I.16 and 2.I.19, isolating  $C_{k,\alpha}^*$  and substituting in Eq. 2.I.18, results:

$$r_{k,\alpha} = -C_{k,\alpha}^{*} \frac{\Theta}{\left[1 + \frac{\delta}{D_{k,\alpha}}\Theta\right]} , \text{ where}$$
(2.I.20)  
$$\Theta = \frac{M_{k}}{z_{k}} nk_{k0} \left\{ exp\left[-\frac{\alpha nF}{RT}\eta\right] - exp\left[\frac{(1-\alpha)nF}{RT}\eta\right] \right\}$$
(2.I.21)

An analysis of Eq. 2.I.20 shows two classic limiting cases:

1) if 
$$\delta \to 0$$
 then  $\left[1 + \frac{\delta}{D_{k,\alpha}}\Theta\right] \to 1$ 

so Eq. 2.I.20 becomes Eq. 2.I.19, that is, when the boundary layer becomes insignificant, due to the prevailing fluid dynamic conditions, the control of the reactive process is due only to intrinsic kinetics.

2) if 
$$\delta \gg 0$$
 then  $\left[1 + \frac{\delta}{D_{k,\alpha}}\Theta\right] \rightarrow \frac{\delta}{D_{k,\alpha}}\Theta$ 

so Eq. 2.I.20 becomes Eq.2. I.16, that is, when the boundary layer becomes significant, due
to the prevailing fluid dynamic conditions, the control of the reactive process is due only to mass transport.

In the most general case, in which none of these limiting cases are applied, the control will be mixed and Eq. 2.I.20 shall be used.

So far, only the case of a single reaction occurring at the electrode has been discussed. If two or more reactions can occur simultaneously, then each of them must be treated as occurring independently. The total current density will be the sum of the current densities due to each of the independent reactions. More complex cases than those discussed here can be better appreciated in the works of Newman  $(1973)^8$ , Vetter  $(1967)^9$ , Bard  $(1980)^{10}$  and Pletcher  $(1982)^{11}$ .

It remains to bring the results developed in terms of the local rate of mass production of the k chemical species per unit of reaction area,  $r_{k,\alpha}$ , for local rate of mass production of k chemical species per unit volume of reaction,  $R_{k,\alpha}$ .

Considering the settings:

$$r_{k,\alpha} = \frac{1}{A_{\alpha}} \frac{d}{dt} (m_{k,\alpha})$$
(2.I.22)

$$R_{k,\alpha} = \frac{1}{V_{\alpha}} \frac{d}{dt} (m_{k,\alpha})$$
(2.I.23)

and where you have the result of interest,

$$R_{k,\alpha} = \frac{A_{\alpha}}{V_{\alpha}} r_{k,\alpha} = a_{\alpha} r_{k,\alpha}$$

$$R_{k,\alpha} = a_{\alpha} r_{k,\alpha} \text{ with } a_{\alpha} \equiv \frac{A_{\alpha}}{V_{\alpha}}$$
(2.I.24)

that is, the parameters are linked by the specific area,  $a_{\alpha}$  of the  $\alpha$  phase.

with Eq. 2.I.20 in Eq. 2.I.24 results the constitutive equation sought:

$$\mathbf{R}_{\mathbf{k},\alpha} = \mathbf{R}_{\mathbf{k},\alpha} (\mathbf{C}_{\mathbf{k},\alpha}, \mathbf{C}_{\mathbf{k},\alpha}^*, \Phi_{\alpha,\dots})$$

<sup>&</sup>lt;sup>8</sup>Newman, JS (1973). Electrochemical Systems. Prentice-Hall 432 p

<sup>&</sup>lt;sup>9</sup>Vetter, KJ (1967). Electrochemical Kinetics. Academic Press 789 p

<sup>&</sup>lt;sup>10</sup>Bard, AJ and Faulkner, LR (1980) Electrochemical Methods- Fundamentals and Applications, John Wiley & Sons, NY

<sup>&</sup>lt;sup>11</sup>Pletcher, D. (1982) Industrial Electrochemistry, Chapman and Hall, NY

#### 2.I.5.-obtaining kinetic parameters

For the determination of kinetic parameters, it is necessary to determine the mass of the k component in the particle at a given time, t. Direct determination is very unusual because it requires a lot of care and a lot of experimental effort. However, indirect methods are widely used. In essence, average values are determined in an individual system through the changes they cause in the external environment. In this sense, taking advantage of the methodology already applied in adsorption, we developed an apparatus based on a recirculating composite system configuration and applied it in an unprecedented way in the study of kinetic mechanisms in particulate systems. Figure 2.I.6 shows a schematic view of a system with continuous recirculation. Figure 2.I.7 shows the built laboratory unit.



FIGURE 2.I.6. - Schematic of the composite system with continuous recirculation.

In a closed system as described, the mass of any chemical constituents present is constant (*cte*). If a given k constituent is distributed among two phases (liquid and solid particles in the present case) then at any time, t will have for the k component in the composite system, *sis*:

$$m_{k,sis}(t) = m_{k,p}(t) + m_{k,f}(t) = cte$$
(2.I.25)

Where,  $m_{k,p}$ , is the mass of the k component in the particulate phase and  $m_{k,f}$ , the mass of the k component in the fluid phase. Consequently.

$$m_{k,p}^{o} + m_{k,f}^{0} = m_{k,p} + m_{k,f}$$
(2.I.26)

in Eq. 2.I.26. the left side represents the initial time, ti, and the right side any instant, t.

If at the initial instant a mass of solid,  $M_s^0$ , completely free of liquid is placed in the presence of a finite volume of liquid,  $V_f^0$  of composition, in mass per unit volume,  $C_{1,f}^0, \dots C_{m,f}^o$  at the temperature and pressure of the system that from that moment is closed then,  $m_{k,p}^o = 0$  and we have by Eq. 2.I.26.

$$m_{k,p} = m_{k,f}^{o} - m_{k,f} = C_{k,f}^{o} V_{f}^{o} - C_{k,f} V_{f}$$
(2.I.27)

once the concentrations are low it is possible to assume that during the experiment there is no change in the volume of the liquid and then:

$$V_f^o = V_f = V_L$$

and,

$$m_{k,p} = V_L (C_{k,f}^o - C_{k,f})$$
(2.I.28)

It is evident that the mass of the particle at any instant depends on the conditions of its surroundings and its value will depend on the accuracy with which the concentration of the bath is measured,  $C_{k,f}$ . Molarity is recommended as the unit of concentration in the electrolyte and the change of concentration units is made by including the molecular mass of the k component,  $M_{m,k}$ . resulting:

$$m_{k,p} = M_{m,k} V_L (C_{k,f}^o - C_{k,f})$$
(2.I.29)

Where do you get the result, you are looking for?

$$\frac{d}{dt}(m_{k,p}) = -M_{m,k}V_L(\frac{d}{dt}(C_{k,f}))$$
(2.I.30)

which is the ion deposition rate, k, in the electrochemical reactor particles. This result immediately follows important parameters such as *current efficiency* and *energy efficiency*.

The *current efficiency* for a given electrochemical system in a given time interval is given by the ratio between the mass of metal actually deposited and the mass of metal that would be deposited if all the electrical current applied to the system were used for this purpose (given by Faraday's law). Thus, we have the following expression for the *current efficiency*:

$$E_{c} = \frac{100}{M_{m,k}} \frac{z_{k}F}{i} \frac{dm_{k,p}}{dt} = \frac{100}{M_{m,k}} \frac{z_{k}F}{i} \left( -M_{m,k}V_{L} \frac{dC_{k,f}}{dt} \right)$$
(2.I.31)

where:

$$\begin{split} E_C &= \text{current efficiency (\%);} \\ F &= \text{Faraday constant (96498 A.s.mol^{-1});} \\ Z_k &= \text{number of electrons involved in the electrochemical reaction of interest;} \\ i &= \text{current applied to the reactor (A).} \end{split}$$

already the *energy efficiency* is given by the amount of mass deposited per unit of energy consumed. This way:

$$E_{E} = \frac{1}{iV} \frac{dm_{k,p}}{dt} = \frac{1}{V.i} \left( -M_{m,k} V_{L} \frac{dC_{k,f}}{dt} \right)$$
(2.I.32)

or, using equation 2.I.31 we have:

$$E_{E} = \frac{M_{m,k}}{100 * z_{k}F} \frac{1}{V} E_{c}$$
(2.I.33)

where:

 $E_E$  = energy efficiency, (kg. s<sup>-1</sup>. V<sup>-1</sup>. A<sup>-1</sup>); V = voltage drop in the reactor (V).

The experimental unit used to carry out these studies consists of the following set of systems: fluid flow, current supply and electrical measurements and has the electrochemical reactor as its main constituent, with the experimental unit represented in the figure 2.I.7.



FIGURE 2.I.7. - Experimental apparatus.

The experiments consist of the following steps:

1-electrolyte preparation;

2-assembly of the electrochemical reactor;

3-filling the reactor with metallic particles;

4-adjustment of the current to be supplied to the reactor;

5-electrical contact connection;

6-activation of the centrifugal pump and opening of the valve, inlet of the electrolyte; 7- connection of electrical source with current supply, and start of timing;

8-withdrawal, from time to time, of an aliquot of the electrolyte at the exit of the reactor and reading, at the same instant, of the voltage drop in the reactor;

9-chemical analysis, in an atomic absorption spectrophotometer, of the aliquots withdrawn from the system.

# 2.I.5.1.-method applications

The described installation as well as the procedure protocol can be used for any type of three-dimensional electrodes (electrochemical reactors). For the application of the technique, we will use one of the most promising types: the fluidized bed, whose constructive details are shown in figure 2.I.8.



1- electrolyte inlet, 2- electrolyte outlet, 3- distributor, 4- lead plate, 5- copper plate.

FIGURE 2.I.8. - Electrochemical reactor: **a**) global view and **b**) detailed view:

The reactor is entirely made of transparent acrylic (plexiglass sheet), which allows the internal visualization of the same during its operation, having as main characteristic the fact that it is built by the juxtaposition of plates, which makes it possible to change its thickness, thus allowing the choice of distance between electrode and counter electrode as shown in figures 2.I.8. a) and b). which allows versatility and easy handling. A rectangular metal plate of copper, called current feeder (cathode) and the other of lead called counterelectrode (anode). are the elements that complement the reactor.

The experiments selected for this example refer to removal of copper ion in a fluidized bed.

### Solid-fluid system.

The particles constituting the bed were 1 mm equilateral cylinders. Before being used, the particles were previously subjected to a chemical treatment with a solution identical to that used in the copper plate.

The electrolyte used was prepared by deionized water, concentrated sulfuric acid and copper sulfate pentahydrate, using 12 liters of electrolyte. Prepared with a copper ion concentration of 0.9 g/l and acid concentration according to the configuration of the experiment to be carried out. After weighing and measuring the quantities of the electrolyte components, they were added to the unit's plastic reservoir where they were mixed and homogenized by activating the pump and circulating only through the "by-pass". After the experiments were carried out, the concentration of  $Cu^{++}$  ions in the electrolyte decreased to concentrations of the order of 1ppm.

During the experiments, the temperature of the electrolyte solution was kept constant around 25°C.

The mass of particles in the bed was that which it gave the bed a resting height of 8 cm and operated fluidized at 12 cm. how the bed thickness can be parameterized in 2.0, 2.5 and 3.0 cm; the mass was respectively 334.99, 444.27 and 536.66 grams, and the flow rates were 65.0, 79.0 and 95.0 cm<sup>3</sup> /s. With chemical analysis, the concentration of copper ions present in the electrolyte at each instant was obtained. and the deposited mass found by equation 2.I.28 and from it the deposition rate of copper ions, (gs<sup>-1</sup>).

#### 2.I.5.1.1. a typical result

Figure 2.I.9 shows the result of a typical experiment.



FIGURE 2.I.9. - Typical behavior of mass transfer kinetics in electrochemical fluidized bed reactor.

In figure 2.I.9. **a**) are the primary results obtained directly from the observation of the fluid behavior during the experiment time and which will be used to obtain the parameters sought: the k ion *deposition rate* in the particles of the electrochemical reactor, *current efficiency* and *energy efficiency*.

In figure 2.1.9. **b**) it is possible to clearly identify three kinetic regimes controlling the reactive process, two of them with immediate identification configured by the straight lines and an intermediary linking the two. being respectively

### - Control by activation

In this case, details shown in figure 2.I.10, there is excess reagent to be used in the electrochemical reaction; this occurs in the initial stages of the process, when t < t\* and C(t) > C\* and I < I<sub>lim</sub>. Under such conditions, the rate of decrease in concentration is constant and proportional to  $E_C = E_C^*$ . because as seen by Eq. 2.I.31. The current efficiency is directly proportional to  $\frac{dC_{k,f}}{dt}$ 

integrating Eq. 2.I.32., results for this regime

$$C_{k,f}(t) = C_o - \left(\frac{1}{100} \frac{E_c I}{z_k F V_L}\right) t \quad ; \ 0 < t < t \ * \tag{2.I.34}$$

Since E<sub>C</sub>, I and C<sub>0</sub> are constant, the concentration drops linearly with time.

- Control by mass transfer

The behavior described above is maintained until the operating time  $t = t^*$ , when then the limiting current,  $I_{lim}$ , equals current I; from this point we have  $t > t^*$ ;  $Ct < C^*$  and  $I > I_{lim}$ , details shown in figure 2.I.10.

The current efficiency from then on is no longer constant, since, as the threshold current drops, as a consequence of the decrease in the reactant concentration, an increasing fraction of the current supplied to the system is diverted to other reactions.

As the reaction becomes controlled by mass transfer, the decay of concentration becomes exponential, and the electrochemical reaction is controlled by mass transfer, and the local current density is given by Eq. 2.I.17.:

$$I_{\rm lim} = -k_L \frac{z_k F}{M_{m,k}} C_{k,f}$$
(2.I.35)

and from equations 2.I.18 in 2.I.24 and 2.I.35 comes out,

$$R_{k,f} = a_p i_{\lim} \frac{M_{m,k}}{z_k F} = -a_p k_L C_{k,f}$$
(2.I.36)

where  $k_L$  is an average mass transfer coefficient (ms<sup>-1</sup>).

Applying the mass balance of Eq. 2.1 to the reactor exits:

$$\frac{\partial}{\partial t} \left[ \varepsilon C_{k,\alpha} \right] + \operatorname{div} \left[ \vec{\varphi}_{k,\alpha} \right] = \varepsilon R_{k,\alpha}$$
(2.I.37)

If the longitudinal dispersion can be neglected, the flux density vector can be considered only convective and given by:

$$\vec{\varphi}_{k,\alpha} = C_{k,\alpha} V_z$$

and,

$$\frac{\partial}{\partial t} \left[ \varepsilon C_{k,\alpha} \right] + \operatorname{div} \left[ C_{k,\alpha} V \right] = \varepsilon R_{k,\alpha}$$
(2.I.38)

and by the uniformity of the velocity along the reactor, it comes out:

$$\operatorname{div}\left[C_{k,\alpha}V_{z}\right] = V_{z}\frac{\partial C_{k,f}}{\partial z}$$

and,

$$\frac{\partial}{\partial t} \left[ \varepsilon C_{k,\alpha} \right] + V_z \frac{\partial C_{k,f}}{\partial z} = -\varepsilon a_p k_L C_{k,f}$$
(2.I.39)

Given this equation, it is possible to adopt several plausible types of reactors to apply it. We will consider two types: PFR and CSTR.

## PFR

when the length of the reactor in the flow direction is too large or the reaction rate is too fast, thus causing an appreciable variation in concentration along z.

# CSTR

When the length is small enough or the reaction rate is slow enough, then the change in concentration along the length z can be neglected. Therefore, the modeling becomes simpler. Both cases will be treated starting with the simplest.

Considering a continuous stirred-tank reactor (CSTR) the concentration uniformity along z, leads to:

$$\frac{\partial}{\partial t} \left[ C_{k,\alpha} \right] = -a_p k_L C_{k,f} \tag{2.I.40}$$

with initial condition,  $t = 0 \rightarrow C_{k,f} = C_0$ 

The integration results in:

$$C_{k,f} = C_0 \exp(-a_p k_L t)$$
(2.I.41)

Summarizing we have:

activation control:

$$C_{k,f}(t) = C_o - \left(\frac{1}{100} \frac{E_c I}{z_k F V_L}\right) t; \ 0 < t < t *$$
(2.I.42a)

mass transfer control:

$$C_{k,f} = C^{**} \exp(-a_p k_L t); t > t^{**}$$
 (2.I.42b)

between t\* and t\*\* we have the mixed control without a specific kinetic model in terms of the experiment performed.

In the figure 2.I.10 the fit of these models to the experimental data is shown. In figure 2.I.10a. we use the model given by Eq. 2.I.42a. at  $0 < t < t^*$  and Eq. 2.I.42b. at  $t > t^{**}$  in figure 2.I.10b. arbitrary choice of the midpoint, tm, between  $t^*$  and  $t^{**}$  for the extension of the models and continuity of the curve. The curve becomes continuous, but it is not differentiable at the point t=tm and as the rate of k ion deposition in the electrochemical reactor particles is proportional to the derivative of the curve as shown in Eq. 2.I.30. this artifice is impaired.



FIGURE 2.I.10. - Experimental data and fitted kinetic models

To the Analysis of the plug flow reactor model (PFR model) is more instructive to look at the composite Reactor-Reservoir system, in order to give scope to the study.

The model for the Tank (electrolyte reservoir), Equation 2.I.43, it simply consists of a mass balance considering the tank perfectly agitated and without reaction.

$$V_T \frac{dC_{k,T}}{dt} = Q_v (C_{k,T}^e - C_{k,T}^s)$$
(2.I.43)

in which:

e=input; s=output; T=tank and yet,

$$C_{k,T} \equiv C_{k,T}^s$$
 and  $\tau = \frac{V_T}{Q_v}$ 

and relieving the notation leaves, for the variation of the concentration in the tank:

$$\frac{dC_T}{dt} = \frac{1}{\tau} (C_{T,e} - C_T)$$
(2.I.44)

For the reactor we have Eq. 2.I.38. where we will consider that the change in composition inside the reactor changes more significantly with position than with time, that is, the concentration profile at time t is not very different from the concentration profile at time (t  $+\Delta t$ ), that is, it is considered a *pseudo-steady state* regime. then to the reactor:

$$V_z \frac{\partial C_R}{\partial z} = -\varepsilon a_p k_L C_R \tag{2.I.45}$$

also relieved notation.

with boundary condition,  $z = 0 \rightarrow C_R = C_{R,0}$ 

Integrating the Equation 2.I.45. Equation 2.I.46 is obtained, which describes the variation in the concentration of the reactant species along the z direction of the electrode.

$$C_{R} = C_{R,0} \exp(-\frac{\varepsilon a_{p} k_{L}}{V_{z}} z)$$
(2.I.46)

at the input of the reactor, z=0 and at the output of the reactor, z=L we will have, respectively:

$$C_R^e = C_{R,0}$$

$$C_R^s = C_{R,0} \exp(-\frac{\epsilon a_p k_L}{V_z} L)$$
(2.I.47)

and Eq. 2.I.47, can be put in the form:

$$C_R^s - C_R^e = -C_R^e \left[ 1 - \exp(-\frac{\varepsilon a_p k_L}{V_z} L) \right]$$
(2.I.48)

but,

$$C_R^e = C_T$$
 and  $C_R^s = C_{T,e}$  so,

$$C_{T,e} - C_T = -C_T \left[ 1 - \exp(-\frac{\varepsilon a_p k_L}{V_z} L) \right]$$

this result in Eq. 2.I.44. gives

$$\frac{dC_T}{dt} = -\frac{C_T}{\tau} \left[ 1 - \exp(-\frac{\varepsilon a_p k_L}{V_z} L) \right]$$
(2.I.49)

with initial condition,  $t = 0 \rightarrow C_T = C_{R,0}$ 

The integral of the Equation 2.I.49 with the initial condition, provides Equation 2.I.50, which expresses, for a bed of length, L, the variation in reservoir concentration as a function of processing time.

$$C = C_0 \exp\{-\frac{1}{\tau} \left[1 - \exp(-\frac{\varepsilon a_p k_L}{V_z}L)\right]t\}$$
(2.I.50)

which obviously has to be tested for a reactor at least 5 times longer than the one being studied at the moment. but that will be analyzed in Chapter 3. At sequence shows the total of the results obtained with the reactor shown in figure 2.I.8.

### Decay of copper ion concentration

The results related to the variation of the concentration of copper ions in the electrolyte with time will be presented, from which the rates of variation of the concentration were taken. Such rates were obtained from linear regression, using regression only at intervals in which the concentration-time relationship was linear, and the results will be presented in groups that will be divided according to the acid concentrations that were used: 0.3; 0.6 and 0.9 molar.

The concentration is represented dimensionless C/Co as a function of time, t (min) in figures 2.I.11.1, 2.I.11.2 and 2.I.11.3, parameterized by the current, for the distances between electrode and counter electrode of 2.0; 2.5 and 3.0 cm; and acid concentrations of 0.3; 0.6 and 0.9 molar, respectively.



FIGURE 2.I.11- Dimensionless of the concentration of copper ions in the electrolyte as a function of time, having as a parameter the current for acid concentration of 0.3, 0.6 and 0.9 molar and bed thickness of: (a) 2.0 cm; (b) 2.5 cm and (c) 3.0 cm.

It can be seen that the rate of deposition of copper ions increases with the increase in current, which is independent of the distance used. However, it turns out that as the distance between electrode and counter electrode increases the rate of decay of the concentration of copper ions in the electrolyte, consequently, the deposition rate becomes smaller for the two smaller currents; whereas for the highest current the rate was little influenced. It is also observed that for the distance between electrode and counter-electrode of 2.0 cm, the currents of 6A and 8A presented practically the same deposition rate, which suggests having reached, for this configuration, a maximum current, the from which any increase in current is unfavorable for the electrodeposition, causing an increase in parallel reactions that will cause a decrease in current efficiency and energy efficiency. As in the configuration with a distance between electrode and counter electrode of 2.0 cm and acid concentration of 0.3 molar (figure 2.I.11.1 (a)), the configuration with the same distance and acid concentration of 0.6 molar (figure 2.I.11.2 (a)) presented practically identical deposition rate for currents 6A and 8A, suggesting that, in the same way as for that configuration, a maximum current was reached for this one, or that is, the increase in the support electrolyte concentration (sulfuric acid) was not enough to change that value. It is observed that the deposition rate increased for all streams with increasing support electrolyte concentration from 0.3 to 0.6 molar. The effect of increasing the concentration of the supporting electrolyte (sulfuric acid) can be verified when comparing the deposition rates for a given current in the three studied distances.

It is verified, however, that the increase in the deposition rates due to the increase in the support electrolyte concentration (sulfuric acid) from 0.6 to 0.9 molar did not provide significant increases in the deposition rates, except for the current of 2A in the distance between electrode and counter electrode of 3.0 cm, which significantly improved the deposition rate. This indicates that an "optimal concentration" of acid was reached for the other configurations, except for the one mentioned above.

For all configurations studied, the deposition rate remains constant until a certain concentration of copper ions is reached in the electrolyte, a concentration that depends on the configuration used, and changes until it becomes zero.

### current efficiency

The relative results will be presented the current efficiency, observing the behavior of such response against the variation of the concentration of copper ions in the electrolyte when the values of the studied parameters change.

Figures 2.I.12.1, 2.I.12.2 and 2.I.12.3 show the *current efficiency*,  $E_c(\%)$  results as a function of the concentration of copper ions,  $C_{cu}$  (mol) present in the electrolyte, parameterized by the currents applied to the reactor for distances of 2.0; 2.5 and 3.0 cm, and acid concentrations of 0.3; 0.6 and 0.9 molar.



FIGURE 2.I.12- Current efficiency of copper ions in the electrolyte as a function of concentration of copper ions,  $C_{cu}$ , having as parameter the current for acid concentration of 0.3, 0.6 and 0.9 molar and bed thickness of: (a) 2.0 cm; (b) 2.5 cm and (c) 3.0 cm.

It is verified that the current efficiency remains constant until a certain concentration of copper ions is reached in the electrolyte, a concentration that depends on the configuration used, and then drops sharply to values close to zero. In the figure 2.I.12.1(a), it can be seen that the best efficiencies were obtained for currents of 4A and 6A, with these values being close. In turn, the efficiency obtained for the 2A current was lower than for the two previously mentioned.

It can be seen, in the figure 2.I.12.1(b), that the best efficiencies were obtained for current 4A and 6A, as before. However, there was an inversion between the 2A and 8A currents, because once the distance between electrode and counter electrode was increased, this favored the higher current and disfavored the lower one.

In the figure 2.I.12.1(c), it is verified that the best efficiency, for this configuration, was obtained for a current of 8A and that the currents of 4A and 6A provided practically identical efficiencies. On the other hand, the lowest efficiency was obtained for the lowest current.

It can be seen that, for all configurations, there was a significant improvement in current efficiency as a result of the increase in the support electrolyte concentration.

With the increase of acid concentration from 0.6 to 0.9 molar, there was an increase in current efficiency for all configurations, being less accentuated than that from 0.3 to 0.6 molar; except for the 2A current at the longest distance. The increase in the support electrolyte concentration, for the current of 8A in the distances of 2.0 and 2.5 cm, did not cause a considerable increase in the current efficiency, that is, it seems that the support electrolyte concentration reached a maximum, for this current at the mentioned distances and a further increase in concentration would only decrease the efficiency.

For a current of 2A at the distance between electrode and counter-electrode of 3.0 cm and acid concentration of 0.9 molar, a considerable improvement in current efficiency is verified in comparison with that obtained for this current, for the same distance when with acid concentration of 0.3 and 0.6 molar. This highlights the great influence of the support electrolyte concentration on the system, as well as the fact that, for this configuration, the maximum value of this parameter has not been reached.

### energy efficiency

The results obtained for energy efficiency will be shown, where the behavior of energy efficiency will be presented against the decay of the concentration of copper ions, present in the electrolyte, throughout the experiment, analyzing the influence of each variable on the answer in question.

Figures 2.I.13.1, 2.I.13.2 and 2.I.13.3 show the *energy efficiency*,  $E_E$  (kg/kwh) results as a function of the concentration of copper ions,  $C_{cu}$  (mol) present in the electrolyte, parameterized by the currents applied to the reactor for distances of 2.0; 2.5 and 3.0 cm, and acid concentrations of 0.3; 0.6 and 0.9 molar, respectively.



FIGURE 2.I.13.1

- FIGURE 2.I.13.2
- **FIGURE 2.I.13.3**

FIGURE 2.I.13.- Energy efficiency of copper ions in the electrolyte as a function of concentration of copper ions,  $C_{cu}$ , having as parameter the current for acid concentration of 0.3, 0.6 and 0.9 molar and bed thickness of: (a) 2.0 cm; (b) 2.5 cm and (c) 3.0 cm.

As verified for the *current efficiency*, the *energy efficiency* remains constant until a certain concentration of copper ions is reached in the electrolyte, a concentration that has its value determined by the configuration in use, dropping sharply to values close to zero.

A fact worthy of comment is that, during the experiments, the voltage drop inside the bed, measured with the help of a multimeter, as mentioned in the methodology, fellas the experiment proceeded, increasing again as the concentration mentioned above was reached. This fact is not expressed in the graphic results presented above, since the voltage difference used to calculate the energy efficiency is a time-weighted average, obtained from the various readings performed during the experiment.

It can be seen that, for the shortest distance, the lowest consumption efficiencies were obtained for the highest currents.

It can be seen that, as if the distance between electrode and counter electrode was increased, this increase favored the higher current and was harmful to the lower current, with little influence being felt for the intermediate currents.

The effect of increasing acid concentration in the electrolyte was clearly seen in the figures 2.I.13.1(a) and 2.I.13.1(c) when compared, respectively, with figures 2.I.13.3 (a) and 2.I.13.3 (c), where in the latter, the significant increase in energy efficiency for current 8A (figure 2.I.13.3 (a)), at the shortest distance, and for current 2A (figure 2.I.13.3 (c)) at the longest distance.

As a main fact, due to the increase in acid concentration from 0.6 to 0.9 molar, the slight decrease in energy efficiency suffered by the current of 8A for a distance between electrode and against electrode of 3.0 cm is observed. This suggests the occurrence of a maximum value for this parameter, which, having its value exceeded, disfavors the current

efficiency and energy efficiency responses. This maximum value depends on the configuration used.

On the other hand, it is important to point out that for the 2A current the increase in acid concentration was extremely favorable, since it was this current that provided the best energy efficiency when using the 0.9 molar acid concentration in the distance between electrode and 3.0 cm counter electrode. However, when using concentrations of 0.3 and 0.6 molar, this current provided the worst efficiencies in the mentioned distance.

From the results obtained and the discussion it is possible to make the following general comments.

- Among all the configurations studied, those containing 4A and 6A currents were the ones that presented the best results, when the value for the configuration's acid concentration was at the lowest value. It is advisable to work with these, since increasing the acid concentration increases the cost of the process, unless the effluent already contains a high concentration.

- For the configurations that contained values of acid concentration of 0.9 molar, all presented excellent results, being little felt the influence of the other parameters.

# CHAPTER 2 Part II. non-electrolytic systems

### **2.II.1.** Preliminary considerations

In the multiphase multicomponent system, the vast majority of problems of interest are almost always biphasic. In this sense, the relevant simplification will be:

k=1, 2, 3,..., m; and α=1,2;

that is, two-phase multicomponent systems.

The most common two-phase systems are related to an extensive fluid as a continuous phase, simply called "bulk", and a dispersed phase in the form of an immiscible fluid, a gel, or a microporous solid, which for the purposes of applications will be denoted by biphasic systems of type I (fluid-fluid), II (fluid-gel) and III (fluid-solid), with the continuous phase always denoted by  $\alpha$ =1 and the fragmented phase by  $\alpha$ =2.

As the idea here is to treat a system *micro* within a *macro* system it will be necessary to make clear the identity of each one.

Since our interest is directed, basically, to two-phase systems, of type III (fluid-solid) we will be referring to a continuous phase, henceforth called fluid, and a particulate phase, henceforth called particle.

#### 2.II.2. two-phase model on the particle

We will consider the possibility that the particulate phase is itself a two-phase system and has a void fraction in its interior characterized by intraparticle porosity,  $\varepsilon_P$ , and that the fluid phase can, under certain conditions, invade this void, characterizing an equilibrium condition and forcing the intra-particular concentration to be different from that found outside (bulk). This requires the configuration of this difference: adopting specific notation for the *particle*, henceforth *micro* system, and for the *fluid particle* system, henceforth *macro* system. So,

#### <u>micro system(particle):</u>

 $C_{k,f}$ : concentration of k chemical species per unit volume of fluid phase;  $C_{k,s}$ : concentration of k chemical species per unit volume of solid phase. by solid phase here, we are understanding the porous solid matrix.

#### macro system (set of particles):

 $C_{k,1}$ : concentration of k chemical species per unit volume of fluid phase;  $C_{k,2}$ : concentration of k chemical species per unit volume of the particulate phase;

in either case the local volume fraction of the  $\alpha$  phase,  $\upsilon_{\alpha}$ , is the porosity itself, when  $\alpha=1$ . and so,  $\upsilon_1 = \varepsilon$ . and consequently,  $\upsilon_2 = (1 - \varepsilon)$ . The link between the *micro* and *macro* system is given by:

$$\frac{\overline{\rho}_{k,p}}{\overline{\rho}_{k,p}} = \left[\varepsilon_p C_{k,f} + (1 - \varepsilon_p) C_{k,s}\right]$$

$$\overline{R}_{k,p} = \left[\varepsilon_p R_{k,f} + (1 - \varepsilon_p) R_{k,s}\right]$$
(2.II.1)

On the other hand, from an operational point of view it does not matter much whether the k component inside the particle is in the solid (porous matrix) or in the pore, and thus more interesting and easily identifiable variables in Eq.2.II.1, representing the particle as a whole were defined:

Assuming that an interior point of the particle can be referenced by a position vector,  $\vec{r}$ , and that the properties may vary over time at this point, then:

$$\Omega = \Omega(\vec{r},t)$$

Where,  $\Omega$ , generally represents any interior property: a scalar like concentration,  $C_{k,\alpha}(\vec{r},t)$  or a vector such as the mass flux density,  $\vec{\varphi}_{k,\alpha}(\vec{r},t)$ , for example.

Eq.1 applied to the micro system results:

$$\frac{\partial}{\partial t} \left[ \varepsilon_p C_{k,f} \right] + \operatorname{div} \left[ \varepsilon_p \vec{\varphi}_{k,f} \right] = \varepsilon_p R_{k,f}; \text{ for the fluid}$$

$$\frac{\partial}{\partial t} \left[ (1 - \varepsilon_p) C_{k,s} \right] + \operatorname{div} \left[ (1 - \varepsilon_p) \vec{\varphi}_{k,s} \right] = (1 - \varepsilon_p) R_{k,s}; \text{ for the solid}$$
(2.II.2)

adding the two equations we have the global balance of the k component, in the particle as a whole,

$$\frac{\partial}{\partial t} \left[ \varepsilon_p C_{k,f} + (1 - \varepsilon_p) C_{k,s} \right] + \operatorname{div} \left[ \varepsilon_p \vec{\varphi}_{k,f} + (1 - \varepsilon_p) \vec{\varphi}_{k,s} \right] = \varepsilon_p R_{k,f} + (1 - \varepsilon_p) R_{k,s}$$
(2.II.3)

with, of course,  $C_{k,f} = C_{k,f}(\vec{r},t)$  and  $C_{k,s} = C_{k,s}(\vec{r},t)$ 

suppose that only diffusive motions prevail in the particle, such that:

$$\vec{\varphi}_{k,f} = \vec{J}_{k,f}$$
, with  $\vec{J}_{k,f} = -D_{k,f}$  grad  $C_{k,f}$ 

and,

and,

$$\vec{\varphi}_{k,s} = \vec{J}_{k,s}$$
, with  $\vec{J}_{k,s} = -D_{k,s}$  grad  $C_{k,s}$ 

and even if there is no chemical reaction inside the particle,

then,

$$\frac{\partial}{\partial t} \left[ \varepsilon_p C_{k,f} + (1 - \varepsilon_p) C_{k,s} \right] + \operatorname{div} \left[ -\varepsilon_p D_{k,f} \operatorname{grad} C_{k,f} - (1 - \varepsilon_p) D_{k,s} \operatorname{grad} C_{k,s} \right] = 0 \quad (2.\text{II.4})$$

Eq.2.II.4, as written, admits diffusion in the pore and in the solid matrix. that is, the k chemical species walks, in parallel, through the fluid and the solid (parallel diffusion model).

suppose that diffusion is negligible in the solid, that is, only the fluid in the pores contributes to the transport of the k chemical species (pore diffusion model). then:

$$\frac{\partial}{\partial t} \left[ \varepsilon_p C_{k,f} + (1 - \varepsilon_p) C_{k,s} \right] + \operatorname{div} \left[ -\varepsilon_p D_{k,f} \operatorname{grad} C_{k,f} \right] = 0$$
(2.II.5)

considering  $D_{k,f}$  and  $\varepsilon_p$  constants, results:

$$\left[\varepsilon_{p}\frac{\partial}{\partial t}C_{k,f} + (1-\varepsilon_{p})\frac{\partial}{\partial t}C_{k,s}\right] = \varepsilon_{p}D_{k,f}LapC_{k,f}$$
(2.II.6)

The equation still imposes a difficulty, as it has two independent variables and, therefore, a new equation must be provided in order to have unique results. This relationship is of the form:

$$f(C_{k,s}, C_{k,f}) = 0$$
  $k = 1..m$  (2.II.7)

this relationship is, in principle, unknown, but it can be elaborated on the basis of local kinetic mechanisms. However, it is clear, whatever the kinetic mechanism adopted, that the solid phase cannot receive more mass from the fluid phase than thermodynamic equilibrium allows, and how, at equilibrium:

$$C_{k,s} = f(T, C_{1,f}, \dots, C_{m,f}) \text{ adsorption isotherm}$$
(2.II.7b)

traditionally, local kinetic mechanisms are disregarded in favor of a local instantaneous equilibrium obeying relations of the type proposed in Eq. 2.II.7b. formulated, thermodynamically, by model or correlation. From Eq.2.II.7b comes:

$$\frac{\partial C_{k,s}}{\partial t} = \frac{df}{dC_{k,f}} \frac{\partial C_{k,f}}{\partial t}$$
(2.II.7c)

which is directly usable in Eq.2.II.6. which results:

$$\left[\varepsilon_{p}\frac{\partial C_{k,f}}{\partial t} + (1 - \varepsilon_{p})\frac{df}{dC_{k,f}}\frac{\partial C_{k,f}}{\partial t}\right] = \varepsilon_{p}D_{k,f}\frac{1}{r^{2}}\frac{\partial}{\partial r}\left(r^{2}\frac{\partial C_{k,f}}{\partial r}\right)$$
(2.II.7d)

or,

$$\left[\frac{\partial C_{k,f}}{\partial t}(\varepsilon_p + (1 - \varepsilon_p)\frac{df}{dC_{k,f}}\right] = \varepsilon_p D_{k,f} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_{k,f}}{\partial r}\right)$$
(2.II.7e)

It remains only to define the coordinate system and the initial and boundary conditions to obtain the concentration fields inside the particle. and therefore,  $C_{k,2}$ , which is the variable of interest in the macro system (set of particles).

From Eq. 2.II.1.

$$\overline{\rho}_{k,p}(\vec{r},t) = \left[\varepsilon_p C_{k,f} + (1 - \varepsilon_p) C_{k,s}\right]$$
(2.II.8)

Simply representing the presence of the k component at a position at a given time within the particle as a whole. However, it is convenient to take for the macro model only its

temporal variation and this is obtained by making, for each time, t a spatial average of the concentration profile for the entire volume of the particle.

$$C_{k,p}(t) = \frac{1}{V_p} \iiint \vec{\rho}_{k,p}(\vec{r}, t) dV$$
(2.II.9)

as the interest is in the temporal variation of  $C_{k,p}(t)$  then:

$$\frac{d}{dt}C_{k,p}(t) = \frac{1}{V_p} \iiint \frac{\partial}{\partial t} \overline{\rho}_{k,p}(\vec{r},t) dV$$
(2.II.9a)

and by Eq.2.II.1.

$$\frac{d}{dt}C_{k,p}(t) = \frac{1}{V_p} \iiint_V \frac{\partial}{\partial t} \left[ \varepsilon_p C_{k,f} + (1 - \varepsilon_p) C_{k,s} \right] dV = \frac{1}{V_p} \iiint_V \operatorname{div} \left[ \varepsilon_p D_{k,f} \operatorname{grad} C_{k,f} \right] = \frac{1}{V_p} \left[ \varepsilon_p C_{k,f} + (1 - \varepsilon_p) C_{k,s} \right] dV$$

and by the divergence theorem.

$$\frac{d}{dt}C_{k,p}(t) = \frac{1}{V_p} \iint_{S} \left[ \varepsilon_p D_{k,f} \operatorname{grad} C_{k,f} \right] \bullet \vec{n} dS$$
(2.II.9b)

Where,  $\vec{n}$  is a unit vector normal to the surface of the particle pointing away from it.

Assuming a spherical particle of radius  $R_p$  and unidirectional flow in the radial variable the Eq. 2.II.9b. becomes.

$$\frac{d}{dt}C_{k,p}(t) = \frac{1}{V_p} \iint_{S} \varepsilon_p D_{k,f} \frac{\partial C_{k,f}}{\partial r} \bigg|_{r=R_p} dS$$
(2.II.9c)

whose integration over the entire surface of the particle results in:

$$\frac{d}{dt}C_{k,p}(t) = \frac{1}{V_p} \left(\varepsilon_p D_{k,f} \frac{\partial C_{k,f}}{\partial r} \right|_{r=Rp} A_p$$
(2.II.10)

$$\frac{d}{dt}C_{k,p}(t) = \frac{3}{R_p} \left(\varepsilon_p D_{k,f} \frac{\partial C_{k,f}}{\partial r} \right|_{r=R_p}$$
(2.II.11)

The concentration has *natural modality* the mass of the k component per unit volume of the  $\alpha$  phase, however for the particulate phase it is more convenient to change the base to the mass of the particulate phase and thus a more practical modality can be defined:

$$q_{k,p} = \frac{m_{k,p}}{m_p}$$
 and therefore

if  $\rho_p = \frac{m_p}{V_p}$  is the apparent density of the particulate phase, then the relationship between the

concentrations is:

$$\rho_p q_{k,p} = C_{k,p} \tag{2.II.12}$$

and Eq.2.II.11 is in its preferred form.

$$\frac{d}{dt}(\rho_p q_{k,p}(t)) = \frac{3}{r_p} \left(\varepsilon_p D_{k,f} \frac{\partial C_{k,f}}{\partial r}\Big|_{r=R_p}\right)$$
(2.II.13)

result that could be obtained only by physical considerations of the type:

$$\frac{d}{dt}(\rho_p q_{k,p}(t)) = \frac{A_p}{V_p} (\varepsilon_p \vec{\varphi}_{k,\alpha} \bullet \vec{n} \mid_{r=R_p})$$
(2.II.14)

In this development Eq. (2.II.7e) is a type of *micro* model and Eq. (2.II.14) a type of *macro* model.

The inclusion of the micro model in the macro model will be discussed more fully in chapter 3.

# 2.II.3. one-phase model on the particle

It is possible, for the *micro* model, to consider the particle as a perfectly mixed system, also called pseudo-homogeneous system, such that Eq.1 applied to the homogeneous system results in:

$$\frac{\partial}{\partial t} \left[ C_{k,p} \right] + \operatorname{div} \left[ C_{k,p} \vec{v}_{k,p} \right] = R_{k,p}$$
(2.II.15)

considering an exclusively diffusion model in the particle given by:

$$C_{k,p}\vec{v}_{k,p} = -D_{k,p}gradC_{k,p}$$
$$\frac{\partial}{\partial t} \left[ C_{k,p} \right] + \operatorname{div} \left[ -D_{p}gradC_{k,p} \right] = R_{k,p}$$
(2.II.16)

if the effective coefficient of diffusion in the particle,  $D_{k,p}$ , can be considered constant gives:

$$\frac{\partial}{\partial t} \left[ C_{k,p} \right] = R_{k,p} + D_p Lap C_{k,p}$$

Assuming that there is no chemical reaction in the particle and that the particle is uniform, the best-known form of diffusion appears.

$$\frac{\partial}{\partial t}(q_{k,p}) = D_p Lap(q_{k,p})$$
(2.II.17)

for a spherical particle and assuming diffusion only in the radial direction, then

$$\frac{\partial q_{k,p}}{\partial t} = D_p \left[ \frac{\partial^2 q_{k,p}}{\partial r^2} + \frac{2}{r} \frac{\partial q_{k,p}}{\partial r} \right]$$
(2.II.18)

that with the initial condition and the boundary conditions will be solved to determine the concentration profile,  $q_{k,p}(r,t)$  inside the particle. Allowing Eq.2.II.8 to obtain its instantaneous mean value.

$$\frac{d}{dt}q_{k,p}(t) = \frac{1}{V_p} \iiint \frac{\partial}{\partial t} q_{k,p}(\vec{r},t) dV$$
(2.II.19)

arriving at:

$$\frac{d}{dt} \left( q_{k,p}(t) \right) = \frac{3}{R_p} \left( \varepsilon_p D_{k,p} \frac{\partial q_{k,p}}{\partial r} \right|_{r=R_p} \right)$$
(2.II.20)

We will not present them here, but the reader may find other general models in the literature, such as: *surface diffusion model* (SDM), pore and surface diffusion model (PSDM) and Shrinking Core Model (SCM).

### **2.II.4.** resistance in the interfacial layer (approach to a linear driving force)

Among the many mass transport mechanisms, those related to the phase boundaries are the most frequent and the least known mechanisms. especially when one of the phases is a fluid, since diffusive and convective elements overlap, the convective ones being highly dependent on the prevailing fluid dynamics. For this case an empirical transport equation based on the existence of a thin film thickness,  $\delta_{\alpha}$ , on each side of the interface is usually accepted to express the mass flow, per unit of transfer area,  $\varphi_{k,\alpha}$ , in the interface and given by:

$$\varphi_{k,f} = \sigma_f \frac{(C_k - C_k^*)}{\delta_f} \text{ on the fluid side film}$$

$$\varphi_{k,p} = \sigma_p \frac{(q_k^* - q_k)}{\delta_p} \text{ on the particle side layer}$$
(2.II.21)

in these equations the coefficients  $\sigma_f$  and  $\sigma_p$  are coefficients similar to diffusion coefficients. on the other hand, incorporating the thickness into these coefficients by the definition:

$$k_{\alpha} \equiv \frac{\sigma_{\alpha}}{\delta_{\alpha}}$$

more familiar forms result:

$$\varphi_{k,f} = k_f (C_k - C_k^*) \text{ and } \varphi_{k,p} = k_p (q_k^* - q_k)$$
 (2.II.22)

where,  $k_f$  and  $k_p$ , are the individual mass transfer coefficients of the k chemical species on the fluid and particle sides, respectively. These are positive numbers and the direction of flow is determined by the concentration gradient. Note that based on figure 2.II.1. the continuity of the flow is observed.

$$\varphi_{k,f} = \varphi_{k,p} \tag{2.II.23}$$

it is easy to observe that the units of  $k_f$  and  $k_p$  are not the same as being a coefficient of proportionality they depend on the definitions of concentrations and mass flow  $\varphi_{k,\alpha}$ .

The concentrations at the interface are determined by thermodynamic equilibrium and are therefore not independent and are represented by the adsorption isotherm:

$$q_k = f(T, C_k)$$
  $k = 1..m$  (2.II.24)

and in the interface.

$$q_k^* = f(T, C_1...C_k^*...C_m)$$

In the last stage of the mass transport process (equilibrium) we will have:

$$C_k^* = C_k \quad \text{and} \quad q_k^* = q_k \tag{2.II.25}$$



FIGURE 2.II.1 transport on the interface

The linear driving force model implies the following kinetic model:

$$\frac{d}{dt}(q_{k,p}(t)) = \frac{3}{r_p}(\varphi_{k,p} \mid_{r=R_p})$$
(2.II.26)

the choice of layer (particle side or fluid side) is arbitrary, meeting a criterion of operational convenience.

### 2.II.5. obtaining kinetic parameters

For the determination of kinetic parameters, it is necessary to determine the average concentration of the k component in the particle at a given instant, t. Direct determination is very unusual because it requires highly complex equipment and a lot of experimental effort. However, indirect methods are widely used.

In this section, among the many methods presented in the literature, we will discuss the one that is perhaps the best known and the most used, when the fluid phase is a liquid, called *finite volume immersion method*, also known among us as *finite bath*. which is why the concentration of the k component in the fluid phase will almost always be referred to as the concentration in the bath,  $Cb_k$ . This method applies to both kinetic and thermodynamic equilibrium studies. It is the *macro* model applied to a closed system.

### 2.II.5.1. finite volume immersion method.

This section will be developed in two parts:

a) Obtaining experimental data;

b) The macro and micro model of interest.

#### a- Obtaining experimental data.

In a closed system the mass of any chemical constituent present is constant (*cte*). If a given k constituent is distributed between two phases (liquid and solid in the present case) then at any time, t will be for the k component in the system, (*sis*):

$$m_{k,sis}(t) = m_{k,p}(t) + m_{k,f}(t) = cte$$
(2.II.27)

Where,  $m_{k,p}$ , is the mass of the k component in the particulate phase and  $m_{k,f}$ , the mass of the k component in the fluid phase. Consequently.

$$m_{k,p}^{o} + m_{k,f}^{0} = m_{k,p} + m_{k,f}$$
(2.II.28)

in Eq. 2.II.28. the left side represents the initial time, t<sub>0</sub> and the right side any instant, t.

If at the initial instant,  $t_0$  a mass of solid,  $M_s^0$ , completely free of liquid, is placed in the presence of a mass of liquid,  $M_f^0$  with composition, in mass fraction,  $w_{1,f}^0, ..., w_{m,f}^o$ , at the constant temperature and pressure of the system that from that moment is closed then,  $m_{k,p}^o = 0$  and we have by Eq.2.II.28.

$$m_{k,p} = m_{k,f}^{o} - m_{k,f} = w_{k,f}^{o} M_{f}^{o} - w_{k,f} M_{f}$$
(2.II.29)

experimentally determining the concentrations  $w_{k,f}$  and the mass  $M_f$  at a given instant t it is possible, through Eq.2.II.29, to determine the total mass of the k component present in the particle (adsorbent). The measurements if carried out in sufficiently long times, symbolically,  $(t \rightarrow \infty)$ , in order to reach the thermodynamic equilibrium can, through Eq.2.II.29, allow the determination of adsorption isotherms.

The apparent simplicity of this equation can lead to the conclusion that conducting experiments is also simple. If, on the one hand, the determination of the concentrations of the liquid phase without changing the system conditions can be carried out, the same does not happen with the determination of the mass,  $M_{f}$ .

In most cases the mass,  $M_f$ , is determined indirectly with an approximate value by making hypotheses that are, in principle, achievable in the laboratory.

In order to provide some directly applicable relationships we will discuss some of these assumptions.

From the global balance in the closed system, we have:

$$M_{f} = M_{f}^{o} - \sum_{k=1}^{m} m_{k,p}$$
(2.II.30)

that taken in Eq.2.II.29. gives the result:

$$m_{k,p} = \frac{M_f^o}{(1 - w_{k,f})} \left[ w_{k,f}^o - w_{k,f} + \frac{w_{k,f}}{M_f^o} \sum_{\substack{j=1\\j \neq k}}^m m_{j,p} \right]$$
(2.II.31)

This equation is particularly useful when at least one of the components of the mixture is not adsorbed. The laboratory conditions imply the adoption of an inert chemical component, that is, with almost negligible selectivity in relation to the other components of the mixture and that, at the same time, does not remove the characteristic of a thermodynamically stable solution from the mixture.

In the case of a two-component solution where one of them is inert, the equation results;

$$m_{k,p} = M_{f}^{o} \left[ \frac{w_{k,f}^{o} - w_{k,f}}{1 - w_{k,f}} \right]$$
(2.II.32)

which is used for studies of the individual components of a mixture. The question that naturally arises is how to make sure that one of the components is inert. So, the equation can only be used correctly if additional information is provided. On the other hand, we have:

$$M_f = \rho_f V_f$$

equation relating the mass of the liquid,  $M_f$ , to its volume,  $V_f$ , through the density,  $\rho_f$ , of the liquid solution. Under these conditions Eq.2.II.29. becomes:

$$m_{k,p} = M_{f}^{o} \left[ w_{k,f}^{o} - w_{k,f} \left( \frac{\rho_{f} V_{f}}{\rho_{f}^{o} V_{f}^{o}} \right) \right]$$
(2.II.33)

consider in the liquid phase the relationship:

$$\Delta V_f = V_f^o - V_f$$

then:

$$m_{k,p} = M_{f}^{o} \left[ w_{k,f}^{o} - w_{k,f} \frac{\rho_{f}}{\rho_{f}^{o}} (1 - \frac{\Delta V_{f}}{V_{f}^{o}}) \right]$$

if the experiment is conducted in such a way that

 $\Delta V_f \ll V_f^o$  then:

$$m_{k,p} = M_{f}^{o} \left[ w_{k,f}^{o} - w_{k,f} \frac{\rho_{f}}{\rho_{f}^{o}} \right]$$
(2.II.34)

equation that, to be rigorously used, depends on the knowledge of the equation of state for the fluid phase:

$$\rho_f = \rho_f(w_{k,f}...w_{m,f})$$
(2.II.35)

Eq.2.II.34 is better known in the form:

$$q_{k,p} = \frac{M_{f}^{o}}{M_{p}} \left[ w_{k,f}^{o} - w_{k,f} \frac{\rho_{f}}{\rho_{f}^{o}} \right]$$
(2.II.36)

In the laboratory, the mass fractions are the most convenient, however the recommendation is to use (mol/gads) in the solid and (mol/cm<sup>3</sup>) in the fluid. So, it becomes necessary the conversion making use of the molecular mass,  $Mm_k$ , of the k component.

$$\Gamma_{k,p} = \frac{1}{Mm_k} q_{k,p}$$
 concentration in the particle  

$$\varsigma_{k,p} = \frac{1}{Mm_k} \rho_f w_{k,f}$$
 concentration in the fluid

volumetric concentrations for fluids are also practical and much appreciated, in this sense, assuming constant fluid density during the experiment. Eq.2.II.36 can be written as:

$$q_{k,p} = \frac{V_f^o}{M_p} \Big[ C_{k,f}^o - C_{k,f} \Big]$$
(2.II.37)

which is the form usually found in the literature.

After determining the concentration at time t, some researchers wait a long enough time to reach thermodynamic equilibrium and find an isotherm point, which experimentally is obtained by:

$$q_{k,p}^{\alpha} = \frac{V_f^o}{M_p} \Big[ C_{k,f}^o - C_{k,f}^{\alpha} \Big]$$
(2.II.38)

remaining under suspicion the constancy of the density of the fluid.

In kinetic studies, it is interesting to consolidate the results in terms of the adsorbed molar fraction "up take rate" defined by:

))

$$\Psi_k = \frac{q_{k,p}}{q_{k,p}^{\alpha}} \tag{2.II.39}$$

### typical equipment

By kinetics of the particulate phase is understood the mechanisms of mass transport in and out of its interior, taking into account possible chemical reactions.

Initially aiming only at transport phenomena, it is important to understand what is sought. It is evident that the demand is directly associated with the proposed transport mechanism, almost always a constitutive equation, presenting phenomenological coefficients to be determined experimentally, for validation of the proposed model.

In this sense, it is desired to separate the mechanisms intraparticle from those occurring outside it. Since, as already mentioned, the measurement of concentrations in its interior is done indirectly and almost always as a function of the changes it causes in its surroundings, special care must be taken in the construction of such experiments.

These precautions consist of guaranteeing;

1- the uniformity of pressure and temperature in the composite system;

2-the complete elimination of resistances to mass transport external to particle;

**3**-the complete characterization of the composite system.

Among these requirements, the second is the most unlikely and is what the equipment should focus on. In fluids, the slowest transport is diffusive. Thus, vigorous agitation uniforms the concentration, eliminating gradients and diffusive flows within it, but, on the surface of the particle, a thick boundary layer,  $\delta$ , harbors a concentration gradient, figure 2.II.1 imposing a diffusive flow represented by Eq. 2.II.22a.

$$\varphi_{k,f} = k_f (C_k - C_k^*)$$
 with  $k_{\alpha} \equiv \frac{\sigma_{\alpha}}{\delta_{\alpha}}$ 

it is imperative then to destroy the gradient so that the concentration at the surface is that of the core of the fluid, that is,  $(C_k \to C_k^*)$  and as the flux is finite implies that  $(k_f \to \infty)$  It is like  $\sigma_{\alpha}$  is a non-zero parameter of the fluid, it remains to be forced ( $\delta_{\alpha} \rightarrow 0$ ) and this is the unique feature of the equipment, printing a high relative particle-fluid velocity in the sense of substantial reduction of the boundary layer, since it will never be null. The simplest equipment that meets the advertised are: the perfectly stirred cell, and the thin layer cell. shown schematically in figure 2.II.2.



a) perfectly stirred cell

b) thin layer cell

Figure 2.II.2 - Cells for kinetic study in finite bath.

In our laboratory, we designed versions of the perfectly stirred cell and in a thin layer cell, with restrictions that ensure the hermetic and isothermal character of the same, where the following prerequisites were satisfied:

-operational ease with regard to assembly, control over the starting conditions of the experiments and collection of samples;

-cell thermostat in order to guarantee the system isothermicity;

-negligible change in the volume of the liquid in the system during the experiment, when aliquots are withdrawn for analysis;

-relative fluid-particle velocity of such an order as to minimize resistance to diffusion of the hydrodynamic boundary layer surrounding the particles;

-minimal mechanical damage to particles in order to keep their size constant over time, throughout the entire experiment.

These cells are shown in the figure. 2.II.3.



a) perfectly stirred cell

b) thin layer cell

Figure 2.II.3 - Devices for kinetic experimental studies.

It is interesting to point out that systems with mechanical agitators often cause damage to the particles and in this case the thin layer equipment, although more sophisticated, proves to be more effective.

### b- The macro and micro model of interest.

In this section we will select kinetic models to illustrate the *finite volume immersion method*.

#### the macro model

the *macro* model in this case is obviously the composite system: the *bath fluid* and the *set of particles*; characterized by uniformity in fluid concentration and particles distribution.

The most significant parameters are defined by the equations:

$$V = V_f + V_p; \quad \varepsilon_b \equiv \frac{V_f}{V}; \quad \rho_p = \frac{M_p}{V_p}$$
(2.II.40)

where  $\varepsilon_b$  is the porosity of the bath,  $\rho_p$ , the apparent density of the particles and V the total volume of the system (fluid and particles). It is important to note that in equations 2.II.40. the defined properties are not independent as they are linked by the equation:

$$\rho_p \frac{(1-\varepsilon_b)}{\varepsilon_b} = \frac{M_p}{V_f}$$
(2.II.41)

The mass balance of the k component in the bath is:

$$\frac{\partial}{\partial t} \left[ \varepsilon_b C_{k,1} + (1 - \varepsilon_b) C_{k,2} \right] + \operatorname{div} \left[ \varepsilon_b C_{k,1} \vec{v}_{k,1} + (1 - \varepsilon_b) C_{k,2} \vec{v}_{k,2} \right] = \varepsilon_b R_{k,1} + (1 - \varepsilon_b) R_{k,2}$$

Assuming no chemical reactions, the result is:

$$\frac{\partial}{\partial t} \left[ \varepsilon_b C_{k,1} + (1 - \varepsilon_b) C_{k,2} \right] + \operatorname{div} \left[ \varepsilon_b C_{k,1} \vec{v}_{k,1} + (1 - \varepsilon_b) C_{k,2} \vec{v}_{k,2} \right] = 0$$

and as the system is uniform the divergence vanishes and thus,

$$\frac{\partial}{\partial t} \left[ \varepsilon_b C_{k,1} + (1 - \varepsilon_b) C_{k,2} \right] = 0$$
(2.II.42)

and,

$$\frac{\partial C_{k,1}}{\partial t} = -\frac{(1-\varepsilon_b)}{\varepsilon_b} \frac{\partial C_{k,2}}{\partial t}$$
(2.II.43)

Eq. 2.II.43 in a notation referring to the bath and an average spatial concentration for the particle, as already seen:

$$\frac{\partial C_{b,k}}{\partial t} = -\frac{(1-\varepsilon_b)}{\varepsilon_b} \frac{d}{dt} C_{k,p}(t)$$
(2.II.43b)

which is the equation (*macro* model) that describes the temporal variation of the concentration of the bath as a function of the temporal variation of the concentration in the particle, this concentration, which is determined by the mass flow conditions on its surface. This can be known, in principle, by the adoption of models that describe this flow, such as those already discussed and summarized below:

$$\frac{d}{dt}C_{k,p}(t) = \frac{3}{R_p} \left(\varepsilon_p D_{k,f} \frac{\partial C_{k,f}}{\partial r} \right|_{r=R_p} \text{ two-phase particle model (PDM)}$$
(2.II.44)

$$\frac{d}{dt}(q_{k,p}(t)) = \frac{3}{R_p} (D_{k,p} \frac{\partial q_{k,p}}{\partial r} \bigg|_{r=R_p}) \text{ pseudo homogeneous model (HDM)}$$
(2.II.45)

$$\frac{d}{dt}(q_{k,p}(t)) = \frac{3}{R_p}k_p(q_k^* - q_{k,p}(t)) \text{ linear driving force (particle side)}$$
(2.II.46)

$$\frac{d}{dt}(q_{k,p}(t)) = \frac{3}{R_p} k_f(C_{k,f}(t) - C_k^*) \text{ linear driving force (fluid side)}$$
(2.II.47)

necessary to include the Langmuir adsorption/desorption rate equation:

$$\frac{d}{dt}(q_{k,p}(t)) = k_a C_{k,f}(1 - \frac{q_{k,p}(t)}{q_{k,p}^s}) - k_d(\frac{q_{k,p}(t)}{q_{k,p}^s})$$
(2.II.48)

Where  $k_a$  and  $k_d$  are, respectively, the kinetic constants of adsorption and desorption.

but in equilibrium;  $\frac{d}{dt}(q_{k,p}(t)) = 0$ , then:

$$q_{k,p} = q_{k,p}^{s} \frac{bC_{k,f}}{1+bC_{k,f}}$$
 with  $b = \frac{k_{a}}{k_{d}}$ ; Langmuir isotherm

combining equations 2.II.47 and 2.II.48 to eliminate  $C_k^*$ , a particularly useful relationship result:

$$\frac{d}{dt}(q_{k,p}(t)) = AC_{k,f}(t) - B$$
(2.II.49)

with,

$$A = 1 - k_a (q_{k,p}(t) - q_{k,p}^s) - \frac{3k_f}{R_p}$$
$$B = k_d q_{k,p}(t)$$

The most common form of quasi-chemical kinetics is given by:

$$\frac{d}{dt}(q_{k,p}(t)) = kC_{k,f}(q_{k,p}^s - q_{k,p}(t))$$
(2.II.50)

These equations 2.II.44 to 2.II.48 and 2.II.50 are also called *kinetic laws*. We do not like this denomination because these equations, being *constitutive*, cannot enjoy the *status* of laws. we prefer the designation of the *adsorption rate equation*, as other authors call them.

### the micro model

The kinetic parameters to be determined experimentally are:

1-  $D_{k,f}$  in the pore diffusion model (PDM); 2-  $D_{k,p}$  in the particle diffusion model (HDM); 3-  $k_p$  in the linear driving force model (LDF).

In summary, the ones used here are presented:

### - Pore diffusion model :

from Eq.(2.II.7e) we have:

$$\frac{\partial C_{k,f}}{\partial t} = \frac{1}{\left[1 + \frac{(1 - \varepsilon_p)}{\varepsilon_p} \frac{dC_{k,s}}{dC_{k,f}}\right]} D_{k,f} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_{k,f}}{\partial r}\right)$$
(2.II.51)

requiring a function:

$$C_{k,s} = f(T, C_{1,f}, \dots, C_{m,f})$$
 adsorption isotherm

most often in the notation:

$$C_{k,s} = C_{k,s}(T, C_{k,f})$$
 (2.II.52)

and the initial and boundary conditions:

$$t = 0, \quad C_{k,f} = C_{k,f}^{O};$$
  

$$r = 0, \quad \frac{\partial C_{k,f}}{\partial r} = 0;$$
  

$$r = R_{p}, \quad C_{k,f} = C_{b,k}$$
(2.II.52b)

for the bath, Eq. 2.II.43b

$$\frac{\partial C_{b,k}}{\partial t} = -\frac{(1-\varepsilon_b)}{\varepsilon_b} \frac{d}{dt} C_{k,p}(t)$$
(2.II.53)

and the "kinetic law" 2.II.44.

$$\frac{d}{dt}C_{k,p}(t) = \frac{3}{R_p} (\varepsilon_p D_{k,f} \frac{\partial C_{k,f}}{\partial r} \bigg|_{r=R_p})$$

results for the finite bath:

$$\frac{\partial C_{b,k}}{\partial t} = -\frac{(1-\varepsilon_b)}{\varepsilon_b} \frac{3}{R_p} \left(\varepsilon_p D_{k,f} \frac{\partial C_{k,f}}{\partial r}\right|_{r=R_p}$$
(2.II.54)

with initial condition,

$$t = 0, \quad C_{b,k} = C_{b,k}^{O}$$
 (2.II.54b)

- Pseudo-homogeneous model.

from Eq.2.II.18 we have:

$$\frac{\partial q_{k,p}}{\partial t} = D_p \left[ \frac{\partial^2 q_{k,p}}{\partial r^2} + \frac{2}{r} \frac{\partial q_{k,p}}{\partial r} \right]$$

requiring a function:

$$q_{k,p} = q_{k,p}(T, C_{b,k})$$
 isotherm

and the initial and boundary conditions:

$$t = 0, \quad q_{k,p} = q_{k,p}^{O};$$
  
$$r = 0, \quad \frac{\partial q_{k,p}}{\partial r} = 0;$$

$$r = R_p \ q_{k,p} = q_{k,p}(T, C_{b,k})$$

considering the density of the particle,  $\rho_p$  constant the equation for the bath is:

$$\frac{\partial C_{b,k}}{\partial t} = -\frac{(1-\varepsilon_b)}{\varepsilon_b} \rho_p \frac{d(q_{k,p}(t))}{dt}$$
(2.II.55)

and the "kinetic law" Eq. 2.II.45.

$$\frac{d}{dt}(q_{k,p}(t)) = \frac{3}{r_p} (\varepsilon_p D_{k,p} \frac{\partial q_{k,f}}{\partial r} \bigg|_{r=Rp})$$

results for the finite bath:

$$\frac{\partial C_{b,k}}{\partial t} = -\frac{(1-\varepsilon_b)}{\varepsilon_b} \rho_p \frac{3}{R_p} D_{k,p} (\frac{\partial q_{k,p}}{\partial r})_{r=R_p}$$
(2.II.55b)

with initial condition,

$$t=0, \quad C_{b,k}=C_{b,k}^O$$

- Model of linear driving force

The equation for the bath is Eq.(2.II.55) and equations 2.II.46 or 2.II.47 can be used.

choosing Eq. 2.II.46.

$$\frac{d}{dt}(q_{k,p}(t)) = \frac{3}{R_p} (\varepsilon_p(k_p(q_k^* - q_{k,p}(t)))$$

results;

$$\frac{\partial C_{b,k}}{\partial t} = -\rho_p \frac{(1-\varepsilon_b)}{\varepsilon_b} \frac{3}{R_p} (k_p (q_k^* - q_{k,p}(t))$$
(2.II.56)

it is interesting to put this last equation with bath data only.

from Eq. 2.II.37 we have:

$$q_{k,p} = \frac{V_{f}^{o}}{M_{p}} \Big[ C_{b,k}^{o} - C_{b,k} \Big]$$

and results for the bath,

$$\frac{\partial C_{b,k}}{\partial t} = -\rho_p \frac{(1-\varepsilon_b)}{\varepsilon_b} \frac{3}{R_p} k_p (q_k^* - \left[C_{b,k}^o - C_{b,k}\right] \frac{V_f^o}{M_p})$$
(2.II.57)

on the other hand, from Eq. 2.II.41.

$$\rho_p \frac{(1-\varepsilon_b)}{\varepsilon_b} = \frac{M_p}{V_f}$$

resulting,

$$\frac{\partial C_{b,k}}{\partial t} = -\frac{M_p}{V_f} \frac{3}{R_p} k_p (q_k^* - [C_{b,k}^o - C_{b,k}] \frac{V_f^o}{M_p})$$
(2.II.58)

which is undoubtedly the simplest model whose integration is hampered by the presence of the isotherm

$$q_{k}^{*} = q_{k}(C_{b,k})$$

which even in its simplest form:

$$q_k = q_k^s \frac{kC_{b,k}}{(1+kC_{b,k})}$$
; Langmuir isotherm

introduces strong nonlinearity into EQ.2.II.58. leading to a numerical procedure.

In many cases, especially *purification* operations, the fluid phase has very low concentrations and the Langmuir equation shows the following limit:

$$q_k = q_k^s k C_{b,k}$$

known as a linear isotherm and almost always represented by:

$$q_k = mC_{b,k}$$

whence,

$$q_k^* = mC_{b,k}$$

resulting for Eq. 2.II.58.

$$\frac{\partial C_{b,k}}{\partial t} = -\frac{M_p}{V_f} \frac{3}{R_p} k_p (mC_{b,k} - [C_{b,k}^o - C_{b,k}] \frac{V_f^o}{M_p})$$
(2.II.58b)

with t = 0,  $C_{b,k} = C_{b,k}^{O}$ 

which can then be solved by direct integration, resulting in:

$$C_{b,k} = \frac{C_{b,k}^{o}}{(1+\xi)} (1+\xi e^{(-k_{p}(1+\xi)t)})$$
(2.II.59)

where,

$$\xi = m \frac{V_s^o}{V_f^o}; \quad separation \ factor \tag{2.II.60}$$

The tables below summarize the results.

Table 2.II.1- synthesis of the pore  
diffusion modelTable 2.II.2- synthesis of the pseudo-  
homogeneous model
$$\frac{\partial C_{k,f}}{\partial t} = \frac{1}{\left[1 + \frac{(1 - \varepsilon_p)}{\varepsilon_p} \frac{dC_{k,s}}{dC_{k,f}}\right]} D_{k,f} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_{k,f}}{\partial r}\right) \\
 C_{k,s} = C_{k,s} (T, C_{k,f}, )$$
$$\frac{\partial q_{k,p}}{\partial t} = D_p \left[ \frac{\partial^2 q_{k,p}}{\partial r^2} + \frac{2}{r} \frac{\partial q_{k,p}}{\partial r} \right] \\
 q_{k,p} = q_{k,p} (T, C_{b,k}, )$$
$$t = 0, \ C_{k,f} = C_{k,f}^{O}; \\
 r = 0, \ \frac{\partial C_{k,f}}{\partial r} = 0; \\
 r = R_p, \ C_{k,f} = C_{b,k}$$
$$t = 0, \ q_{k,p} = q_{k,p}^{O}; \\
 r = R_p \ q_{k,p} = C_{b,k}$$
$$\frac{\partial C_{b,k}}{\partial t} = -\frac{(1 - \varepsilon_b)}{\varepsilon_b} \frac{3}{R_p} (\varepsilon_p D_{k,f} \frac{\partial C_{k,f}}{\partial r} \Big|_{r=R_p}$$
$$\frac{\partial C_{b,k}}{\partial t} = -\frac{(1 - \varepsilon_b)}{\varepsilon_b} \rho_p \frac{3}{R_p} D_{k,p} (\frac{\partial q_{k,p}}{\partial r})_{r=R_p}$$
$$t = 0, \ C_{b,k} = C_{b,k}^{O}$$
$$t = 0, \ C_{b,k} = C_{b,k}^{O}$$
Table 2.II.3- synthesis of the linear driving force model

$$\frac{\partial C_{b,k}}{\partial t} = -\rho_p \frac{(1-\varepsilon_b)}{\varepsilon_b} \frac{3}{R_p} (k_p (q_k^* - q_{k,p}(t)))$$
Or
$$\frac{\partial C_{b,k}}{\partial t} = -\frac{M_p}{V_f} \frac{3}{R_p} k_p (q_k^* - [C_{b,k}^o - C_{b,k}] \frac{V_f^o}{M_p})$$

$$q_k^* = q_k (C_{b,k})$$

$$t = 0, \quad C_{b,k} = C_{b,k}^o$$

# 2.II.5.2. applications of the finite volume immersion method

Finishing the preparation of the method, we will exemplify with a specific problem.

Consider treating wastewater using ion exchange resin as an adsorbent.

The system was characterized and the following data were obtained:

| Characterization of Ion Exchange Resin                    | Particle characterization                           |
|-----------------------------------------------------------|-----------------------------------------------------|
| type/structure: strong acid/macropore;                    | $R_p = 0.03575$ cm, particle radius                 |
| matrix; styrene;                                          | $\varepsilon_{\rm p} = 0.732$ , particle porosity   |
| functional group: -SO <sup>3-</sup> ;                     | $\rho_{ade} = 2.578 \text{ g/cm}^3$ solid density   |
| ionic form: Na <sup>+</sup> ;                             | $p_{aus} = 2.576 \text{ g/cm}^3$ , solution donsity |
| <b>H<sub>2</sub>O retention capacity (%)</b> : (45 - 50.) | pf =1.0 g/cm, solution density                      |

Table 2.II.4- Characterization of the adsorbent

Thermodynamic equilibrium data showed a good correlation with the Sips equation

| Table 2.II.5 - ado | pted isotherm |
|--------------------|---------------|
|--------------------|---------------|

|                                                                                            | whose adjusted parameters are:                                                                                |
|--------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------|
| $q_{k} = q_{k}^{s} \frac{(kC_{b,k})^{\frac{1}{t}}}{(1 + (kC_{b,k})^{\frac{1}{t}})};  Sips$ | $q_k^s = 0.083 \text{ g/cm}^3;$<br>$k = 1503370 \text{ cm}^3/\text{g};$<br>t = 2.33<br>$T = 30^\circ\text{C}$ |

and whose graph is shown below:



FIGURE 2.II.4 - isotherm: resin water copper system

a - Applying the model in Table 2.II.1., whose numerical solution was implemented by the orthogonal placement method coupled to a parameter adjustment program, we obtained:



FIGURE 2.II.5. - Concentration in the bath as a function of time. Experimental data and fitted for *pore diffusion model* 

After adjustment of experimental data for the pore diffusion coefficient,

 $D_{k,f} = 0.1009 \text{ x } 10^{-6} \text{ cm}^2/\text{s};$ 

compatible with diffusion values in liquids and literature data for adsorbents.

b) - Applying the model in Table 2.II.2., whose numerical solution was implemented by the orthogonal placement method coupled to a parameter adjustment program, we obtained:



FIGURE 2.II.6. - Concentration in the bath as a function of time. Experimental data and fitted for *pseudo-homogeneous model*.

After adjustment resulted for the diffusion coefficient in the particle,

 $D_{k,p} = 0.75 \text{ x } 10^{-8} \text{ cm}^2 /\text{sec};$ 

acceptable value for short exposure times, but very poor to represent the experimental data, in fact this is a characteristic of this model it is reasonably good for actually homogeneous particles such as gels, but fails with porous particles.

c)- Applying the model in Table 2.II.3 with a numerical solution coupled to a parameter adjustment program resulted:



FIGURE 2.II.7 - concentration in the bath as a function of time. Experimental data and fitted for *linear driving force model*.

After adjustment resulted for the mass transfer coefficient in the particle,

 $k_p = 0.35 \text{ x } 10^{-6} \text{ cm/s}$ 

acceptable value for short exposure times, but very poor to represent the experimental data.

On the other hand, in the case of a *diluted solution*, a linearization of the isotherm is possible, analytically obtaining Eq. 2.II.59. In figure 2.II.7b. experimental data and a model of the linear driving force with linear isotherm are shown.



FIGURE 2.II.7b - concentration in the bath as a function of time. Experimental data and *linear driving force model with linear isotherm.* 

After adjustment resulted for the mass transfer coefficient in the particle,

 $k_p = 0.281 \times 10^{-5} \text{ cm/s}.$ 

Due to the good agreement between model and experimental data, it is also shown that for dilute solutions a linear isotherm can be adopted. In view of the quality of representing the experimental data, the pore diffusion model (PDM) and the linear driving force model (LDF) with linear isotherm are equivalent in this experiment.

At the end of this section, it is instructive to appreciate the phenomenon of diffusion within a single particle within an *infinity bath* of uniform concentration,  $C_{k,f}$ .



FIGURE 2.II.8 particle concentration profile in *infinite bath* with time as parameter.

At the beginning of time, the particle is free from the k component; as time passes by a front of concentration of the k component advances from the interface towards the interior of the interface until the particle is saturated at a uniform concentration,  $q_k^*$ , such that:

$$q_k^* = f(C_{k,f})$$

as required by thermodynamic equilibrium.

## 2.II.6. Packed column method

This method applies to both liquids and gases. It is the use of a particular *macro* system for studies of important parameters of adsorptive processes.

We will consider a fixed bed, as a packed column, filled uniformly by adsorbent particles in equilibrium with a desorbent or diluent (some fluid).



FIGURE 2.II.9 - Cell for kinetic study in fixed bed

Let us observe the k component concentration profile in the fluid phase, as a function of time and position within the bed from an initial instant where the bed is fed by a fluid stream of constant velocity and concentration of some adsorbable substance.

The phenomenon is inherently transient and a mass transfer zone begins to form from the moment the feed is established and takes definitive shape from the moment the adsorbent at the bed entrance reaches equilibrium with the incoming fluid. From that moment on, the mass transfer zone moves through the bed like a wave. This phenomenon is illustrated in Fig.2.II.10 Where is the concentration of the solution in the fluid phase as a function of the position, z along the bed for increasing values of time.



FIGURE 2.II.10 - fluid concentration profiles along the z axis of the bed, with time as a parameter.

If the solute concentration in the bed effluent is measured as a function of time, it is observed a curve similar to the one in figure 2.II.11. called the *breakthrough curve*. No solute is detected in the early stages so rupture occurs when the wavefront of the mass transfer zone reaches the end of the bed and the solute is detected in increasing amounts until its concentration equals that of the fluid entering the bed. The bed is completely saturated and can no longer retain solute.



FIGURE 2.II.11 - history of concentration at the exit of the column (*breakthrough curve*)

The process described was that of adsorption. if it is, in sequence, fed by a stream of the diluent (desorbent) we will have the desorption process; Figure 2.II.12 shows a general representation of the solute concentration in the fluid phase as a function of position, z and time, t. The plane normal to the t-axis at position t=0 shows the initial condition and the plane normal to the z-axis at position z=L shows the rupture curve (*breakthrough curve*)



FIGURE 2.II.12 - space-time representation of concentration in the fluid phase inside the column.

Instead of a step-shaped disturbance, a peak-shaped disturbance can also be used, sometimes called a Dirac disturbance, it is a pulse of infinitesimal duration that suddenly introduces into the bed a finite amount of a solution containing solute and then entrained through the feed at a constant rate of the diluent. The pulse (peak) changes its height and shape as it walks inside the bed. The factors that influence the wave in the case of the step disturbance are the same that influence the peak in the case of the pulse disturbance. In this case the method is sometimes called chromatographic.

Although both types of perturbations can be used in any type of fixed bed, peak perturbation is mostly used in short beds. A bed is considered short when, in the case of a step disturbance, the rupture occurs before the adsorbent layer at the entrance of the bed comes into equilibrium with the fluid that enters.

For the case of the experiment with step perturbation, it is advisable that the bed has at least two lengths of the mass transfer zone (concentration wave) after fully developed. The

bed diameter must be at least 20 times larger than the average diameter of the particles and uniformly filled with them.

The factors that affect the mass transfer zone (peak or step) as well as its velocity within the bed are linked to the mechanisms involved in adsorption, which belong to three major classes: *thermodynamic*, *fluid dynamic* and *kinetic*.

*Thermodynamics* are those that determine the solute distribution between the phases. They include local properties such as total fluid concentration, bed porosity, and adsorbent capacity as a function of fluid concentration in addition, of course, to temperature and pressure. This information is essentially contained in the adsorption isotherms (*equilibrium laws at interfaces*).

The *fluid dynamics* are those that determine the dispersion. They include the fluid flow regimes (laminar or turbulent) geometric effect such as, for example, preferential channels due to bed packing, gravitational instabilities producing segregation or even digitization and mainly diverse heterogeneities.

*Kinetics* are those that determine local mass transfer rates throughout the system and are greatly affected by capacitive or thermodynamic and dynamic effects... The overall result is evidently an enlargement of the mass transfer zone (*kinects laws*).

In studies related to the packed column method, the global results of mass transfer are analyzed through the *breakthrough curves*, which have the solute concentration as a function of time or effluent volume, since both are proportional. Data processing is based on the conservation of certain global properties.

In this case, global material balances can be expressed simply by examining the areas under the curves. In the figure 2.II.13 the *breakthrough curves* are presented in terms of solute concentration in the fluid phase in (mole per unit volume) as a function of volume so that the area has the dimension of the number of moles.



FIGURE 2.II.13 - global mass balances relative to the breakthrough curves.

A material balance in global terms of the type *quantity entering minus quantity leaving equals accumulated quantity*, we have, based on figure 2.II.13 where  $C_0$  is the concentration of solute in the bed at the initial instant and  $C_f$  is the concentration of solute in the feed that percolates through the column at constant flow from the beginning of the time count gives:

leaves (leakage), L

Figure 2.II.13a illustrates the amount that leaves, which is the amount of solute that enters and that was not retained by the bed, when a volume V of fluid percolates through the bed.

$$L = \int_{0}^{V} (C - C_0) dV$$

goes into(input), I

Figure 2.II.13b illustrates the amount that enters, which is the amount of solute that actually enters when a volume V of the fluid percolates through the bed.

$$I = \int_{0}^{V} (C_{f} - C_{0}) dV = (C_{f} - C_{0})V$$

accumulated(storage), S

Consequently, the amount accumulated in the bed will be figure 2.II.13c.

$$S = I - L = \int_{0}^{V} (C_f - C_0) V$$

**maximum accumulation** (maximum storage),  $S_{\infty}$ 

In figures 2.II.13d. and 2.II.13e. maximum accumulated values are illustrated and are obtained for large values of the effluent volume  $(V \rightarrow \infty)$  so,

$$S_{\infty} = \int_{0}^{\infty} (C_f - C) dV = \int_{C_0}^{C_f} V dC$$

whose particular case, figure 2.II.13e., concerning the initially solute-free bed ( $C_0 = 0$ ) gives the total sorption capacity for a given feed concentration, Cf,

$$Q = S_{\infty}(C_0 = 0) = \int_0^{C_f} V dC$$

in figure 2.II.13f. is showing the unused capacity effectively and representing the difference between the maximum capacity and the capacity at a given instant. so,

lost capacity (unused capacity), U

$$U = S_{\infty} - S = \int_{0}^{Q} (C_f - C) dV$$

in the figures 2.II.13g. and 2.II.13h. we have the definition of the average rupture volume, also called stoichiometric volume. So,

average rupture volume (mean breakthrough volume),  $\overline{V}$ 

$$\overline{V} = \frac{1}{(C_f - C_0)} \int_{C_0}^{C_f} V dC = \frac{S_{\infty}}{(C_f - C_0)}$$

which implies in

$$S_{\infty} = \overline{V}(C_f - C_0)$$

All these parameters are directly used in the evaluation of the adsorption system and process. In our kinetic studies using the packed column method, we equipped the laboratory with benchtop devices.2.II.14 and pilot 2.II.15.



FIGURE 2.II.14 - benchtop fixed bed adsorption unit

- 1. Solution reservoir;
- 2. Reservoir for eluent solution;
- 3. Bypass valve;
- 4. Bypass valve;
- 5. Peristaltic Pump (MCP ISMATEC);
- 6. Adsorption column (a), (b) and (c);
- 7. Sampling valves;
- 8. sampler bottles;
- 9. acrylic support for glass adsorbent columns;
- 10. Reservoir for collection, treatment and disposal of solutions.

On a pilot scale we designed and an interested company installed the plant schematically shown in figure 2.II.15.



FIGURE 2.II.15 - plant for studies of the adsorption phenomena showing an enlarged detail of the packed column.

It basically consists of an adsorption column in a fixed bed, two piston-type positive displacement pumps, two stainless steel reservoirs, two sets of solenoid valves for directing the currents and a double-tube heat exchanger at the exit of the column, for liquid cooling, and a pneumatic valve to control the pressure inside the system. The adsorption column, whose construction detail is enlarged in the figure 2.II.13 consists of a stainless-steel tube whose heating and thermal control is carried out by electrical resistance and special sensors. The installation is fully controlled and allows operation with both step and pulse (peak) disturbance.

Some of the typical results we obtained are shown in terms of mass fraction as a function of time in *breakthrough* curve tests in the figure 2.II.16. and 2.II.17.



Figure 2.II.16 - *breakthrough* curves having the input concentration as a parameter.



Figure 2.II.17 - *breakthrough* curves for a multicomponent system in a desorption process. (p-xylene, m-xylene, o-xylene, ethylbenzene, n-octane)

The bench device has as main purpose kinetic studies aiming at the feasibility of adsorptive processes to separation and purification operations. The advantage is that it is suitable for an exploratory study; the amounts of material are small and the manipulations acceptable in terms of initial concentration, operating time, temperature effect and its control during the adsorptive process, among others, this requires many tests and repetitions, making it expensive on a pilot scale. The purpose of the pilot scale is to respond to the following demand: The company has an industrial plant, a high cost of adsorbent replacement and some manufacturers offering a supposedly equivalent material at a better cost.

To end this section, we will present a methodology for obtaining the parameters of the global mass balances related to the rupture curve. The procedure begins with the experimental obtaining of the *breakthrough* curve itself, followed by the selection of an arbitrary function to fit the data. There are functions that appear, naturally, in the adoption of models for predicting rupture curves, as will be seen in Chapter 3. Unfortunately, those that best represent the phenomenon have a high numerical cost. Some functions, as they originate from solutions of models proposed for the description of rupture curves, are of desired interest, such as the one obtained by Bohart and Adams (1920)<sup>12</sup>who adopted in the macro model the adsorption rate equation given by the quasi-chemical kinetics of Eq.2.II.35e.; whose best-known result is:



Figure 2.II.18 - breakthrough curve and fitted kinetic parameters relative to the chosen model.

It is necessary to emphasize that there are three temporal parameters of interest with particular importance in the generalization of the results, which are: the *breakthrough time*, **tb**, when the first traces of the k component are detected at the exit of the bed, the time to exhaustion of the adsorbent(*saturation time*), **ts** when the concentration of the k component is that of entry in the column and the *breakthrough average time*,  $\bar{t}_{b}$ .

The relationship between the elapsed time, t and the injected volume, V is, of course, the volumetric operating flow, Qv, given by:

<sup>&</sup>lt;sup>12</sup>Bohart, GS, Adams, EQ Journal of the American Chemical Society, 42, 523-544 (1920).

$$t = \frac{V}{Q_V}$$

whose substitution in the fitting equation transforms the natural results  $C_{bt,k} = f(t)$  in  $C_{bt,k} = f(V)$  which is the usual way of treating the global balance as discussed from figure 2.II.12. In view of the friendly nature of the correlation  $C_{bt,k} = f(V)$ , obtaining L, I, S,  $S_{\alpha}$ , Q,  $U \in \overline{V}$  can be undertaken by easy-to-execute direct integration. This is the complete *breakthrough curve analysis*.

As will be seen in Chapter 3, the rupture curve will be practically the only way to obtain data from the inside of the column from measurements in the outside environment only.

Although chapter 3 is the appropriate place for construction and analysis of adsorptive systems seems to us from a didactic point of view that the treatment of the fixed bed column should be presented here.

Therefore, on the basis of Fig. 2.II.9. a fixed bed of diameter, D and length, L, uniformly filled with adsorbing particles of radius,  $R_p$ , characterized by uniform porosity, $\varepsilon_L$  and not subject to chemical reactions. For such a system, as already seen, the mass balance is:

$$\frac{\partial}{\partial t} \left[ \varepsilon_L C_{k,f} + (1 - \varepsilon_L) C_{k,s} \right] + \operatorname{div} \left[ \varepsilon_L \vec{\varphi}_{k,f} + (1 - \varepsilon_L) \vec{\varphi}_{k,s} \right] = 0$$
$$\frac{\partial}{\partial t} \left[ \varepsilon_L C_{k,f} + (1 - \varepsilon_L) \rho_p q_{k,p} \right] + \operatorname{div} \left[ \varepsilon_L \vec{\varphi}_{k,f} + (1 - \varepsilon_L) \vec{\varphi}_{k,s} \right] = 0$$

suppose that the transport in the particles is only intraparticular and that in the external fluid they are only dispersive and convective such that:

$$\vec{\varphi}_{k,s} = 0$$
  
$$\vec{\varphi}_{k,f} = -D_{d,f} \operatorname{grad} C_{k,f} + C_{k,f} \vec{V}_{f}$$

Where,  $D_{d,f}$  and  $\vec{V}_f$  are, respectively, the fluid phase dispersion coefficient and the local interstitial fluid velocity.

$$\frac{\partial}{\partial t} \left[ \varepsilon_L C_{k,f} + (1 - \varepsilon_L) \rho_p q_{k,p} \right] + \operatorname{div} \left[ \varepsilon_L (-D_{d,f} \operatorname{grad} C_{k,f} + C_{k,f} \vec{V}_f) \right] = 0$$
(2.II.62)

The column evidently suggests a cylindrical system of references, but for a first treatment of Eq. 2.II.62. radial and angular movements are neglected, leaving only axial variations in the z direction as shown in figure 2.II.9. assuming further that we can consider the dispersion coefficient of the fluid phase constant, it results:

$$\frac{\partial}{\partial t} \left[ \varepsilon_L C_{k,f} + (1 - \varepsilon_L) \rho_p q_{k,p} \right] + \left[ \varepsilon_L (-D_{az,f} div(grad C_{k,f}) + div(C_{k,f} \vec{V}_f)) \right] = 0$$

$$\frac{\partial C_{k,f}}{\partial t} + \frac{(1 - \varepsilon_L)}{\varepsilon_L} \rho_p \frac{\partial q_{k,p}}{\partial t} - D_{az,f} \frac{\partial^2 C_{k,f}}{\partial z} + C_{k,f} \frac{\partial V_z}{\partial z} + V_z \frac{\partial C_{k,f}}{\partial z} = 0$$
(2.II.63)

Suppose the column is fed by a volumetric flow rate, Qv, then the surface velocity, u, is by definition:

$$u \equiv \frac{Q_v}{A}$$

and the interstitial velocity:

$$V_Z = \frac{u}{\varepsilon_L}$$

For a constant volumetric flow,  $u = u_o$  and results:

$$V_z = \frac{u_o}{\varepsilon_L}$$

and leave,

$$\frac{\partial C_{k,f}}{\partial t} + \frac{(1 - \varepsilon_L)}{\varepsilon_L} \rho_p \frac{\partial q_{k,p}}{\partial t} - D_{ax} \frac{\partial^2 C_{k,f}}{\partial z} + \frac{u_o}{\varepsilon_L} \frac{\partial C_{k,f}}{\partial z} = 0$$
(2.II.64)

for the treatment of this macro model, it must be complemented with a micro model generically represented by:

$$\frac{\partial q_{k,p}}{\partial t} = \text{"kinect law"}$$
(2.II.65)

and equilibrium laws at the interface, usually the isotherm.

The selection of the "kinetic law" may be one of those presented in the equations 2.II.44 to 2.II.48 and 2.II.50 or proposal based on specific mechanisms even adopting pseudo-adsorption reactions. The initial and boundary conditions complete the model:

at t=0 
$$C_{k,f} = C_{k,f}(z)$$
 and  $q_{k,p} = q_{k,p}(z)$ 

in 
$$z=0$$
  $\vec{\varphi}_{k,f}\Big|_{z=0^-} = \vec{\varphi}_{k,f}\Big|_{z=0^+}$  flow continuity

z=L 
$$C_{k,f}\Big|_{z=L^-} = C_{k,f}\Big|_{z=L^+}$$
 concentration continuity

or, in another way,

$$u_o C_{k,f}^0 = u C_{kf} - D_{d,f} \frac{\partial^2 C_{k,f}}{\partial z^2};$$

simply,

z=0 
$$u_o(C_{k,f}^0 - C_{kf}) = -D_{d,f} \frac{\partial^2 C_{k,f}}{\partial z^2}$$
 and z=L  $\frac{\partial C_{k,f}}{\partial z} = 0$ 

In chapter 3 we will deal in more detail with the model represented by these equations. The solution of the model necessarily involves numerical techniques, given the strong nonlinear character it presents. Some simplifications that, although removing relevant information from the model, such as axial dispersion, may, depending on the kinetic model, result in plausible results for obtaining the rupture curve. In the figure 2.II.19 shows what is expected from the mathematical results of the model presented, (fixed bed). This figure shows the spatial displacement of the mass transfer zone in the rupture time and in the saturation time, observe how the rupture curve is already drawn at the z=L dimension of figure b). Figure 2.II.20 shows the temporal evolution of concentrations in the liquid phase and in the solid phase.



FIGURE 2.II.19 - fluid concentration profile,  $C_{k,f}(z,t)$ , inside the column of length, L

(2.II.66)



FIGURE 2.II.20 - fluid concentration profiles,  $C_{k,f}(z,t)$ , and the adsorbent,  $q_{k,p}(z,t)$  inside the column of length, L

## CHAPTER 3. TRANSPORT PHENOMENA

In this Chapter we propose to present the subject related to transport phenomena. As in Chapters 1 and 2, the subject will be treated in two parts, as specific cases of the formulation:

- Part I- Electrolytic systems (three-dimensional electrodes, (ELT));
- Part II- Adsorptive Systems;

## **3.1. Introduction**

For the purpose of observing the phenomena involved, consider the movement of a material system containing multiple phases, generically described by the symbol  $\alpha$ , and that in each of these phases there are multiple chemical species, described generically by the symbol k. Suppose that, in each of these phases, one can define macroscopic properties, resulting from a statistical process of averages, in an infinitesimal volume element, and that, with respect to stationary axes, any of these properties can be considered as functions continuous time and spatial coordinates adopted for their description. Suppose that all phases are "uniformly" distributed in a representative volume element of the spatial coordinate system so that all phases, and all material chemical species, are present at any point in the space of so that the following settings can be made:

dV = infinitesimal volume element;dA = infinitesimal surface element; $dV_{\alpha} = volume occupied by the <math>\alpha$  phase inside dV;  $dmk_{,\alpha} = mass of k$  chemical species inside  $dV_{\alpha}$ .

$$dV = \sum_{\alpha} dV_{\alpha}$$
(3.1)

$$v_{\alpha} = \frac{dv_{\alpha}}{dV}$$
;  $\sum_{\alpha} v_{\alpha} = 1$  (3.2)

$$C_{k,\alpha} = \frac{dm_{k,\alpha}}{dV_{\alpha}} \quad ; \quad \rho_{\alpha} = \frac{\sum_{k} dm_{k,\alpha}}{dV_{\alpha}} \quad (3.3)$$

In these equations,  $\upsilon_{\alpha}$  is the local volume fraction of the  $\alpha$  phase,  $Ck_{,\alpha}$  the local concentration of the k chemical species within the  $\alpha$  phase and  $\rho_{\alpha}$  the local density of the  $\alpha$  phase.

If, within the  $\alpha$  phase, a given k chemical species is an ion, with a charge number  $Z_k$ , and a molecular mass,  $M_k$  then the electrical charge of this chemical species, per unit volume of  $\alpha$  phase, it will be:

$$Q_{k,\alpha} = F \frac{Z_k}{M_k} C_{k,\alpha}$$
(3.4)

In this equation  $Q_{k,\alpha}$ , is the local concentration of electric charges of the k chemical species inside the  $\alpha$  phase;

#### **3.2.** The transport equations

The formulation of the transport problem, as will be presented below, will be directly associated with the thermodynamic concept of phases. Thus, with respect to fixed axes and non-time-dependent control volume, balances will be postulated in the following ways:

Mass balance of k component in a phase-

$$\frac{\partial}{\partial t} \left[ \upsilon_{\alpha} C_{k,\alpha} \right] + \operatorname{div} \left[ \upsilon_{\alpha} C_{k,\alpha} \vec{v}_{k,\alpha} \right] = \upsilon_{\alpha} R_{k,\alpha}$$
(3.5)

In this equation  $\vec{v}_{k,\alpha} \in R_{k,\alpha}$  are, respectively, the local velocity vector of the k chemical species inside the  $\alpha$  phase and the local rate of mass production of the k chemical species per unit volume of the  $\alpha$  phase.

Mass balance of the k component in the mixture-

$$\frac{\partial}{\partial t} \left[ \overline{\rho}_k \right] + \operatorname{div} \left[ \overline{\rho}_k \vec{v}_k \right] = \mathbf{R}_k; \qquad (3.6)$$

Where:

$$\overline{\rho}_{k} = \sum_{\alpha} \upsilon_{\alpha} C_{k,\alpha}; \quad \vec{v}_{k} = \frac{\sum_{\alpha} \upsilon_{\alpha} C_{k,\alpha} \vec{v}_{k,\alpha}}{\sum_{\alpha} \upsilon_{\alpha} C_{k,\alpha}}; \quad R_{k} = \sum_{\alpha} \upsilon_{\alpha} R_{k,\alpha}$$
(3.7)

In these equations,  $\overline{\rho}_k$ , is the local partial density of the k component;  $\vec{v}_k$  is the local velocity vector of the k chemical species inside the mixture and  $R_k$  is the local rate of mass production of the k chemical species per volume element of the mixture.

Overall mass balance of the mixture-

$$\frac{\partial}{\partial t} \left[ \rho \right] + \operatorname{div} \left[ \rho \vec{v} \right] = 0 \tag{3.8}$$

where

$$\rho = \sum_{k} \overline{\rho}_{k}; \quad v = \frac{\sum_{k} \overline{\rho}_{k} \overline{v}_{k}}{\sum_{k} \overline{\rho}_{k}}; \quad \sum_{k} R_{k} = 0$$
(3.9)

In these equations,  $\rho$ , is the local density of the mixture and  $\vec{v}$  is the local velocity vector of the mixture moving as a single body. Eq. 3.9c meets the principle of conservation of mass.

Electric charges balance of k component in a phase-

$$\frac{\partial}{\partial t} \left[ Q_{k,\alpha} \right] + \operatorname{div} \left[ \upsilon_{\alpha} \vec{i}_{k,\alpha} \right] = \upsilon_{\alpha} F \frac{Z_k}{M_k} R_{k,\alpha}$$
(3.10)

where:

$$\vec{i}_{k,\alpha} = F \frac{z_k}{M_k} C_{k,\alpha} \vec{v}_{k,\alpha}$$

is the local current density vector of the k chemical species within the  $\alpha$  phase;

Electric charges balance of k component in the mixture-

$$\frac{\partial}{\partial t} \left[ \overline{\mathbf{Q}}_{k} \right] + \operatorname{div} \left[ \vec{\mathbf{i}}_{k} \right] = F \frac{\mathbf{Z}_{k}}{\mathbf{M}_{k}} \mathbf{R}_{k}$$
(3.11)

where:

$$\overline{Q}_{k} = F \frac{z_{k}}{M_{k}} \overline{\rho}_{k} \quad e \quad \vec{i}_{k} = F \frac{z_{k}}{M_{k}} \overline{\rho}_{k} \vec{v}_{k}$$

In these equations,  $\overline{Q}_k$ , is the local partial charge density of the k component,  $\vec{i}_k$  is the local current density vector of the k chemical species inside the mixture.

Overall Electric charges balance of the mixture-

$$\frac{\partial}{\partial t} [Q] + \operatorname{div} [\vec{i}] = 0 \tag{3.12}$$

where:

$$Q = \sum_{\alpha} \sum_{k} \upsilon_{\alpha} F \frac{Z_{k}}{M_{k}} C_{k,\alpha}; \vec{i} = \sum_{\alpha} \sum_{k} \upsilon_{\alpha} \vec{i}_{k,\alpha}; \sum_{\alpha} \sum_{k} \upsilon_{\alpha} F \frac{Z_{k}}{M_{k}} R_{k,\alpha} = 0$$
(3.13)

In these equations Q is the local charge density of the mixture and  $\vec{i}$  is the local current density vector of the mixture moving as a single body. Eq. 3.13c meets the principle of conservation of electric charge.

A complete description of the phases, their movements and interactions in terms of exchanges of mass, energy and momentum is necessary for a complete understanding of the phenomena involved. Therefore, the balances referring to the phases are as follows:

## Global a phase mass balance-

Adding both members of Eq.3.5, for all k, results:

$$\frac{\partial}{\partial t} \left[ \overline{\rho}_{\alpha} \right] + \operatorname{div} \left[ \overline{\rho}_{\alpha} \vec{v}_{\alpha} \right] = \mathbf{R}_{\alpha}; \qquad (3.14)$$

where:

$$\overline{\rho}_{\alpha} = \sum_{k} \upsilon_{\alpha} C_{k,\alpha} \; ; \; \overline{v}_{\alpha} = \frac{\sum_{k} \upsilon_{\alpha} C_{k,\alpha} \overline{v}_{k,\alpha}}{\sum_{k} \upsilon_{\alpha} C_{k,\alpha}} \; ; \; R_{\alpha} = \sum_{k} \upsilon_{\alpha} R_{k,\alpha} \tag{3.15}$$

In these equations,  $\overline{\rho}_{\alpha}$ , is the local partial density of the  $\alpha$  phase;  $\vec{v}_{\alpha}$  is the local velocity vector of the  $\alpha$  phase and  $R_{\alpha}$  the local rate of global mass production, in the $\alpha$  phase, by the volume unit of the  $\alpha$  phase. It is easy to verify that  $\overline{\rho}_{\alpha} = \upsilon_{\alpha}\rho_{\alpha}$ .

## Global a phase Electric charges balance-

Adding both members of Eq.3.10, for all k, results:

$$\frac{\partial}{\partial t} \left[ \overline{Q}_{\alpha} \right] + \operatorname{div} \left[ \upsilon_{\alpha} \vec{i}_{\alpha} \right] = \sum_{k} \upsilon_{\alpha} F \frac{Z_{k}}{M_{k}} R_{k,\alpha}; \qquad (3.16)$$

Where:

$$\overline{\mathbf{Q}}_{\alpha} = \sum_{k} \upsilon_{\alpha} F \frac{\mathbf{Z}_{k}}{\mathbf{M}_{k}} \mathbf{C}_{k,\alpha} ; \ \vec{\mathbf{i}}_{\alpha} = \sum_{k} F \frac{\mathbf{Z}_{k}}{\mathbf{M}_{k}} \mathbf{C}_{k,\alpha} \vec{\mathbf{v}}_{k,\alpha}$$
(3.17)

In these equations  $\overline{\mathbf{Q}}_{\alpha}$  is the local partial electric charge density of the  $\alpha$  phase and  $\vec{i}_{\alpha}$  is the local current density vector of the  $\alpha$  phase. The amount  $\upsilon_{\alpha} \vec{i}_{\alpha}$  is the current density calculated over the unit area as a whole (projected area) and not over the individual unit area of the phase.

Postulating that each phase, individually, is electrically neutral, then:

$$\sum_{k} \frac{Z_k}{M_k} C_{k,\alpha} = 0 \tag{3.18}$$

and results for Eq. 3.16:

$$\operatorname{div}\left[\upsilon_{\alpha}\vec{i}_{\alpha}\right] = \upsilon_{\alpha}F\sum_{k}\frac{Z_{k}}{M_{k}}R_{k,\alpha}$$
(3.19)

and adding to all  $\alpha$ , results:

$$\sum_{\alpha} \operatorname{div} \left[ \upsilon_{\alpha} \vec{i}_{\alpha} \right] = \operatorname{div} \left[ \sum_{\alpha} \upsilon_{\alpha} \vec{i}_{\alpha} \right] = \operatorname{div} \left[ i \right] = \sum_{\alpha} \sum_{k} \upsilon_{\alpha} F \frac{Z_{k}}{M_{k}} R_{k,\alpha}$$
(3.20)

and as the last term is null by Eq. 3.13c results:

$$\sum_{\alpha} \operatorname{div}[\upsilon_{\alpha} \vec{i}_{\alpha}] = 0 \tag{3.21}$$

a phase linear momentum balance-

$$\bar{\rho}_{\alpha} \left[ \frac{\partial \vec{v}_{\alpha}}{\partial t} + (grad \ \vec{v}_{\alpha}) \bullet \vec{v}_{\alpha} \right] = \operatorname{div} T_{\alpha} + \bar{\rho}_{\alpha} \vec{\ell}_{\alpha} + \bar{\rho}_{\alpha} \vec{b}_{\alpha} + R_{\alpha} \vec{v}_{\alpha}$$
(3.22)

where:

$$\sum_{\alpha} \overline{\rho}_{\alpha} \vec{\ell}_{\alpha} = 0 \tag{3.23}$$

In these equations  $T_{\alpha}$  is the local partial stress tensor;  $\vec{\ell}_{\alpha}$  is the supply of linear momentum, per unit mass of the  $\alpha$  phase and  $\vec{b}_{\alpha}$  the external force field per unit mass of the  $\alpha$  phase.

Eq.3.23 meets the principle of conservation of linear momentum.

a phase angular momentum balance-

$$\mathbf{T}_{\alpha}^{t} - \mathbf{T}_{\alpha} = \mathbf{L}_{\alpha}; \tag{3.24}$$

where:

$$\sum_{\alpha} L_{\alpha} = 0 \tag{3.25}$$

In these equations  $T_{\alpha}^{t}$  is the transpose of  $T_{\alpha}$  and  $L_{\alpha}$  is the internal supply of angular momentum per unit volume of the  $\alpha$  phase. Eq. 3.25 meets the principle of conservation of angular momentum.

 $\alpha$  phase energy balance-

$$\overline{\rho}_{\alpha} \left[ \frac{\partial e_{\alpha}}{\partial t} + \left( \text{grad } e_{\alpha} \right) \bullet \vec{v}_{\alpha} \right] = -\operatorname{div} \vec{q}_{\alpha} + \overline{\rho}_{\alpha} r_{\alpha} + \overline{\rho}_{\alpha} \vec{\ell}_{\alpha} \bullet \vec{v}_{\alpha} + \overline{\rho}_{\alpha} \vec{b}_{\alpha} \bullet \vec{v}_{\alpha} +$$

$$+T_{\alpha} \bullet \operatorname{grad} \vec{v}_{\alpha} + R_{\alpha}u_{\alpha} + e'_{\alpha}$$
(3.26)

where:

$$\mathbf{e}_{\alpha} = \mathbf{u}_{\alpha} + \frac{1}{2} \vec{\mathbf{v}}_{\alpha} \vec{\mathbf{v}}_{\alpha}; \qquad (3.27a)$$

and

$$\sum_{\alpha} e'_{\alpha} = 0 \tag{3.27b}$$

In these equations  $u_{\alpha}$  is the internal energy per unit mass of the  $\alpha$  phase;  $\vec{q}_{\alpha}$  is the heat flux density vector;  $r_{\alpha}$  is the external heat supply per unit mass of the  $\alpha$  phase and  $e'_{\alpha}$  the internal energy supply per unit volume of the  $\alpha$  phase. Eq. 3.27b meets the principle of conservation of energy.

### $\alpha$ phase Entropic inequality-

$$\overline{\rho}_{\alpha} \left[ \frac{\partial s_{\alpha}}{\partial t} + \left( \text{grad } s_{\alpha} \right) \bullet \vec{v}_{\alpha} \right] + \text{div } \frac{\vec{q}_{\alpha}}{T_{\alpha}} - \frac{\overline{\rho}_{\alpha} r_{\alpha}}{\theta_{\alpha}} + R_{\alpha} s_{\alpha} + s_{\alpha}' \ge 0 \quad (3.28)$$

where:

$$\sum_{\alpha} \mathbf{s}'_{\alpha} = 0 \tag{3.29}$$

In these equation  $s_{\alpha}$  is the entropy per unit mass of the  $\alpha$  phase;  $T_{\alpha}$  the absolute temperature of the  $\alpha$  phase and  $S'_{\alpha}$  the entropy supply per unit volume of the  $\alpha$  phase. Eq. 3.29 is accepted by postulate.

For the use of Eqs. 3.5 to 3.29 there is a need for state and constitutive equations, which complete the formulation.

## 3.2.1 The equations of state

The equations of state are those presented by Eqs. I.4. of chapter 1 part I. However, when the fundamental equation of thermodynamics is reformulated and the state is worked in terms of Gibbs free energy, it is characterized by temperature, pressure and molar fractions. Thus, a set of equations equivalent to the one given by Eqs. I.4 is:

$$c_{P,\alpha} = c_{P,\alpha} (T_{\alpha}, P_{\alpha}, x_{1,\alpha}, \dots, x_{m,\alpha})$$
(3.30)

$$\rho_{\alpha} = \rho_{\alpha}(T_{\alpha}, P_{\alpha}, x_{1,\alpha}, \dots, x_{m,\alpha})$$
(3.31)

In these equations  $c_{P,\alpha} e \rho_{\alpha}$  are, respectively, the molar heat at constant pressure of the  $\alpha$  phase and the  $\alpha$  phase density

## 3.2.2. The constitutive relationships

The phenomenological terms, which appear naturally in the balance equations, are generally made up of an arbitrary part and a purely material-dependent, that is, constitutive, part. Very little progress has been made in terms of establishing this relationship, and it is often necessary to resort to concepts applicable to homogeneous mixtures and, also, to a lot of simplification. Only the equations related to linear momentum, mass transport and electric charges and reaction kinetics will be presented here.

### resistive force

Considering isothermal systems, in which reaction rates do not play an important role in the linear motion equation of the phases, and where the partial stress tensor only has an arbitrary part, containing an arbitrary quantity P, interpreted as a local pressure (Silva, 1990)<sup>13</sup>, and that the only important external field is that of gravity, and that the local acceleration of the phase can be neglected. It then results for Eq. 3.22:

$$\vec{0} = -\upsilon_{\alpha} \text{ grad } P + \overline{\rho}_{\alpha} \vec{\ell}_{\alpha} + \overline{\rho}_{\alpha} \vec{g}; \text{ where } \overline{\rho}_{\alpha} = \upsilon_{\alpha} \rho_{\alpha}$$

or

<sup>&</sup>lt;sup>13</sup>Silva, A.S. (1990) Meio poroso com restrição de incompressibilidade e sua aplicação em sedimentação. Cap.1, p. 1 - 59. In: Tópicos especiais em sistemas particulados. Gráfica da UFSCar, 382p., Freire, J.T. e Gubulin, J.C. (Editores).

$$(\text{grad } \mathbf{P} - \rho_{\alpha} \vec{\mathbf{g}}) = \frac{1}{\upsilon_{\alpha}} \overline{\rho}_{\alpha} \vec{\ell}_{\alpha}$$
(3.32)

a constitutive relationship is necessary for  $\vec{\ell}_{\alpha} = \vec{\ell}_{\alpha}(\upsilon_{\alpha}, \vec{v}_1, \vec{v}_2, ...)$ .

For two-phase systems fluid (1) solid (2) it is very common to use an Ergun type relationship given by:

$$\frac{1}{\nu_{1}}\overline{\rho_{1}}\vec{\ell}_{1} = \left[\frac{\mu_{1}}{K_{2}} + C_{2}\rho_{1}\|\vec{V_{r}}\|\right]\vec{V_{r}}$$
(3.33)

and by Eq. 3.23

$$-\bar{\rho}_1\vec{\ell}_1 = \bar{\rho}_2\vec{\ell}_2$$
 and  $\vec{V}_r = (v_1\vec{V}_1 - v_2\vec{V}_2)$ 

In this equation  $K_2$ ,  $C_2$ ,  $\mu_1$  and  $\rho_1$ , are, respectively, the *intrinsic permeability* of the porous matrix, a *factor* related to the porous matrix(sometimes called the *Forchheimer factor*), density and viscosity of the fluid.

For a stationary solid and a fluid percolating unidirectionally at a low flow rate (darcyan regime) we have:

$$grad \wp = -\frac{\mu_f}{K} \upsilon_f V_z \tag{3.33b}$$

in which

$$\wp = P + \rho_{\alpha}gh$$

is the piezometric pressure of the fluid and h a distance in the opposite direction to the g field at the measurement point and measured from a horizontal reference plane on the ground.

for a two-phase solid-fluid system  $v_f = \varepsilon_L$ , and  $\varepsilon_L V_z = u$  where u is the surface or Darcy velocity. and Eq. 3.33b remains in its classic form.

$$grad \wp = -\frac{\mu_f}{K}u$$
; Darcy's equation (3.33c)

### Mass flux densities (calculated per unit area of phase)

when the  $\alpha$  phase allows the flow of a k chemical species in its interior, this movement can be attributed to numerous mechanisms. In general, the following mechanisms are assumed to apply: Diffusion, Dispersion, Convection and Migration. So you will have:

$$C_{k,\alpha}\vec{v}_{k,\alpha} = \vec{J}_{k,\alpha} + \vec{\delta}_{k,\alpha} + \vec{\zeta}_{k,\alpha} + \vec{\eta}_{k,\alpha}$$
(3.34)

where:

$$\begin{split} \vec{J}_{k,\alpha} &= -D_{k,\alpha} \text{ grad } C_{k,\alpha} \text{ (diffusion)} \\ \vec{\delta}_{k,\alpha} &= -D_{d,\alpha} \text{ grad } C_{k,\alpha} \text{(dispersion)} \\ \vec{\zeta}_{k,\alpha} &= C_{k,\alpha} \vec{v}_{\alpha} \text{(convection)} \\ \vec{\eta}_{k,\alpha} &= -F \, z_k C_{k,\alpha} \, \mu_{k,\alpha} \text{ grad } \Phi_{\alpha} \text{ (ionic migration)} \end{split}$$

In these Equations  $D_{d,\alpha}$  and  $D_{k,\alpha}$  are, respectively, the  $\alpha$  phase dispersion coefficient and the diffusion coefficient of the k chemical species inside the  $\alpha$  phase; F is Faraday's constant;  $Z_k$  the number of charges of the k chemical species (ion) ;  $\mu_{k,\alpha}$  the ionic mobility of the k ion within the  $\alpha$  phase and  $\Phi_{\alpha}$  the electric potential in the  $\alpha$  phase. This results for Eq. 3.34:

$$C_{k,\alpha}\vec{v}_{k,\alpha} = -D_{k,\alpha}^{\text{ef}} \operatorname{grad} C_{k,\alpha} + C_{k,\alpha}\vec{v}_{\alpha} - F z_k C_{k,\alpha} \mu_{k,\alpha} \operatorname{grad} \Phi_{\alpha} \quad (3.35)$$

where, usually by simplification:

$$\mathbf{D}_{\mathbf{k},\alpha}^{\mathrm{ef}} = (\mathbf{D}_{\mathbf{k},\alpha} + \mathbf{D}_{\mathbf{d},\alpha}) \tag{3.36}$$

is an effective diffusion coefficient.

#### ionic current flows densities (calculated per unit area of phase)-

If a given k chemical species is an ion, with a charge number,  $Z_k$ , and a molecular mass,  $M_k$ , then, as a function of the movement of this chemical species, an *ionic current* will arise within the  $\alpha$  phase, as discussed above. This will be according to Eqs 10, 17, 35 and 36:

$$\vec{i}_{\alpha} = -\sum_{k} F \frac{z_{k}}{M_{k}} D_{k,\alpha}^{\text{ef}} \text{grad } C_{k,\alpha} - \sum_{k} F^{2} \frac{z_{k}^{2}}{M_{k}} C_{k,\alpha} \mu_{k,\alpha} \text{grad } \Phi_{\alpha}$$
(3.37)

where, by the condition of Eq. 3.18:

$$F\vec{v}_{\alpha}\sum_{k}\frac{Z_{k}}{M_{k}}C_{k,\alpha}=0$$

Eq.3.37 can be rewritten in the form:

$$\vec{i}_{\alpha} = -\sum_{k} F \frac{Z_{k}}{M_{k}} D_{k,\alpha}^{\text{ef}} \text{grad} C_{k,\alpha} - \kappa_{\alpha} \text{grad} \Phi_{\alpha}$$
(3.38)

where:

$$\kappa_{k,\alpha} = F^2 \frac{Z_k^2}{M_k} C_{k,\alpha} \mu_{k,\alpha} \quad e \qquad \kappa_{\alpha} = \sum_k \kappa_{k,\alpha}$$
(3.39)

In these equations  $\kappa_{k,\alpha} \in \kappa_{\alpha}$  are, respectively, the ionic conductivity of the k species inside the  $\alpha$  phase (fluid) and the ionic conductivity of the  $\alpha$  phase as a whole.

When diffusion and dispersion are negligible in the face of convection then:

$$\vec{i}_{\alpha} = -\kappa_{\alpha} \operatorname{grad} \Phi_{\alpha} \tag{3.40}$$

Assuming that, with solid phases, the current is electronic and that it follows Ohm's law, then:

$$\vec{i}_{\alpha} = -\sigma_{\alpha} \operatorname{grad} \Phi_{\alpha}$$
 (3.41)

Where  $\sigma_{\alpha}$  is the electronic conductivity of the  $\alpha$  phase (solid).

Electrode kinetics-

The equations, as presented, can describe systems with chemical reactions within the phases and with specific reactions at the phase separation interface. In the case of electrochemical systems, in most cases, only the reactions of transfer charges between phases are of interest and are of the type:

$$\mathbf{R}_{\mathbf{k},\alpha} = \mathbf{R}_{\mathbf{k},\alpha} (\mathbf{C}_{\mathbf{k},\alpha}, \mathbf{C}_{\mathbf{k},\alpha}^*, \Phi_{\alpha,\dots})$$

In this equation  $C_{k,\alpha} \in C_{k,\alpha}^*$  are, respectively, the concentrations of the k chemical species within the  $\alpha$  phase and on the  $\alpha$  phase-side electrode "surface". So, if, the  $a_{\alpha}$ , is the specific area of the  $\alpha$  phase and, $\lambda_{\alpha}$ , is the fraction of the area  $a_{\alpha}$  effectively used for the reaction, then based on Eq. 2.I.24 there will be:

$$\mathbf{R}_{\mathbf{k},\alpha} = \mathbf{r}_{\mathbf{k},\alpha} \lambda_{\alpha} \mathbf{a}_{\alpha}$$

In terms of mass or current flows, we will have:

$$R_{k,\alpha} = -\frac{\vec{i}_{k,\alpha} \bullet \vec{e}_n}{F \frac{z_k}{M_k}} \lambda_\alpha a_\alpha = -C_{k,\alpha} \vec{v}_{k,\alpha} \bullet \vec{e}_n \lambda_\alpha a_\alpha$$
(3.42)

Where  $\vec{e}_n$  is a local unit vector normal to the  $\alpha$  phase surface and pointing out of it. In terms of intrinsic kinetics at the electrode, one will have:

$$\mathbf{R}_{\mathbf{k},\alpha} = \mathbf{i}_{\kappa,\alpha}^* \frac{\mathbf{M}_{\mathbf{k}}}{\mathbf{z}_{\mathbf{k}} \mathbf{F}} \lambda_{\alpha} \mathbf{a}_{\alpha}$$
(3.43)

a constitutive relationship is necessary for  $i_{k,\alpha}^* = i_{k,\alpha}^*(C_{k,\alpha}^*, \Phi_{\alpha}, ...)$ , such as the *Butler-Volmer equation*.

Assuming that in a film of thickness  $\delta$  (boundary layer) lying at the electrode interface the mass flow is due only to diffusion in the thick boundary layer  $\delta$  then:

$$\mathbf{R}_{\mathbf{k},\alpha} = -\mathbf{C}_{\mathbf{k},\alpha} \vec{\mathbf{v}}_{\mathbf{k},\alpha} \bullet \vec{\mathbf{e}}_{\mathbf{n}} \lambda_{\alpha} a_{\alpha} = -\lambda_{\alpha} a_{\alpha} \frac{\mathbf{D}_{\mathbf{k},\alpha}}{\delta} (\mathbf{C}_{\mathbf{k},\alpha} - \mathbf{C}_{\mathbf{k},\alpha}^{*})$$
(3.44)

Assuming that at the electrode surface the reaction is due only to intrinsic kinetics then:

$$\mathbf{R}_{\mathbf{k},\alpha} = \lambda_{\alpha} \mathbf{a}_{\alpha} \frac{\mathbf{M}_{\mathbf{k}}}{\mathbf{z}_{\mathbf{k}} \mathbf{F}} \mathbf{i}_{\mathbf{k},\alpha}^{\mathbf{n}} (\mathbf{C}_{\mathbf{k},\alpha}^{*}, \Phi_{\alpha}^{*}, \dots)$$
(3.45)

when  $C_{k,\alpha}^* \to 0$  the reaction is controlled by mass transport. when  $C_{k,\alpha}^* \to C_{k,\alpha}$  the reaction is controlled by intrinsic kinetics.

In any other case the control will be mixed. Eqs. 3.44 and 3.45 will be linked together through concentration at the interface,  $C_{k,\alpha}^*$ , as seen in chapter 2: item 2.I.4.-*Kinetics and controlling factors*.

CHAPTER 3. Part I. Electrolyte Systems

## 3.I.1. Initial considerations three-dimensional electrodes.

In *three-dimensional porous electrodes*, **ELT**, the porosity of the system is decisive. The volume not occupied by the solid becomes a reservoir of soluble chemical species available for consumption and, also, the space necessary for the storage of products coming from the solid material. In addition, numerous macroscopic properties of the systems are dependent on the porosity value. Phenomenological coefficients such as the effective diffusion coefficients, the electrical conductivity of the porous matrix and the ionic conductivity of the electrolyte solution are also of fundamental importance. It is very important that these parameters are determined experimentally or predicted by appropriate equations. The formulation presented here provides the basis for a detailed examination of the specific behavior of electrochemical systems, such as primary and secondary batteries, as well as electrochemical reactors operating with three-dimensional porous electrodes, percolated by an electrolyte solution.

When the reactor is a fixed bed and the solid phase is gaining mass, the porosity will be decreasing and, consequently, increasing the pressure drop in the system. When the bed is mobile and the solid phase is gaining mass, the porosity may remain constant and, consequently, there will be an increase in bed volume and a small increase in pressure drop.

In the case of electrochemical reactors with porous electrodes, percolated by electrolytic solutions, works have shown, although under very restrictive conditions, an excellent fit between theory and experimentation, Olive and Lacoste (1980)<sup>14</sup>.

With regard to reaction rates (polarization equations), applicable to a given process, it appears that they are subject to a complex set of relative phenomena to the morphology of the electrode, formation of the double layer and the intrinsic processes of charge transfer. Also, objects of interest are the complete analysis of the porous electrochemical cell, the prediction of the polarization curve of a given battery, the dynamic behavior of fluid flow in multiphase systems and the complete optimization of a given electrochemical process in particulate systems. Therefore, there are many problems that the scientific community working in this sector must face. Among its main attractive features, the following stand out: the recovery of the metal in its pure form; selectivity, applying appropriate potential differences; versatility, being able to process small and large volumes; energy efficiency; ease of data acquisition, automation and control; environmental compatibility, using only electrical energy; and the low cost of construction and operation (Ibanez, Rajeshwar and Swain,<sup>15</sup>.

Although the most interesting technological application is the recovery of precious metals from produced water, our interest has always been more ecological than economic, since industrial effluents containing heavy metals, even in low concentrations, are highly toxic. Electrochemical techniques, especially the three-dimensional electrode, are promising in the treatment of these effluents.

Electrochemical processes for cleaning and recovering heavy metals use special reactors known as electrochemical reactors. These reactors, crossed by electrolytic solution, can be two-dimensional, when they are constituted by parallel flat plates; or three-dimensional, by being filled with electronically conductive particles.

Regarding the configuration, electrochemical reactors can be classified as parallel, when the current and electrolyte solution flows are following the same direction; or perpendicular, when the flows intersect orthogonally.

Three-dimensional electrochemical reactors are often preferred when working with low

<sup>&</sup>lt;sup>14</sup>Olive, H. and Lacoste, G. (1980) Application of volumetric electrodes to the recovery of metals in industrial effluents - II. Design of an axial field flow through porous electrodes". Electroquimica Acta, v. 25, p. 1303-1308.

<sup>&</sup>lt;sup>15</sup>Ibanez, JG, Rajeshwar, K. and SWAIN, GM (1994). "Electrochemistry and the Environment". Journal of Applied Electrochemistry. vol. 24, p. 1077-1091.

concentration solutions, less than 2000 ppm. This type of reactor, due to its large specific surface area, can offer high rates of heat and mass transfer along the bed, and a good distribution of potential in the liquid phase (Goodridge, Holden and Plimley, 1971).<sup>16</sup>.

## **3.I.2.** porous or three-dimensional electrodes

Three-dimensional electrodes basically consist of a porous solid matrix and an electrolyte solution that percolates through it, providing a wide variety of chemical and electrochemical reactions.

Assigning the indices  $\alpha = 1$  for the solid and  $\alpha = 2$  for the electrolyte solution and noting that, in this case,  $\upsilon_2 = \varepsilon$ , Where  $\varepsilon$  is the porosity of the matrix, then equation (5) results for the solid and for the fluid:

$$\frac{\partial}{\partial t} \left[ (1 - \varepsilon) C_{k,1} \right] + \operatorname{div} \left[ (1 - \varepsilon) C_{k,1} \vec{v}_{k,1} \right] = (1 - \varepsilon) R_{k,1}$$
or  $\rho_{\mathrm{m}} \frac{\partial \varepsilon}{\partial t} = -(1 - \varepsilon) R_{m,\alpha}$  (solid like a pure metal)
$$\frac{\partial}{\partial t} \left[ \varepsilon C_{k,2} \right] + \operatorname{div} \left[ \varepsilon C_{k,2} \vec{v}_{k,2} \right] = \varepsilon R_{k,2}$$

$$R_{k,\alpha} = \frac{\lambda_{\alpha} a_{\alpha}}{F \frac{z_{k}}{M_{k}}} i_{k,\alpha}^{n} (C_{k,\alpha}, \phi_{\alpha,\dots})$$
(3.I.1)

and from equations (3.34) to (3.41) result:

$$\vec{j}_{1} = \upsilon_{1}\vec{i}_{1} = -\sigma_{1} \operatorname{grad} \phi_{1}$$

$$\vec{j}_{2} = \upsilon_{2}\vec{i}_{2} = -\kappa_{2} \operatorname{grad} \phi_{2} \text{ where : } \kappa_{2} = \varepsilon F^{2} \sum_{k} \frac{z_{k}^{2}}{M_{k}} C_{k,2} \mu_{k,2}$$
and
$$div \ \mathbf{j}_{1} + div \ \mathbf{j}_{2} = 0 \text{ where :}$$

$$div \ \mathbf{j}_{1} = F \sum_{k} \frac{z_{k}}{M_{k}} \upsilon_{1} R_{k,1}$$

$$div \ \mathbf{j}_{2} = F \sum_{k} \frac{z_{k}}{M_{k}} \upsilon_{2} R_{k,2}$$
2)

(3.I.2)

of the equations (7c) and (9e) results:

<sup>&</sup>lt;sup>16</sup>Goodridge, F., Holden, DI and Plimley, RF (1971). "Fluidized Bed Electrodes. Part I: A Mathematical Model of the Fluidized Bed Electrode". trans. Instn. Chem. Engs. vol. 49, p. 128-136.

$$v_1 R_{k,1} = -v_2 R_{k,2} \tag{3.I.3}$$

Assuming that the reaction is controlled only by diffusion in the thickness boundary layer  $\delta$  then:

$$\upsilon_{\alpha} R_{k,\alpha} = \upsilon_{\alpha} \frac{i_{k,\alpha}^{n}}{F \frac{z_{k}}{M_{k}}} \lambda_{\alpha} a_{\alpha} = \upsilon_{\alpha} \lambda_{\alpha} a_{\alpha} \frac{D_{k,\alpha}}{\delta} (C_{k,\alpha} - C_{k,\alpha}^{*})$$
(3.I.4)

assuming operation under limit current conditions, where  $\boldsymbol{C}_{\boldsymbol{k},\alpha}^{*}=0,$  results:

$$\upsilon_{\alpha} \mathbf{R}_{\mathbf{k},\alpha} = \lambda_{\alpha} \mathbf{a}_{\alpha} \mathbf{K}_{\mathbf{k},\alpha} (\upsilon_{\alpha} \mathbf{C}_{\mathbf{k},\alpha}) \tag{3.I.5}$$

where  $K_{k,\alpha}$  is the mass transfer coefficient of the k chemical species inside the  $\alpha$  phase.

Of the equations (3.I.2c), (3.I.2d), (3.I.2e) and (3.I.5) result:

$$\operatorname{div} \vec{j}_{1} = -\operatorname{div} \vec{j}_{2} = F \sum_{k} \frac{Z_{k}}{M_{k}} \lambda_{2} a_{2} K_{k,2}(\varepsilon C_{k,2})$$
(3.I.6)

assuming, as a final simplification, that  $\sigma_1$  and  $\kappa_2$  is constant, and that we are considering negligible diffusion and dispersion in relation to convection, which implies that  $\vec{v}_{k,2} = \vec{v}_2$ , then results:

$$\rho_{\rm m} \frac{\partial \varepsilon}{\partial t} = \lambda_2 a_2 \mathbf{K}_{\mathbf{k},2} (\varepsilon \mathbf{C}_{\mathbf{k},2}) \qquad \text{(solid like a pure metal)}$$

$$\frac{\partial}{\partial t} [\varepsilon \mathbf{C}_{\mathbf{k},2}] + \operatorname{div} [\varepsilon \mathbf{C}_{\mathbf{k},2} \vec{v}_2] = -\lambda_2 a_2 \mathbf{K}_{\mathbf{k},2} (\varepsilon \mathbf{C}_{\mathbf{k},2})$$

$$Lap \ \phi_1 = + \frac{1}{\sigma_1} F \sum_{\mathbf{k}} \frac{z_k}{M_k} \lambda_2 a_2 \mathbf{K}_{\mathbf{k},2} (\varepsilon \mathbf{C}_{\mathbf{k},2})$$

$$Lap \ \phi_2 = -\frac{1}{\kappa_2} F \sum_{\mathbf{k}} \frac{z_k}{M_k} \lambda_2 a_2 \mathbf{K}_{\mathbf{k},2} (\varepsilon \mathbf{C}_{\mathbf{k},2})$$

$$\vec{j}_1 = \upsilon_1 \vec{i}_1 = -\sigma_1 \operatorname{grad} \phi_1$$

$$\vec{j}_2 = \upsilon_2 \vec{i}_2 = -\kappa_2 \operatorname{grad} \phi_2$$
(3.1.7)

When the local velocity of the electrolyte and an equation for the mass transfer coefficient are known, this set of equations allows the determination of the porosity profile and the composition of the chemical species in the reactor (equations (3.I.7a) and (3.I.7b)),

and with these results, the potential profiles (equations (3.I.7c) and (3.I.7d)), and with these results, the profiles of currents (equations (3.I.7e) and (3.I.7f)).

When the velocity of the fluid and the solid are not known, it will also be necessary to solve, simultaneously, the equations (3.22) and (3.23).

## 3.I.2.1. behavior of three-dimensional electrodes.

## **3.I.2.1.1.** prediction of current efficiency in the electroseparation of toxic metals.

For the application illustration, a fluidized bed reactor will be considered as shown in figure 3.I.1. aiming at application in the extraction of copper from produced (waste) waters.



FIGURE 3.I.1.: Schematic representation of an electrochemical fluidized bed reactor

The mathematical model used is based on the mass transport and electric charge equations proposed here, considering relevant simplifications, the main one being the hypothesis of practically uniform concentrations within the reactor, so that mass transport can be disregarded. and if we work only with the transport of electrical charges, we obtain for the solid (m) and fluid (s) phases:

$$\operatorname{div}\left[(1-\varepsilon)\vec{i}_{m}\right] = -\varepsilon F \sum_{k} \frac{z_{k}}{M_{k}} R_{k,s}$$
(3.I.8.1)

$$\operatorname{div}\left[\varepsilon \,\overline{i}_{s}\right] = \varepsilon F \sum_{k} \frac{Z_{k}}{M_{k}} R_{k,s}$$
(3.I.8.2)

$$i_{\rm m} = -\sigma_{\rm m} {\rm grad} \phi_{\rm m}$$
 (3.I.8.3)

$$\vec{i}_s = -\sigma_s \operatorname{grad} \phi_s$$
 (3.I.8.4)

The index k in these equations refers to the reactive chemical species present in the electrolyte solution, which is indicated by the index s.

The reaction rate of the k chemical species within the s phase, can be symbolically represented by the equation:

$$R_{k,s} = a_{m} \frac{(1-\varepsilon)}{\varepsilon} \frac{i_{k,s}^{*}}{F \frac{Z_{k}}{M_{k}}};$$

$$i_{k,s}^{*} = i_{k,s}^{*}(\phi_{s}, \phi_{m}, C_{1,s}, C_{2,s}, ....)$$
(3.I.8.5)

In this equation,  $i_{k,s}^*$  is the reaction rate of the k chemical species in terms of charge per unit area of liquid phase, s (electrolyte solution).

## kinetics

For electrochemical reactions (copper and hydrogen) the classic Butler-Volmer model was adopted:

$$\mathbf{i}_{k,s}^{*} = \mathbf{i}_{k,s}^{o} \left\{ \exp[\alpha Y \eta] - \exp[(\alpha - 1)Y \eta] \right\}$$
(3.I.8.6)

where:

$$\eta = \phi_{\rm m} - \phi_{\rm s} - \left[ E_0 + \frac{1}{Y} \ln \left( C_{\rm k,s}^* \right) \right]$$
(3.I.8.7)

and

$$Y \equiv \frac{n_k F}{RT}$$

Equation (3.I.8.7) defines the overpotential  $\eta$  of the metal/solution system.

This model is particularly interesting when working with concentrated solutions, since it is assumed that the ionic transport from the bulk of the solution to the particle is much faster than the transfer of electrons at the solid/fluid interface.

### Potential distribution in the reactor

Applying Equations (3.I.8.1) to (3.I.8.4) to an electrochemical fluidized bed reactor with a rectangular base and perpendicular configuration and assuming that: The potential and current density depend only on the x variable; The surface velocity of the electrolyte solution is high enough to ensure that the change in concentration along the bed height is negligible; The operation is isothermal; the potential in the metallic and liquid phases is obtained, respectively:

$$\frac{d^2\phi_m}{dx^2} = \frac{1}{\sigma_m} \frac{\varepsilon}{(1-\varepsilon)} F \sum_k \frac{z_k}{M_k} R_{k,s}$$
(3.I.8.8)

$$\frac{d^2\phi_s}{dx^2} = -\frac{1}{\sigma_s} F \sum_k \frac{z_k}{M_k} R_{k,s}$$
(3.I.8.9)

## **Boundary Conditions**

In the feeder plate (x=X), practically all the current is carried by the liquid phase. On the receiving plate (x=0) the opposite occurs. So:

$$x = 0, \quad \frac{d\phi_s}{dx} = 0 \tag{3.I.8.10}$$

$$\mathbf{x} = \mathbf{X}, \ \frac{\mathrm{d}\phi_{\mathrm{m}}}{\mathrm{d}\mathbf{x}} = 0 \tag{3.I.8.11}$$

If the system operates under constant potential condition, then:

$$\mathbf{x} = \mathbf{0}, \quad \boldsymbol{\phi}_{\mathrm{m}} = \boldsymbol{\phi}_{\mathrm{mo}} \tag{3.I.8.12}$$

$$\mathbf{x} = \mathbf{X}, \ \mathbf{\phi}_{\mathrm{s}} = \mathbf{\phi}_{\mathrm{so}} \tag{3.I.8.13}$$

If the system operates under constant current condition, then:

$$x = 0, \quad \frac{d\phi_m}{dx} = -\frac{i_m}{\sigma_m} = -\frac{I}{(1-\varepsilon)\sigma_m A}$$
(3.I.8.14)

$$x = X, \ \frac{d\phi_s}{dx} = -\frac{i_s}{\sigma_s} = -\frac{I}{\varepsilon \sigma_s A}$$
 (3.I.8.15)

Next, Equations (3.I.8.8) and (3.I.8.9) are presented as they were solved, by the orthogonal placement method, considering the parallel reaction of hydrogen reduction. The k=1 index refers to copper and the k=2 index to hydrogen.

In these equations, N is the number of internal placement points. For the boundary conditions, the most complex case was chosen, which is the one related to the reactor operating under constant current condition:

## **Equations:**

$$\sum_{i=1}^{N+2} B_{ji} \phi_{mi} = \frac{1}{\sigma_m} \frac{\varepsilon}{(1-\varepsilon)} \Omega; \qquad (3.I.8.16)$$

$$\sum_{i=1}^{N+2} B_{ji} \phi_{si} = -\frac{1}{\sigma_s} \Omega;$$
(3.I.8.17)

where:

$$\Omega = F\left(\frac{z_1}{M_1}R_{1,s_j} + \frac{z_2}{M_2}R_{2,s_j}\right)$$
  
j = 2,..., N+1
(3.I.8.18)

## **Boundary conditions:**

x = 0, 
$$\sum_{i=1}^{N+2} A_{1i} \phi_{mi} = -\frac{I}{A\sigma_m(1-\epsilon)}$$
 (3.I.8.19)

$$x = X, \sum_{i=1}^{N+2} A_{N+2i} \phi_{mi} = 0$$
 (3.I.8.20)

$$x = 0, \quad \sum_{i=1}^{N+2} A_{1i} \phi_{si} = 0$$
 (3.I.8.21)

$$x = X, \sum_{i=1}^{N+2} A_{N+2i} \phi_{si} = -\frac{I}{A\sigma_s \epsilon}$$
 (3.I.8.22)

From N=4, good results are already obtained. However, we worked with N=6.

It should be noted that in the simulations in which only copper reduction was considered, the condition applied:

 $R_{2,s_j} = 0 \tag{3.I.8.23}$ 

For the simulations, copper recovery at room temperature was considered.

The values used for the system parameters are shown in Table 3.I.1 and were based on laboratory studies.

Table 3.I.1: System parameters.

| Parameter         | adopted value        |
|-------------------|----------------------|
| a <sub>m</sub>    | 6000 m <sup>-1</sup> |
| Α                 | 0.008 m <sup>2</sup> |
| C* <sub>k,s</sub> | 1.0 mol/L            |
| α                 | 4.5 A/m <sup>2</sup> |
| σ <sub>m</sub>    | 250.0/(Ωm)           |
| σs                | 50.0 <b>/(</b> Ωm)   |

### Case1. Simulations disregarding parallel reactions.

In this case the condition expressed by Equation (3.I.8.23) was used in the analysis. It should be noted that under this condition the reactor necessarily operates with 100% efficiency.

The operational parameters adopted were: porosity (36; 43 and 50%); bed thickness (0.019; 0.024 and 0.029 *m*), and applied current (3.5; 6.25 and 9.0 *A*). For better visualization of the results, the graphs presented are normalized with respect to the reactor length.

In Figures 3.I.2a, 3.I.2b and 3.I.2c are shown profile graphs in the phases being, respectively, potential; current and overpotential.

In Figure 3.I.2c, together with simulation data, the experimental results of the overpotential profile, obtained by Germain and Goodridge (1975) are shown.<sup>17</sup>. It is important to point out that some fundamental operational parameters were not mentioned by the authors, making a quantitative comparison unfeasible. There was, therefore, no adjustment of parameters in this comparison, but an overlap of experimental and simulated results, based on maintaining the same range of overpotentials. Note the excellent qualitative compatibility between the experimental data and the simulation results. In Figure 3.I.2a, it is observed that the potential in the solid phase remains more uniform throughout the length of the bed when compared to the potential in the fluid phase. This can be justified by the conductivities of the phases. That of the metal is significantly greater than that of the solution. In addition, the potential in the solution was always higher than that of the metal.



<sup>&</sup>lt;sup>17</sup>Germain, S. and Goodridge, F. (1975). "Cooper Deposition in a Fluidized Bed Cell". Electrochimica Acta. 1976. Vol. 21. p. 545-550.
FIGURE 3.I.2: Typical profiles inside the electrochemical reactor as a function of x/X.

The values obtained for the overpotential (Figure 3.I.2c) were always negative, which shows that there are no regions of metal dissolution inside the bed (regions of anodic behavior).

Figures 3.I.3a, 3.I.3b and 3.I.3c show the *reaction rate* profile graphs showing the influences of applied current, bed thickness and porosity.



FIGURE 3.I.3: Typical profiles of reaction rates inside the electrochemical reactor as a function of x/X.

In all cases, the highest reaction rates were found in approximately 30% of the bed close to the counter electrode. It was observed that the higher the applied current, the higher these rates. On the other hand, for small currents, the rate is practically constant over the entire length of the bed, resulting in a more uniform deposition.

Porosity significantly influences the distributions of overpotentials and reaction rates. The highest absolute values for these overpotentials are obtained at higher porosities, while for the reaction rates the opposite occurs.

The bed thickness has little influence on the reaction rate distribution. It should be noted, however, that as this thickness increases, the hypothesis of uniform electrolyte concentration becomes less and less realistic, since the highest reaction rates in the vicinity of the current feeder tend to decrease drastically the concentration values in that part of the bed.

# Case 2. Simulations considering parallel reactions (hydrogen reduction).

Considering the parallel hydrogen reduction reaction, the exchange current densities for copper and hydrogen were adjusted  $(i_{0,1} \text{ and } i_{0,2})$  using experimental data of current efficiency as a function of bed thickness, obtained by Ponte and Gubulin (1998). The operational parameters used in the adjustments were the same as those described by these authors in their work.

The adjustments made are shown in Figures 3.I.4a, 3.I.4b and 3.I.4c, respectively for thicknesses of 0.019, 0.024 and 0.029 m.

When considering uniform electrolyte concentration in the bed, as is the case here, bed thickness and exchange current density do not influence current efficiency. It is a kinetic parameter that depends on the reactant species and its concentration. However, the adjustments made were quite significant, showing very satisfactory agreement between the predicted and observed values. It is believed that the adjustments will be even more significant when considering concentration profiles within the bed and mixed kinetic control involving the mass transfer coefficient (Gubulin, 1998).



FIGURE 3.I.4: Current efficiency as a function of current density for different thicknesses.

The information provided by the simulations can be summarized as follows:

- The model used was able to describe qualitatively and quantitatively the behavior of three-dimensional electrochemical fluidized bed reactors.

- the applied current is the parameter that most influences the results. Considering only the copper reduction, the greater the applied current, the greater its deposition rate. When introducing hydrogen reduction, an optimal current is verified in which the ratio between the copper and hydrogen reduction rates is maximum;

- The porosity of the bed is a parameter that also significantly interferes in the results. However, its influence may be greater than that verified in the simulations. The electrical conductivity of the solid phase is strongly dependent on porosity, which was not considered in this work;

- Disregarding parallel reactions, the bed thickness has little influence on the results. With the introduction of hydrogen reduction, this parameter significantly interferes with current efficiency. Considering, still, regions of different concentrations inside the bed, it is believed that this thickness would have fundamental importance in the viability of electrochemical fluidized bed reactors.

- The adjustments made for the current efficiency were very interesting and motivating, showing very good agreement between the experimental and theoretical values.

As reported from item 3.I.1. when the reactor is a fixed bed and the solid phase is gaining mass, the porosity will be decreasing and, consequently, increasing the pressure drop in the system. When the bed is mobile and the solid phase is gaining mass, the porosity may remain constant and, consequently, there will be an increase in bed volume and a small increase in pressure drop. In this sense, to complete the section, we will address these two

cases.<sup>18,19</sup>, In chapter 4 these works are shown in full. We present here only the results and discussion.

#### 3.I.2.1.2. porosity field study

The results of interest are:



FIGURE 3.I.5: Distributions of overpotentials, $\eta$ , of the porosities, $\epsilon$ , as a function of x/X taking time as a parameter.



Figure 3.I.6: Evolution of the bed porosity as a function of time, for different thicknesses X of the reactors, R1 and R3, having other variables as parameters.

It can be seen that the greatest changes, both in the overpotential and in the porosity, occur in the vicinity of the counter-electrode, that is, in the vicinity of the microporous diaphragm.

It is observed that, although the average rate of reaction within the bed is constant, since the current applied to the reactor remains constant throughout the operating time, both the overpotential and the porosity of the porous matrix change significantly in the space at as the operating time progresses.

<sup>&</sup>lt;sup>18</sup>Ehirim, E.O. ; Gubulin, J.C. (1997). "comportamento de um eletrodo de leito fixo: modelo matemático para o estudo do campo de porosidades", XXV ENEMP.

<sup>&</sup>lt;sup>19</sup>Ehirim, E.O. ; Gubulin, J.C. (1998). "comportamento de um eletrodo de leito fluidizado: modelo matemático para um leito em expansão", XXVI ENEMP.

It is verified, at any time, that the value of the overpotential being more expressive in the region closest to the diaphragm, indicates that this is the most active region, electrochemically, and, therefore, more favorable to the copper electrodeposition reactions.

It can be seen, in Figure 3.I.6, over time, that the porosity, in view of what was observed above in relation to the overpotential, tends to decrease considerably in the region closest to the diaphragm, confirming that this is the region more active, electrochemically. This local decrease in porosity, the faster the higher the applied operating current, leads the reactor to a short useful life since, in a few hours of operation, the bed reaches zero porosity (complete closure of the pores) in the vicinity of the diaphragm. From then on, only the x/X=1 plane is active and the bed loses its three-dimensional characteristics.

The cathodic increase of the overpotentials, in the region close to the diaphragm (membrane that prevents the short circuit between the particles and the metallic plate), may be due, probably, to the physical barrier that the membrane imposes to the electrons and to the discharge in the metallic plate, causing a greater concentration of negative charges in the particles near the diaphragm, thus favoring the electrochemical reactions in this place.

The sharp local increase in the overpotential, in the cathodic sense, for increases in time, is due to the narrowing of the pores as the mass transfer takes place, because with this narrowing there is a decrease in the local area and a consequent local increase in the density of current, 3.I.

Other important data obtained show the influence of the copper concentration, for a given reactor that operates under the same applied current conditions. The influence of the reactor thickness is verified, under the same conditions of applied current and copper concentration. It is important to note that, for a given operating current, the reactor with a less concentrated solution takes longer to close the pores, that is, it takes longer to become inoperative. This behavior is due to the fact that the deposition rate is a function of the copper concentration, that is, lowering the concentration of the solution means decreasing the number of copper ions present in it, available to react with electrons and, consequently, , cause a decrease in the deposition kinetics.

## 3.I.2.1.3. bed expansion study

The results of interest are:



FIGURE 3.I.7: a) relative position of the bed surface with time, b) increase in bed height with time

The proposed model figure 3.I.7.(a) is able to satisfactorily describe the behavior of an expanding fluidized bed electrode, as observed in the laboratory figure 3.I.7.(b), in

addition assures us a direct application to more complex systems, such as those operating with mixed reaction systems (control by mass transfer and intrinsic reaction).

In order to qualify and quantify better ELT systems, three-dimensional reactors of different designs were studied: fixed bed, spouted bed, vortex bed and fluidized bed (conventional and pulsating)

The experimental proof of this formulation forced us to develop numerous techniques for experimental determination of overpotentials inside the reactor, in chapter 4 a technique applied to the vortex bed is presented.<sup>20</sup>.

CHAPTER 3. Part II. adsorptive systems

# **3.II.1. Initial considerations**

Due to the simplicity of their equipment, ease of construction, operation and control, adsorptive processes have been attractive for applications in three large groups of separation processes:

- 1- Purification;
- 2- Solute recovery;
- 3- Mixture separation.

In this sense, we will deal with some of these processes, assuming that kinetic studies have already anticipated which adsorbents are recommended and quantitative information is available on the forms of adsorption isotherms and kinetic parameters of transport within the adsorbent.

# 3.II.2. adsorptive processes

## 3.II.2.1. packed column adsorption

We will start by resuming a study, purposely, not completed in chapter 2., so that it could be dealt with here. It refers to the system called fixed bed adsorption column whose model is represented by equations 2.II.64 and 2.II.65 of chapter 2. being, respectively:

<sup>&</sup>lt;sup>20</sup>C.A. Rodrigues, M.J.J.S. Ponte e J.C. Gubulin (1990), "obtenção de um sistema para a realização de medidas de potenciais em eletrodos tridimensionais", XXVI ENEMP.

$$\frac{\partial C_{k,f}}{\partial t} + \frac{(1 - \varepsilon_L)}{\varepsilon_L} \rho_p \frac{\partial q_{k,p}}{\partial t} - D_{az} \frac{\partial^2 C_{k,f}}{\partial z^2} + \frac{u_o}{\varepsilon_L} \frac{\partial C_{k,f}}{\partial z} = 0$$
(3.II.1)

$$\frac{\partial q_{k,p}}{\partial t} = \text{"lei cinética"} \tag{3.II.2}$$

Before a more rigorous treatment, it is interesting to ask: What would be the simplest model?

Evidently, it is the one that facilitates the solution the most, and can be configured by:

1- isothermal and isobaric operation (the temperature is constant and the fluid moves with negligible pressure drop);

2- instantaneous local equilibrium at each point of the bed such that,  $q_{k,p} = q_k^*$  (no resistance to transport is offered by the particle);3- the velocity of the fluid is assumed to be constant across any cross-section "plug flow" (there is no type of dispersion at the front of the flow or variation of its velocity); under these conditions Eq. 3.II.1. becomes,

$$\frac{\partial C_{k,f}}{\partial t} + \frac{(1 - \varepsilon_L)}{\varepsilon_L} \rho_p \frac{\partial q_k^*}{\partial t} + \frac{u_o}{\varepsilon_L} \frac{\partial C_{k,f}}{\partial z} = 0$$
(3.II.3)

and still,

$$q_k^* = f(C_{k,f})$$
 isotherm

whence:

$$\frac{\partial q_k^*}{\partial t} = \frac{df}{dC_{k,f}} \frac{\partial C_{k,f}}{\partial t} = f'(C_{k,f}) \frac{\partial C_{k,f}}{\partial t} \text{ and then,}$$

$$\frac{\partial C_{k,f}}{\partial t} + \frac{(1 - \varepsilon_L)}{\varepsilon_L} \rho_p f'(C_{k,f}) \frac{\partial C_{k,f}}{\partial t} + \frac{u_o}{\varepsilon_L} \frac{\partial C_{k,f}}{\partial z} = 0 \text{ whence,}$$

$$\{\frac{\varepsilon_L}{u_0} (1 + \frac{(1 - \varepsilon_L)}{\varepsilon_L} \rho_p f'(C_{k,f}))\} \frac{\partial C_{k,f}}{\partial t} + \frac{\partial C_{k,f}}{\partial z} = 0$$

or

$$\lambda(C_{k,f})\frac{\partial C_{k,f}}{\partial t} + \frac{\partial C_{k,f}}{\partial z} = 0$$
(3.II.4)

with,

$$\lambda(C_{k,f}) = \{ \frac{u_0}{\varepsilon_L} (1 + \frac{(1 - \varepsilon_L)}{\varepsilon_L} \rho_p f'(C_{k,f})) \}$$
(3.II.5)

defining,

$$\beta \equiv \left[1 + \rho_p \frac{(1 - \varepsilon_L)}{\varepsilon_L} f'(C_{k,f})\right]$$

results:

$$\frac{u_o}{\varepsilon_L} = V_z = \frac{\lambda(C_{k,f})}{\beta}$$
(3.II.6)

imposing a last simplification which is to adopt a linear isotherm, then,

 $q_k^* = m.C_{k,f}$  and so  $\lambda(C_{kf}) = cte = \lambda_f$  and so the equation 3.II.4. reduces to an equation in partial derivatives of the first order and finds its general solution, given by:

 $C_{k,f}(z,t) = g(z + \lambda_f t)$  where g is an arbitrary differentiable function.

With:

$$\left. \frac{dz}{dt} \right|_{C_{k,f}} = \lambda_f$$
; the characteristic equation.

introducing typical values into Eq. 3.II. 5 to obtain  $\lambda_f$ , the model can be solved. Figure 3.II.1 presents the solution:



FIGURE 3.II.1 - graphic result of the distribution of fluid concentrations inside the adsorption column

When solved analytically or numerically, the model allows obtaining the rupture curve.

Although it has a reduced probability of being put to technical use in view of the severe simplification resource, it provides a remarkable didactic resource.

1- Shows that packed column adsorption is a *wave phenomenon* with a wave traveling at a velocity,  $\lambda(C_{kf})$ , along the bed;

2- Each concentration,  $C_{k,f}$ , travels along the column at its own velocity;

3- The propagation velocity of a given concentration,  $\lambda_{C_k}$  is inversely proportional to the slope of the isotherm,  $f'(C_{k,f})$ , Eq.3.II.6.

4- Allows you to evaluate the it influences several operational parameters such as the form and concentration of the fluid at the column inlet, flow and, mainly, the type of isotherm including analysis of dispersive fronts.

We will now deal with a more complex analysis. Therefore, for Eq. 3.II.1. applied to a column of length L, we will define dimensionless variables given by:

$$\hat{C}_{k} \equiv \frac{C_{k,f}}{C_{k,f}^{0}} \text{ and } \hat{q}_{k} \equiv \frac{q_{k,p}}{q_{k,p}^{0}}; \text{ for concentrations}$$
$$\xi \equiv \frac{z}{L} \quad \tau \equiv \frac{tu_{0}}{\varepsilon_{L}L}; \quad \text{for the coordinates}$$
$$q_{k,p}^{0} = f(C_{k,f}^{0}) \quad \text{for equilibrium law (isotherm)}$$

resulting,

$$\frac{\partial \widehat{C}_{k}}{\partial \tau} + \rho_{p} \left(\frac{(1 - \varepsilon_{L})}{\varepsilon_{L}} \frac{q_{k,p}^{0}}{C_{k,f}^{0}}\right) \frac{\partial q_{k,p}}{\partial t} - \left(\frac{\varepsilon_{L} D_{az}}{u_{0}L}\right) \frac{\partial^{2} \widehat{C}_{k}}{\partial \xi^{2}} + \frac{\partial \widehat{C}_{k}}{\partial \xi} = 0$$
(3.II.7)

and yet, in a more compact form,

$$\frac{\partial \hat{C}_{k}}{\partial \tau} + \varsigma_{L} \frac{\partial q_{k,p}}{\partial t} - \frac{1}{P_{eL}} \frac{\partial^{2} \hat{C}_{k}}{\partial \xi^{2}} + \frac{\partial \hat{C}_{k}}{\partial \xi} = 0$$
(3.II.8)

with,

$$\varsigma_{L} = \left(\frac{(1 - \varepsilon_{L})}{\varepsilon_{L}} \frac{\rho_{p} q_{k,p}^{0}}{C_{k,f}^{0}}\right); \text{ capacity factor } \left(\frac{\text{mass in adsorbent}}{\text{mass in fluid}}\right)$$

$$P_{eL} = \frac{u_o L}{\varepsilon_L D_{az}}$$
; Peclet number

This simple action allows an enormous generalization reducing the problem to studies of practically two operational parameters: the capacity factor,  $\zeta_L$  and the Peclet number,  $P_{eL}$ , immediately imposing the following limits:

$$P_{eL} \rightarrow \infty \rightarrow$$
 fluid flow without dispersion "plug flow"  
 $\varsigma_L \rightarrow 0 \rightarrow$  non-adsorptive process (inert particles)

The model described by Eq. 3.II.8 is what we have called the *macro* model, so the column process will only be completed by selecting the *micro* model of arbitrary choice among those available in the literature and the new ones that may be proposed: it follows, therefore, a very wide range of possibilities for describing and predicting adsorption in a fixed bed or in a column. For an overview we recommend reading the material (review) developed by  $Xu^{21}$  and collaborators.

To obtain the breakthrough curve, it will be necessary to solve Eq.3.II.7, with a kinetic equation for the adsorption rate consistent with equilibrium (adsorption isotherm) and respective initial and boundary conditions.

In order to properly describe the process with a significant reduction in computational effort, Biscaia jr. and Andrade Jr.<sup>22</sup>developed a numerical resolution of the multicomponent separation in a fixed bed column using a microcomputer. Figures 3.II.2a and 3.II.2b are representative of the results obtained by them, which allow an analysis of the separation efficiency as well as the dynamic capacity of the adsorbent.



<sup>&</sup>lt;sup>21</sup>Xu et al. / J Zhejiang Univ-Sci A (Appl Phys & Eng) 2013 14(3):155-176

<sup>&</sup>lt;sup>22</sup>E.C. Biscaia jr. e J. S. Andrade jr. (1986), "Modelagem matemática de colunas de adsorção em leito fixo", Anais do XIV ENEMP,99-113.

FIGURE 3.II.2 - a) Transient profiles of metaxylene and paraxylene concentrations at the column outlet, b) Transient profiles of average metaxylene, paraxylene and total average concentrations.

According to the authors, the technique was providentially designed with the objective of consistently evidencing an explanation for the occurrence of the peak of metaxylene concentration at the exit of the column, at a certain moment, during the dynamic simulation of the process transient, as shown in Figure 3. II.2a. For this purpose, the transients of the average concentrations of the two components were computed throughout the column, in the adsorbed phase, figure 3.II.2b. The authors conclude with this analysis that at the beginning of the process, while paraxylene accumulates in the initial region, the metaxylene that was not captured there will be adsorbed in the terminal region of the column until it is finally expelled by the mobile wave (mass transfer zone) of adsorption that travels through the bed.

This is one of the few works dealing with modeling in multicomponent systems.

For the formulation to be completed, it is necessary to consider the movement of the fluid inside the column of length, L.

Considering incompressible fluid in unidirectional flow at low flow in the column it is possible to use Eq. 3.33c. which integrated yields:

$$\Delta \wp = \left(\frac{\mu_f}{K}u\right)L\tag{3.II.9}$$

and the head loss, exclusively in the column, given by:

$$H_{col} = \frac{\Delta \wp}{\rho_f g} = \left(\frac{\mu_f}{K}u\right)\left(\frac{L}{\rho_f g}\right)$$
(3.II.10)

Where,  $\wp$ , is the piezometric pressure.

*Packed columns* for their simplicity of construction, operation and control, in addition to their low cost, are the most abundant choice. However, in specific cases, other adsorptive systems may be more attractive. In this sense, we will deal with them in the sequence.

## 3.II.2.2. batch adsorption

It is basically an agitated vessel containing a volume,  $V_f^0$ , of fluid to a concentration  $C_{k,f}^0$ , in agitation in which a mass is suddenly placed,  $M_p$ , of activated adsorbent,  $q_{k,p}^0 = 0$ , keeping the system perfectly agitated. Two questions of interest arise.

1- Given the mass of the adsorbent, what is the final concentration of the fluid;

2- For a desired final concentration of the fluid (degree of purification) what is the adsorbent mass.

Both answers are possible with the second question being the one of greatest interest.

In a sense this system has already been dealt with in Chapter 2. whose model is represented by equation 2.II.28. being:

$$q_{k,p} = \frac{V_f^o}{M_p} \Big[ C_{k,f}^o - C_{k,f} \Big]$$
(3.II.11)

Also called operating line

At adsorbent saturation (equilibrium)

$$q_{k,p}^{*} = \frac{V_{f}^{o}}{M_{p}} \Big[ C_{k,f}^{o} - C_{k,f}^{*} \Big]$$
(3.II.12)

equation that must be satisfied by the isotherm of the solid fluid system:

$$q_{k,p}^* = f(C_{k,f}^*)$$
 (3.II.13)

The answer to the questions mentioned above results from the simultaneous resolution of the equations 3.II.12 and 3.II.13, which represent functions traceable in the qC plane and their intersection is the graphical solution of the process.

Pictorially, the process can be seen in Fig. 3.II.3. system: resin-water-copper already referenced in chapter 2.



FIGURE 3.II.3 - **qC** diagram for analyzing the behavior of batch adsorption.

In the figure 3.II.3 points 1, 2 and 3 are all on the straight line established by the mass balance given by Eq. 3.II.11. Point 1 is fixed and represents the initial state of the fluid,  $C_{k,f}^0$ 

points 2 and 3 are mobile as they depend on the initial relationship between the volume of the solution,  $V_f^0$  and the adsorbent mass,  $M_p$ .

Point 3 is given by:

$$q_{k.p} = \frac{V_f^o C_{k,f}^0}{M_p}$$
 in  $C_{k,f} = 0$ 

the slope (slope) of the operating line is, of course,

$$b = -\frac{V_f^o}{M_p}$$

so as point 3 moves on the ordinate point 2 moves on the isotherm. point 2 in any situation is the end of the process, i.e. the equilibrium state, with coordinates,  $C_{k,f}^* = q_{k,p}^*$  which represent the final conditions of the system. For the case of the system shown in the figure the numerical resolution results in  $C_{k,f}^* = 0,00007 \text{ mg/ml}$ , with the aim of purifying the fluid, that is,  $C_{k,f}^* \rightarrow 0$  it will be necessary, if plausible, to increase the adsorbent mass. The limiting factor in the process is the ratio of fluid volume to adsorbent volume, determining the porosity that must be greater than or equal to the minimum fluidization for the system to be perfectly agitated, this leads us almost automatically to the new topic that is adsorption in a fluidized bed. Before, however, it is interesting to ask the question: how much time is spent for the operation to be completed?

This answer requires knowledge of the kinetic behavior of the adsorptive system, which in this case is known because we have already dealt with the subject in Chapter 2. For that, we will look for the results of the pore diffusion model figure 2.II.5 of chapter 2, the result of which was:



# FIGURE 3.II.4 - concentration in the bath as a function of time. Experimental data and model of diffusion in the adjusted pore.

To obtain the result, the equation is integrated until the time when the concentration reaches the equilibrium value, in the case  $C_{k,f}^* = 0,00007$  time being exactly 230 s, or obtained directly from the graph. An interesting thermodynamic observation regarding the subject is interesting; In the **qC** diagram shown in figure 3.II.3 the points on the straight line between points 1 and 2 are the states assumed by the system in the process that leads the initial concentration to its final value, at the operating temperature.

When working with moderate or high concentrations, it is almost always necessary to use several stages of separation as illustrated in figure 3.II.5. in which to obtain a final concentration,  $C_{k,f}^{f}$  from an initial solution,  $C_{k,f}^{0}$  **n** number of separation stages will be established as shown in the figure. As it is about batch separation, only two similar equipment operating in a cyclic way are sufficient although multiple operations in a single equipment is equally plausible.



FIGURE 3.II.5 - qC diagram for analysis of separation by stages in batch adsorption

## 3.II.2.3. fluidized bed adsorption

Fluidization is a system, usually two-phase, solid fluid with its own characteristics called *homogeneous fluidization* in the case of solid-liquid system and particulate fluidization in the solid-gas case. three-phase solid-liquid-gas systems are less abundant. As for the type of operation, they can be open or recirculating.



FIGURE 3.II.6 - fluidized bed systems: a) open; b) recirculating.

Practically, the only operating parameters that have any effect on the behavior of a fluidized bed system are bed height, particle size, fluid velocity and operating temperature.

The height of the bed is crucial for the selection of simplifying operating models. For cylindrical beds in which the height is less than the diameter it is reasonable to assume a perfectly agitated behavior of the type (CSTR) and for long beds in which the height is greater than 10 times the diameter it is reasonable to assume a plugged behavior of the type (PFR).

The total mass of k component inside the bed is:

$$m_{k,L} = V_f C_{k,f} + V_s C_{k,s}$$

For open system:

mass flow at the inlet:  $C_{k,f}^e V_f^e A^e = QC_{k,f}^e$ mass flow at the output:  $C_{k,f}^s V_f^s A^s = QC_{k,f}$ 

# 3.II.2.3.1. CSTR type fluidized bed adsorption

Considering a CSTR-type system without constant flow reaction and equality of cross-sectional areas at the inlet and outlet of the bed we have for mass balance:

$$QC_{k,f}^{e} = QC_{k,f} + V_{f} \frac{\partial C_{k,f}}{\partial t} + V_{s} \frac{\partial C_{k,s}}{\partial t}$$
(3.II.14)

and per bed volume unit:

$$\frac{Q}{V}(C_{k,f}^{e} - C_{k,f}) = \varepsilon_{L} \frac{\partial C_{k,f}}{\partial t} + (1 - \varepsilon_{L}) \frac{\partial C_{k,s}}{\partial t}$$
(3.II.15)

and in the usual notation;

$$(C_{k,f}^{e} - C_{k,f}) = \tau(\varepsilon_{L} \frac{\partial C_{k,f}}{\partial t} + (1 - \varepsilon_{L})\rho_{p} \frac{\partial q_{k,p}}{\partial t})$$
(3.II.16)

with

$$\tau = \frac{V}{Q}$$

completing with a "kinetic law", equilibrium relations and initial conditions, it is possible to determine the temporal evolution of the system.

# 3.II.2.3.2. PFR type fluidized bed adsorption

The mass balance of the k component in the fluidized bed, FB is:

$$\frac{\partial}{\partial t} \left[ \varepsilon_L C_{k,1} + (1 - \varepsilon_L) C_{k,2} \right] + \operatorname{div} \left[ \varepsilon_L C_{k,1} \vec{v}_{k,1} + (1 - \varepsilon_L) C_{k,2} \vec{v}_{k,2} \right] = \varepsilon_L R_{k,1} + (1 - \varepsilon_L) R_{k,2}$$

Assuming no chemical reactions, the result is:

$$\frac{\partial}{\partial t} \left[ \varepsilon_L C_{k,1} + (1 - \varepsilon_L) C_{k,2} \right] + \operatorname{div} \left[ \varepsilon_L C_{k,1} \vec{V}_{k,1} + (1 - \varepsilon_L) C_{k,2} \vec{V}_{k,2} \right] = 0$$
(3.II.17)

One of the characteristics of fluidization is the random movement of particles it can always be considered that the properties of the particle do not depend on its position in the bed and that its distribution is uniform thus,

$$\frac{\partial}{\partial t} \left[ \varepsilon_L C_{k,1} + (1 - \varepsilon_L) C_{k,2} \right] + \operatorname{div} \left[ \varepsilon_L C_{k,1} \vec{V}_{k,1} \right] = 0$$
(3.II.17b)

for the fluid it is assumed a piston motion with surface velocity, constant and equal to  $u_0 \equiv \frac{Q}{A} = \varepsilon_L \vec{V}_{k,1}$  where Q is the volumetric flow rate of the fluid and A is the cross-sectional area of the bed and so,

$$\frac{\partial}{\partial t} \left[ \varepsilon_L C_{k,1} + (1 - \varepsilon_L) C_{k,2} \right] + \mathbf{u}_0 \frac{\partial C_{k,1}}{\partial z} = 0$$
(3.II.17c)

from the porosity uniformity results for the fluidized bed:

$$\frac{\partial C_{k,1}}{\partial t} + \frac{(1 - \varepsilon_L)}{\varepsilon_L} \rho_p \frac{\partial q_{k,p}}{\partial t} + \frac{\mathbf{u}_0}{\varepsilon_L} \frac{\partial C_{k,1}}{\partial z} = 0$$
(3.II.17d)

$$\frac{\partial C_{k,1}}{\partial t} + \frac{u_0}{\varepsilon_L} \frac{\partial C_{k,1}}{\partial z} = -\frac{(1 - \varepsilon_L)}{\varepsilon_L} \rho_p \frac{\partial q_{k,p}}{\partial t}$$
(3.II.17e)

To the fluidized bed, FB, we have Eq. 3.II.17e that complemented with a "kinetic law", equilibrium relations, initial and boundary conditions allow the determination of the spatial time evolution of the system and the rupture curve. Being, as already shown, the rupture curve is the most significant result for the treatment of experimental data and understanding of the adsorptive process figure 3.II.7 shows part of the results obtained by Homem<sup>23</sup> related to open fluidized bed studies. In the nondimensionalization of time, the saturation time **ts** was used.



FIGURE 3.II.7 - Comparison of experimental values with the model of Renken et al (1998), for adsorption of lead in zeolite Baylith 986 (Bayer).

Open systems in fluidized bed adsorption are rarely found in the literature. They are particularly attractive in *particulate fluidization* by the kinetic speed finding interest in the activation or regeneration of the adsorbent by means of a gas stream at high temperature. Operation not recommended in the open if the adsorbed substance is harmful to the environment.

## **3.II.2.3.3.** adsorption in a moving bed associated with an agitated tank.

Mobile bed is a common denomination to differentiate the fixed bed, it is, therefore, particulate systems in which the particle has wide mobility. The association *mobile bed stirred tank*, (MBST), figure 3.II.8, is a simple system, low cost, easy to operate and maintain and very efficient in the treatment of wastewater by adsorption.

or

<sup>&</sup>lt;sup>23</sup>E. M. Homem (2001) "Remoção de Chumbo, Níquel e Zinco em Zeólita utilizando um Sistema de Leito Fluidizado", (Dissertação) UNICAMP, 112.



FIGURE 3.II.8 - system combining moving bed, MB and stirred tank (reservoir), ST

Modeling is greatly facilitated considering a closed composite system. One of the individual systems being the solid phase and the other the fluid phase, such that the composite system is equivalent to the batch system described in section 3.II.2.2. and whose representative equation is given by:

$$\frac{d}{dt}(m_{k,p}) = -V_f\left(\frac{d}{dt}(C_{k,f})\right)$$
(3.II.18)

or yet,

$$M_{p}\frac{d}{dt}(q_{k,p}) = -V_{f}(\frac{d}{dt}(C_{k,f}))$$
(3.II.19)

Where,  $V_f$ , is the volume of fluid in the stirred tank, and  $M_p$ , the mass of the particulate solid.

This arrangement, MBST, was widely used in our laboratory to explore scales larger than the bench-top ones, both for the fluidized bed, figure 3.II.9a, and the vortex bed, figure 3.II.9b. one of the mechanical characteristics of these devices was the gyrate to remove the particles.



FIGURE 3.II.9 - Moving bed association stirred tank (MBST) for: a) electrochemical, b) fluid dynamic studies.

# **3.3. Final considerations**

For the conclusion of this chapter, we intend to couple the parts aiming at relevant application.

For introduction to the subject and motivation for the study we will consider an environmental problem related to Galvanic Industries.

The Galvanic Industries are the main generators of toxic metals (heavy metal) Copper, Nickel and Chromium, among others. The effluent treatment process used in the vast majority of these industries is through the physical-chemical process, which consists of the reduction and chemical precipitation of the metal followed by filtering in a filter press, which is not efficient to remove residual concentrations of metals. An important problem of this process, which must be taken into account, is the production of relatively large amounts of sludge contaminated with metals, which later need to be sent to industrial landfills for final disposal. In this context, the proposal here is to present the electrochemical and/or ion exchange technology as an alternative to the conventional physical-chemical treatment.

## the copper bath

This bath is one of the oldest applications in the history of electroplating. When prepared on the basis of sulfate, it is used for decorative and technical purposes. This bath is, on a large scale, applied as a layer prior to nickel plating. Due to its great leveling power, it allows a less demanding iron polishing and, in many cases, direct nickel plating on the shiny copper layer, without the intermediate polishing of this layer, resulting in great labor savings.

In galvanic processes, in addition to the baths themselves, there are "waterfalls" through which washing or rinsing water is recirculated. The scheme of a wash is simple and consists of large tanks that are fed with good quality water, and where there is a constant replacement of this water. Normally, the wash water is fed continuously and with a regulated flow in relation to the number of substrates being washed, thus preventing the concentration of a given metal in the wash water from being high. For example, when a substrate passes through the copper bath, it must pass through the copper wash water before going to the nickel bath, which must pass through the nickel wash water to finally go to the chromium bath if this is the final objective of the treatment of the part in question. The function of these washing waters is to remove excess metals from a bath that remain on the surface of the substrate in liquid form. If these excesses are not removed, there will be contamination of the subsequent baths by dragging the metals, seriously affecting the quality of the process. The water intended for washing the substrates is continuously replaced by good quality water (public supply standard), being fed in the 1st stage and discarded in the last stage. The washing water works by difference in quotas, the 1st stage being the highest; the water overflows to the 2nd stage and so on, preventing mixing of the waters contained in the different stages. As mentioned, the wash water contained in the last stage has an appreciable amount of metal and cannot be discarded directly. This water is normally directed to a storage tank for further chemical treatment. If added, these large volumes of water constitute more than half of all effluent to be treated for disposal.

As a problem to be studied, the case of a galvanic in São Paulo will be considered, where the washing water, directed to the storage and treatment tank, has an average content of 300 mg/L of copper at an average continuous flow of 100 l/h The treatment of which will require that it has no more than 2 ppm in reuse and disposal.

We will consider that a minimum infrastructure already exists and that, in this case, the chemical treatment tank with a minimum capacity of  $20m^3$  will be used, where the effluent arrives by gravity and awaits a technical procedure for treatment.



FIGURE 1 - reservoir for reception and chemical treatment of effluent.

For the purpose of a demonstration study of the technical feasibility of treating this polluting stream, by alternative technologies, we intend to follow the following procedures:

- 1- Purely electrochemical technique;
- 2- Purely adsorptive technique;
- 3- Electrochemical technique associated with adsorptive technique.

In order to take advantage of practically all the results of the bench studies, we will adopt the fluidized bed in the MBST arrangement (Mobile bed associated with an agitated tank) as equipment, that is, just stretching the apparatus in Figure 2.I.8. from part I of chapter 2. In this system, for concentrations lower than 500 mg/L, as noted, the kinetics is controlled by mass transfer, and so the design will be based on equation 2.I.50. from part I of chapter 2 given by:

$$C = C_0 \exp\{-\frac{1}{\tau} \left[1 - \exp(-\frac{\varepsilon a_p k_L}{V_z}L)\right]t\}$$

$$\tau = \frac{V}{Q}$$
(3.46)

The parameter to be determined is the height of the bed, L, required to lower the concentration to 2 mg/L in 3 h of operation, assuming all other parameters are known:

# filling:

The constituent particles of the fluidized bed are equilateral cylinders of copper with:

$$d_{p} = 0.1cm \text{ (particle diameter)}$$
  

$$\phi = 0.874 \text{ (sphericity)}$$
  

$$\rho_{p} = 8.96 \frac{g}{cm^{3}} \text{ (particle density)}$$
  

$$a_{p} = \frac{6}{d_{p}} = \frac{60}{cm} \text{ (particle specific area)}$$

# fluid:

The fluid is the industrial effluent considered a copper electrolyte solution

$$C_{0} = 300 \frac{mg}{L} (concentration)$$

$$\rho_{f} = 1 \frac{g}{cm^{3}} (fluid density)$$

$$Q = 100 \frac{L}{h} (volumetric flow rate)$$

Bed:

The bed is a column with a rectangular base, formed by flat walls housing metal plates feeding and receiving current separated by a distance of 2 cm and with a width of 10 cm and a height of 200 cm, as shown in figure 2. the minimum height L, of the filling, that is, the mass of particles, which will meet the criterion of maximum concentration for local industrial reuse (floor cleaning or similar),  $C_{cu,final} = 1ppm$ in the case.



FIGURE 2 - proposed geometry and size for the pilot scale

To use Eq.3.46, data from  $\tau$  k<sub>L</sub> and V<sub>z</sub>:

Bench studies for good quality fluidization have shown that one should operate with a 35% expansion of the fixed bed, that is, a porosity above that of minimum fluidization, this regime being given by:

$$u_{z} = 11.335 \frac{cm}{s} ; (fluid surface velocity)$$
  

$$\varepsilon_{L} = 0,585 ; (bed porosity)$$
  

$$V_{z} = \frac{u_{z}}{\varepsilon_{L}} = 19,39 \frac{cm}{s}; (interstitial fluid velocity)$$

The mass transfer coefficient, in addition to the fluid dynamic conditions, also depends on the intensity of the applied current. On the bench, we worked with currents of up to 10 Ampere and in this prototype, it will be possible to use up to 1000 Ampere. In this sense, the mass transfer coefficient is still undetermined. It is intended to use 400 A. As the fluid dynamic conditions are the same and they are the most relevant, we will assume that the coefficient obtained with 8 A is usable. given by:

$$k_L = 0,007692 \ \frac{cm}{s}$$

$$Q = Au_z = 226.7 \frac{cm^3}{s}$$

The effluent production is 100 liters per hour, generating a volume of 300 liters in 3 hours, so taking V=300000 cm<sup>3</sup>, the last parameter required is obtained.

$$\tau = \frac{V}{Q} = 1323.33$$
s

The initial concentration in the tank is  $C_0=300$  mg/liter, all this data in Eq. 3.46 results in an operating time of 3 hours:

$$C_{cu} = C_{cu}(L) \tag{3.47}$$

whose graph is shown in figure 3.



FIGURE 3 - copper concentration in the tank at the end of 3 hours of operation, for a given height of particles inside the apparatus

It is verified that heights greater than 60 cm practically deplete the copper in the tank. For the mathematical solution of the problem, just use the final value of 1 ppm in Eq.3.47 and solve for L, obtaining:

L = 70 cm

and then:

$$V_L = AL = 20.70 = 1400 \, cm^3$$
; (bed volume)  

$$V_s = (1 - \varepsilon_L)V_L = 581 \, cm^3$$
; (volume of solids)  

$$m_s = \rho_p V_s = 10035 . 2g$$
; (mass of solids)  

$$A_s = a_p V_s = 34860 \, cm^2$$
; (total surface area of solids)

In practical terms, the result sought is the required mass of solids,  $\mathbf{m}_s$ , to obtain the desired result. It is interesting to note that the proposed apparatus is 200cm high and only 70cm will be used, leaving a useful volume for operational adjustments.

Before presenting the strategy for solving the problem, we will insert relevant information: Silva (1996, 2000) after substantial work on the laboratory scale<sup>24</sup> undertook the pilot-scale study<sup>25</sup>. With significant financial support from FAPESP<sup>26</sup>, we were able together to develop scale expansion in the pilot mode.

## **Pilot plant**

The experimental unit proposed, built and tested for the application of this technique is schematized in figure 4.



FIGURE 4 - Schematic of the pilot experimental unit.

The reactor used in the tests is built in acrylic material (plexiglass sheets) and its total dimensions are 2.00 m high, 0.16 m wide and 0.05 m deep. The current feeder and the counter electrode are made of copper and lead plates, respectively. The diaphragm that covers the counter electrode to prevent short circuits is formed of plastic mesh followed by polyamide blanket.

The bed consists of copper particles in the form of cylinders with a diameter and length of 1 mm (produced by a device built by us aiming at the perfect cut of 1m diameter copper wires). The electrolyte was composed of a mixture of distilled water, copper sulfate

<sup>&</sup>lt;sup>24</sup>SILVA, A.P. (1996). Eletrodeposição de cobre em leito fluidizado. Dissertação de Mestrado, Universidade Federal de São Carlos, São Carlos, 114 p.

<sup>&</sup>lt;sup>25</sup>SILVA, A. P. (2000), Eletrosseparação de íons cobre, em eletrodo de leito fluidizado, em escala piloto. Tese de Doutorado, Universidade Federal de São Carlos, São Carlos - SP, 153p.

<sup>&</sup>lt;sup>26</sup>Fundação de Amparo à Pesquisa do Estado de São Paulo. (Foundation for Research Support of the State of São Paulo, Brazil).

pentahydrate and sulfuric acid. The sulfuric acid concentrations used were 0.55 M and 0.80 M.

The electrolyte was stored in a polypropylene reservoir with a capacity of up to 600 l, and the volume used in the tests was 300 l. The electrolyte solution was recirculated between the reactor and the reservoir through a 3.0 hp centrifugal pump, whose parts in contact with the fluid were made of plastic. The electrical current fed to the system came from a direct current rectifier with a capacity of up to 1000 A, and the measurement of the current applied to the reactor and the voltage drop presented by the same were obtained with the use of an ammeter pliers and a digital multimeter, respectively.

To control the temperature of the electrolyte, a heat exchanger in plastic material connected to a cooling tower was used, with water as the cooling fluid. In the latter, a frequency inverter and a programmable logic controller were added to the experimental unit, in order to achieve the electrolyte flow variation that characterizes the electrode as pulsating. In figure 5, the final form of the pilot plant is shown, which was tested as a fluidized bed and a pulsating bed with an innovative proposal for the functionality of the latter.



FIGURE 5- Pilot experimental unit,

In this equipment, a C(t) vs t curve of the pollutant concentration decay as a function of operating time can be drawn. This curve from which all other parameters originate.

In figure 6 a typical result is shown. It is clearly evident that it is possible to bring the effluent concentration from 2000 ppm to practically 1 ppm in about 300 minutes.



FIGURE 6- Copper concentration in the electrolyte as a function of time, having as parameters the applied current I=400 A, initial particle height  $L_0=100$  cm if fixed bed and L=135 cm if fluidized bed.

The points are data obtained in the tests and the curve is a fit of these points and is well represented by the equation:

$$C_{cu}(t) = 1780. \, e^{(-0.024t)} \tag{3.48}$$

The resolution of Eq. 3.48 for a final concentration of 1 ppm is t=311.85 min. Note that the initial concentration of the bath is 2000 ppm and we operate with up to 3000 ppm, emphasizing that this study is necessary because the concentration in the industrial reservoir can reach these values when the exhausted baths are added. Note that if the initial concentration is 300 ppm, then 237.65 minutes will be needed to reduce the concentration to 1 ppm. This post follows analysis of the initial problem with the proposition of application strategies in the industrial environment.

# 3.3.1.1. Operational arrangements in the industrial environment

## a) -Continuous treatment

The operating strategy aimed at continuous treatment is shown in figure7. and operates according to the protocol:

The effluent arrives by gravity to the reservoir, to accumulate, as if it were going to do the usual chemical treatment. The process starts with a command activating the pump, **B1**, for an adjusted time, so that they are transferred from the main reservoir to the tank, **T**, exactly 300 liters and, in the sequence, the pump **B1** is turned off and the pump **Bs** is activated, to bed fluidization and current source, both with pre-set flow and current adjustments. After 3 hours of operation, the processing of a batch is finished. The command switches off the pump **Bs**, and the current source and opens the valve, **Vd**, for almost instantaneous discharge from the tank **T**, to the *auxiliary reservoir* and, in the sequence, closes the valve, **Vd**, activates the pump **B1** and the cycle is repeated until the moment when the increase in the volume of the

particles, due to the removal of copper, requires its removal and replacement. At each cycle, the **B2** pump removes the treated water from the *auxiliary reservoir* and sends it to an elevated reservoir where it can be directly to *suitable reused*. (Sanitary installations or floor cleaning, etc...) or any other with legal permission.



FIGURE 7. - arrangement with an electrochemical fluidized bed reactor, FB, an associated tank T and properly positioned reservoirs.

In the kinetic studies it was found that at concentrations below 500 ppm the current efficiency drops a lot and consequently the energy consumption increases. At the in the case of this test, the average current efficiency was 37.52% and the average energy consumption was 186.78 kWh/kg.

The chemical treatment for installations like the ones presented are weekly. For economic considerations we will take this time as a basis. considering 24 hours of continuous work per day, resulting in 168 hours of operation and 16800 liters of washing water and 5.04 kg of copper (II) to be removed.

# **Operating costs with the pilot unit**

Treatment of 16800 liters of wastewater containing copper (II) in 168 h.

The power of the fluid recirculation pump is 3.0 hp, that is, 3. (735.5W) =2206.5W=2.2kW consuming an amount of energy given by 2.2 kW in operation. (168h) =369.6 kWh.

The rated consumption of the current source is 6kW and will yield to the process 6kW. (168h) =1008kWh.

The total electricity consumption is then 369.6+1008=1377.6kWh. Considering that the price of industrial electricity in SP is 0.8 R\$/kWh, the cost of operation would be R\$ 1102.08. On the other hand, the price of electrolytic metal is 32.00 R\$/kg copper, for example, and we would have sold the recovered metal R\$ (5.04) (32.00) =171.8. The real cost of the operation would thus be R\$ 929.28.

It would be instructive for the reader to estimate the cost of treatment by the chemical process classically used.

As previously, we will operate in the sense of taking advantage of practically all the results of preliminary studies; in this case the work of Catunda Pinto<sup>27</sup>. We will adopt the fixed bed as equipment, determining the dimensions of the adsorption column compatible with the industrial need in question. The main experimental information needed is the *breakthrough curves* of a laboratory scale test column. Among the known techniques, our favorite is the *kinetic approach*. This information has already been explored in part II of chapter 2. item 3.II.4. which we repeat here to facilitate the reader:



FIGURE 8.- Studies of *breakthrough curves* on a laboratory scale and model for kinetic adjustment; **a**) experimental data from Catunda Pinto (2001); **b**) model from Boharth and Adams (1920).

It is well established that the kinetic parameters remain unchanged if the same laboratory scale conditions are maintained at the enlarged scale. Among the many conditions studied by Catunda Pinto, the data shown in Figure 8 were conducted under the conditions of the industrial environment in question. For this condition, the data were selected:

L=8cm; column length; u=0.7325 cm/min; surface velocity; D=1.5 cm; column diameter; C<sub>0</sub>=0.10267 mg/cm<sup>3</sup>; effluent concentration; q<sub>0</sub>=0.0017 mg/cm<sup>3</sup>; kinetic parameter; k=165.5 min<sup>-1</sup>; kinetic parameter; ts=4240.2 min; column saturation time.

<sup>&</sup>lt;sup>27</sup>CATUNDA PINTO, C. H. (2001), Remoção de metais pesados de soluções aquosas diluídas via processo adsortivo por troca iônica utilizando vermiculita, Tese de Doutorado Universidade Federal de São Carlos, São Carlos - SP,151p.

resulting for any L and Co

$$C_b = \frac{C_0}{1 + e^{(0.3833L - 0.039C_o t)}}$$
(3.49)

For reasons that will be clarified later, we will adopt a length of 100 cm for the scale increase. The flow rate will be that of the washing water production, 100 l/h, that is, Q=1666.7 cm<sup>3</sup>/min at a concentration of 0.3 mg/cm<sup>3</sup>. Keeping, from the laboratory test, the filtration speed, u=0.7325 cm/min, the packing density of the adsorbent,  $\rho$ =1.17 g/cm<sup>3</sup> we will have for the column area; A=2275.3 cm<sup>2</sup>, the volume V=227531.3cm<sup>3</sup> and the adsorbent mass, M<sub>ads</sub>=266211.6g; thus, being completely determined, the dimensioning of the adsorption system. It remains, therefore, to determine the rupture time and the saturation time of this column, using Eq. 3.49, and replacing in this the values of the enlarged scale, L=100 cm and Co=0.3 mg/cm<sup>3</sup>, resulting:

$$C_b = \frac{0.3}{1 + e^{(38.33 - 0.117t)}} \tag{3.50}$$

considering a widely used criterion that at break time,  $C_b = 0.1C_0$ , and at saturation time  $C_b = 0.99C_0$  results by substituting these values into Eq. 3.50,

$$t_r = 3085.9min$$
  
 $t_s = 3666.0min$ 

In the figure 7 the dynamic kinetic behavior of the new column is shown. highlighting the rupture and saturation times based on the adopted criterion.



FIGURE 9.- behavior of the breakthrough curves for an enlarged scale.

it is easy to see from figure 9 that the column supplies water, practically free of copper for a period of 3000 minutes, which we will consider as operating time,  $t_{op}$ =50 hours from which the column must be unloaded, according to the operation protocol to be described below. Substituting t=t\_op in Eq. 3.49 results in the output concentration, C<sub>s</sub>=0.011 mg/cm<sup>3</sup>, that is,

the water starts to become contaminated. We only want good quality water, to return to the process, which is a great consumer of water. A graphical analysis of figure 7 according to the technique concerning the *global mass balances* relative to the rupture curve shown in figure II.12. of chapter 2 part II, presents the following parameters of interest:

Imp=1.388kg (in, *input*); L=0.00013kg (out, *leakage*); S=1.388kg (accumulated, *storage*); U=0.248kg (useless, *unused*)

The volume treated in 48 h is 4800 liters at a concentration of 300mg/l and, therefore, with 1.44 kg of copper. This data compared with the predicted result of accumulation of 1.388 kg is very satisfactory validating and ensuring confidence in the project.

The equipment we are suggesting is shown in figure 8 and will be in two states a) in the adsorption period and b) in the moment of withdrawal of the saturated adsorbent; It can be built with a cylindrical or parallelepipedic body. It is a tilting column for fast and complete removal of the exhausted adsorbent. The 1 m high adsorption column is contained within a complementary column and, attached to it, constitutes a single piece, whose function is the discharge by gravity of the copper-free permeate that, through the bed jacket, goes to the *auxiliary tank*, for about two days, until the time of rupture, when then the supply switches with the second bed and the first rocker bed as shown in figure 8.



FIGURE 10 - suggestion of adsorption unit a) bed in adsorption b) tilted bed after saturation.

The system will operate with two identical columns 1 and **2** as shown in figure 11 working alternately as shown in figure 12.



FIGURE 11 - suggestion of adsorption system



FIGURE 12 - arrangement of the adsorption system

At the beginning of the process, the two columns are filled with raw vermiculite and the control system (CS) takes over; closes valves  $V_1$  and  $V_2$  and, subsequently, opens valve  $V_1$  and activates pump  $B_1$  to feed column 1 for the operating time,  $t_{op}$ =48 hours, (2 days exactly) in which the rupture time of column 1 is about to be reached; closes valve  $V_1$  and opens  $V_2$  to feed column 2 by operating time,  $t_{op}$ . Immediately, a company worker uncouples column 1 from the feed line and tilts it to remove the adsorbent, which, by gravity, falls onto the saturated adsorbent receiving trolley, as seen in figure 13, and sends it to drying in a natural environment, arranged in a thin layer, awaiting appropriate procedure. It then replaces fresh adsorbent in column 1 for sequential use. This protocol is repeated, alternately and indefinitely. In this modality, it is not intended to reuse the adsorbent, as it is a low-cost and abundant material. It is solid waste produced in smaller quantities than chemical sludge and more easily repositioned in nature. At the end of a month of operation, 72 m<sup>3</sup> of water (standard industrial use) was recovered, returning to the process 3993.1 kg of solid waste, equivalent to 3.413 m<sup>3</sup>, with a very attenuated risk classification.



FIGURE 13 - removal of the exhausted adsorbent

In a more elaborate version, the tilting column is automatic and the adsorbent is removed by a conveyor belt.

## **3.3.2.1.** adsorbent recovery (regeneration)

To make a more economical adsorption process, it is necessary that the adsorbent is regenerated, that is, recycled. Through experimental data of adsorption, desorption and recovery of copper (II) ion, Catunda Pinto (2001), we verified that only 24.93% is recovered when using an eluent solution of NaCl (0.5 eq/L). However, this value increases to 97.17% when using an HCl solution (0.5 eq/L). This is an indication that the nature of ion exchange is greatly influenced, when the presence of acidic solution, in the sorption processes, it also indicates that the copper (II) ion was adsorbed by stronger interactions with the adsorbent vermiculite. Therefore, vermiculite can be regenerated (recycled) for a new use by acid treatment. If desorption is not desired, this vermiculite material plus the adsorbed ion  $(Cu^{2+})$ , can serve as a substrate for plants that need the copper (II) ion present in the substrate for their development, as well as being incorporated as a binder in the civil industry, and we can also suggest that this material is incorporated into, or sent to, a relevant class landfill. Needing, therefore, an economic study for the final destination of the adsorbent with the incorporated ion. Catunda Pinto (2001) showed that the adsorbent can be regenerated in the adsorption column itself or outside it in a perfectly stirred system. Before presenting our proposal for recovery in the column itself, it is natural to continue the previous process where the adsorbent is preferably discarded for operational simplification. If the company is interested in opting for an additional operation, we propose the following formulation: Recovery of the adsorbent in a batch system whose equipment is practically the same as shown in Figure 8, slightly modified by the introduction of an agitation element as seen in Figure 12 In the case of the proposal, the agitator is attached to an *automatic jib crane* and can go up and down through a synchronous motor to position itself in the tank: lowered it will promote agitation; raised will allow the tank to tilt to discharge the regenerated adsorbent. At the bottom of the tank, a segment of pipe fitted, in its portion anterior to the valve Vd, with a filtering element of acceptable permeability, so that the gravitational flow of the solution is carried out through the opening of the discharge valve Vd.



FIGURE 14 – suggestion of desorption unit a) desorption bed b) tilted bed after activation of the adsorbent.

When the valve, Vd, is closed, the operation begins with the introduction of a mass,  $M_{ads}$ , of adsorbent and a volume,  $V_{sol}$ , of desorbent solution, respectively. The control system (CS) starts the agitation motor and starts timing. At the end of the desorption time, the command turns off the agitation, opens the valve, Vd, and the extractor solution is discharged to an *auxiliary reservoir*, similar to the one shown in figures 11 and 13. At the end of the extraction solution flow time, the CS commands the closing the valve, Vd, lifts the agitation system and delivers the command to the operator who tilts the tank, so that the activated adsorbent falls onto the regenerated adsorbent receiving trolley and taken to the drying sector. Then the operator feeds the tank again with  $M_{ads}$  and  $V_{sol}$  and delivers the system to the CS, to start a new batch and so on until all adsorbent is recovered.

In a slightly more elaborate version of the project developed, the desorption tank in Figure 14 is a fluidized bed, for rapid drying, if desired. In this version, the desorbent is removed by evacuation using the suction of the same radial compressor, **RC** which is used to supply the hot air. For the suction and the discharge, we have two-way valves so that the suction and the discharge work in the same line with a single **RC**, whose operation of evacuation of the desorbent is initially carried out in the form of a gravity filter followed by vacuum filtration so that only the residual saturation remains in the adsorbent followed by the entry of hot air for drying in a fluidized-agitated bed, a triple function. With an electronic speed variator (frequency inverter), the speed of rotation of the agitator is adjusted. Combined fluidization and agitation promote drying kinetics.

For the operation of the system will be considered, for a batch, the following data:

 $V_{sol}$ =238 liters of water at a concentration in HCl (0.5 eq/L);  $M_{ads}$ =88 kg dry mass.

According to Catunda Pinto (2001) in 90 minutes, 97.17% (476336.8mg) of the adsorbed copper will be in the solution, resulting in a solution with a concentration of 2001 mg/liter, whose destination will be the *auxiliary reservoir*, for a short period and, subsequently, an *accumulation reservoir*. It should be noted that the recovery of the adsorbent has an operational cost, which is the accumulation of an effluent with 2001 ppm that must be properly treated either by the conventional process or an alternative technique such as electrochemistry, for example.

The mass of adsorbent in the adsorption column (proposed for adsorption) is 266211.6g and as 88000g is the proposed mass treated in a batch, so 3 batches will be enough to recover the entire column. Exactly 4.5 hours of desorption time are spent. Considering the pause for the operator to feed and unload the bed, 5 hours can be considered the total time of bed regeneration.

After this adsorbent recovery proposal, the following item becomes almost mandatory.

#### 3.3.3. Electrochemical technique associated with adsorptive technique

In the proposal above, the electrochemical technique is suggested as a complementary treatment, waiting for the volumetric limit of the *accumulation reservoir* to be reached before starting. In the following proposal, the technique will be incorporated into the process.

The idea here is to use the electrochemical technique to bring concentrations from 2001 ppm to concentrations of 300 ppm because in this range of concentrations the current efficiency is greater than 90%; in the sequence enter with adsorptive process. In this case we will not discard vermiculite; it will be activated by acid treatment in desorption in a stirred tank and dried in a natural environment, producing fresh adsorbent and an acidic copper solution with adequate concentration (2001ppm) for recovery by electrochemical technique. The integration of adsorptive and electrochemical techniques promotes the recovery of water, adsorbent and metal. No waste will be generated. In figure 13 we are suggesting a flow diagram of the treatment unit.



FIGURE 15 - treatment plant suggestion combining adsorptive and electrochemical techniques.

With the material already presented so far the design of this strategy can be undertaken. The complete and specific dimensioning including peripherals such as pumps and reservoirs as well as automatic control suggestions will be left to the reader so that he can exercise his vocation as an engineer and designer. The minimization of the physical area, surface available on the property for building the plant, should receive special attention, because older companies don't have enough anymore.

# Appendix A

# KINETIC AND HYDRODYNAMIC STUDY OF COPPER ION ELECTRODEPOSITION IN THREE-DIMENSIONAL FIXED BED ELECTRODES\*

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Abstract - The objective of this work was to study the kinetic behavior of a fixed bed reactor in terms of current efficiency (EC) and energy efficiency (EE), having as operational parameters the bed thickness (L) and the applied electric current density (i). It was found that the fixed bed, for certain applied thicknesses and current densities, presents high current efficiencies (close to 100%) in the removal of copper ions. It was also observed that the increase in current density causes a powdery deposit to appear, which becomes more and more intense. Once the kinetic characteristics of the reactor were known, the experimental conditions that would be used in the hydrodynamic study were established. It was found that the pressure drop data as a function of flow velocity fit the quadratic equation of Forchheimer. The electrode was characterized by its permeability and c facto as a function of its porosity. During the process, there was a decrease in flow and porosity, however, these had no influence on the EC, which remained practically constant, the same not occurring with the EE. Through the kinetic and hydrodynamic results obtained, it was then possible to establish an expression for the optimal operating time of the reactor as a function of the applied current density, which remained practically constant, the same not occurring with the EE. Through the kinetic and hydrodynamic results obtained, it was then possible to establish an expression for the optimal operating time of the reactor as a function of the applied current density. which remained practically constant, the same not occurring with the EE. Through the kinetic and hydrodynamic results obtained, it was then possible to establish an expression for the optimal operating time of the reactor as a function of the applied current density.

# **INTRODUCTION**

As mentioned in Ruotolo and Gubulin (1997), the treatment of industrial waste containing metallic ions is necessary due to both ecological and economic factors.

Traditional methods of treating wastewater containing heavy metals basically consist of precipitation and ion exchange techniques.

In the 1960s, the electrochemical method emerged, which, unlike conventional methods,

does not produce permanent waste, thus being a completely clean technology. From an economic point of view, this method is also promising because it has advantages such as: reduction of labor, partial or total elimination of storage areas, reduction of the final cost of the product, almost total reuse of by-products and reintegration of metals into the main process due to their high degree of purity, Rajeshwar and Ibañez, (1997).

The low current efficiency and high energy consumption resulting from the use of

the conventional flat electrode led to the creation of a new generation of electrochemical reactors using electrodes with a large surface area, called three-dimensional electrodes, such as the electrodes of particulate beds, among which the fixed bed reactor stands out, which is characterized as being the most efficient in the electrodeposition of metals. However, the fixed bed reactor has the inconvenience of closing the porous matrix due to the metallic deposit. However, due to the fact that for diluted ionic solutions the operating time becomes very long, this fact would justify its use in the form of refills. In view of this, this work addresses the behavior of the electrochemical reactor under two aspects: 1) kinetic: aims to study the influence of current density and bed thickness parameters on the current efficiency and energy efficiency of the process; 2) hydrodynamic: aims to relate the hydrodynamic properties of the bed and the system in order to obtain a relationship that establishes an optimal operating time as a function of the current density imposed on it.

# **GENERAL ASPECTS**

The current efficiency, Equation 1, comprises the ratio between the mass of the metal effectively deposited in a certain time interval and the mass of the metal that would be electrodeposited in that same time if all the applied electrical current were used for this purpose, while the efficiency Energy, Equation 2, is given by the ratio between the mass of copper effectively electro processed in a given time interval and the electrical energy transferred to the system in this same time interval.

$$EC = \frac{z_i F}{M_i I} \frac{\Delta m}{\Delta t}$$
(1)

$$EE = \frac{1}{I.V} \frac{\Delta m}{\Delta t}$$
(2)

With the results of the kinetic study, it was then possible to establish the best conditions in which the highest current and energy efficiencies were obtained in a fixed bed thickness in which the electrode presents the lowest possible thickness of inactive regions in terms of electrodeposition. As for the hydrodynamics of the reactor, the effect of pore closure on the hydrodynamics of the system can be evaluated through the parameters permeability (k) and c factor, using a quadratic equation of the Forchheimer type, Equation 3, which is applied to the flow of fluids in porous media Scheidegger, (1974; Massarani, (1997).

$$\frac{\Delta P}{L} = \frac{\mu}{k(\varepsilon)} \cdot q + \frac{c(\varepsilon) \cdot \rho}{\sqrt{k(\varepsilon)}} \cdot q^2$$
(3)

With regard to the porosity of the fixed bed, an efficient method was not achieved for its experimental measurement along the thickness of the bed (the pore closure rate is not uniform along the thickness). In view of this, it was decided to use an average porosity that was calculated from a mass balance in the system.

As the system operated in a closed circuit with finite amounts of solution and copper particles, the following relationship between  $\varepsilon$  and C<sub>Cu</sub> was obtained, as shown in Equation 4.

$$\varepsilon = \varepsilon_{o} - \frac{m_{io}^{s}}{\rho_{m} \cdot V_{L}} \left[ 1 - \frac{C_{i}}{C_{io}} \right], \quad i = Cu^{2+} \quad (4)$$

Through the experimental measurement of the pressure drop curve in the bed as a function of the flow velocity, it was then possible to adjust a curve through which the hydrodynamic parameters were obtained, through Equation 3, as a function of the porosity that the bed presented in a given instant, calculated by Equation 4.

## **MATERIALS AND METHODS**

An overview of the equipment used in both the kinetic and hydrodynamic studies, as well as the schematic figure of the reactor used in the kinetic studies can be found, respectively, in Figures 1 and 2 by Ruotolo and Gubulin (1997).

The electrolyte used was prepared using copper sulfate at the desired concentration and sufficient sulfuric acid to obtain a concentration of 0.5 M. The electrolyte flow was downward and the reactor configuration was parallel in terms of current flow directions and electrolyte. A porous cathode whose particles consisted of equilateral copper cylinders, measuring 1 millimeter, was used. The electrochemical reactor used in the kinetic experiments had a cross-sectional area of 12.6 cm<sup>2</sup> (diameter of 4.0 cm) and its parts are all made of plexiglass.

The experimental procedure consisted of the following sequence of steps: preparation of the electrolyte; filling the bed with the particles to a predetermined bed height; adjustment of the electric current source so that a fixed current density is provided; coupling of electrical contacts; admission of electrolyte into the cell with a pre-established flow rate; supply of electrical current to the system and start of timing. At periodic time intervals, the voltage drop in the bed was measured and samples were taken for later analysis of copper concentration in the electrolyte, using a Varian atomic spectrophotometer, absorption model SpectrAA100. This was followed by the closure of the passage of electric current, the reassembly of the reactor, the adjustment of a new current and the restart of timing, voltage drop measurement and sample collection. In all experiments, the flow rate was kept constant and the temperature maintained within a controlled range (25-27°C). This procedure was repeated for the four bed heights and for the four initial concentrations studied.

Figure 1 shows an illustration in which the reactor used in the hydrodynamic study is represented.

Like the previous one, this reactor had a cylindrical acrylic body composed of moving parts that were joined by means of tie rods. This reactor has a fluid passage cross-sectional area three times larger than the previous one. The liquid distributor was inserted in the electrolyte inlet region, followed by a perforated lead plate that constituted the counter-electrode.

The main difference between this reactor and the one described above is that it has two 1.0 mm holes through which it was possible to measure the pressure drop in the bed.

The experimental procedure adopted consists of once the pump is turned on and the electrolyte is admitted to the reactor, a measurement of the pressure drop in the bed is then taken and the initial flow is measured with the main line valve completely open. The bypass valve is kept closed throughout the experiment. Then the valve was closed by placing it in 3 or 4 positions between open and closed. In each of these valve positions, the corresponding flow rate and also the pressure drop in the bed were measured. With these values, it is possible to calculate the permeability of the system and the Forchheimer c factor for a given porosity of the bed.



Figure 1. Reactor used in hydrodynamic studies.

Once the previous step has been completed, the main line valve is fully opened and electricity is supplied to the system and timing begins. The voltage drop in the reactor was also measured and samples were taken for analysis of the initial concentration.

After a time interval, that allowed for an appreciable variation in the height difference in the manometer that measures the flow, a new measurement of the voltage drop in the reactor, the flow, the pressure drop in the bed was then carried out and samples of electrolyte were taken. for further concentration analysis. Once again, the procedure of closing the main line valve, measuring the flow rate and pressure drop is repeated. Then again, the main line valve is fully reopened for the experiment to proceed.

The experiment is conducted until the electrolyte flow is practically zero. At the end of the experiment, the reactor was dismantled,
the particles removed and replaced by new ones.

Using the previous kinetic experiments as a basis, this type of hydrodynamic experiment was carried out only for a bed thickness of 0.5 cm (because it was the region in which the deposition reaction actually occurred) and for two current densities: 318 and 477 A/m<sup>2</sup>, which correspond to those where the best current efficiencies were obtained without the formation of powdery deposits.

The particles used were the same as in the kinetic study, which provides an initial porosity of 33% and the composition of the electrolyte was 0.5 M of sulfuric acid and approximately 5000 ppm of copper ions, which was the amount sufficient for guarantee that at the end of the experiment the electrode was completely blocked and the concentration was not less than 100 ppm, Ruotolo and Gubulin, (1997).

#### **RESULTS AND DISCUSSIONS**

#### **Kinetic Study**

The constant kinetic study in this work seeks knowledge of the phenomena that occur when high current densities are applied, thus complementing the work previously carried out by Ruotolo and Gubulin (1997), in which they verified that even the studied current of 1600  $A/m^2$ , for beds with thicknesses greater than 2.0 cm, the EC and EE increased, which motivated us to find out what would happen when the current density was increased, as there could be a highly desirable condition in which the reactor could operate with high EC values and EE and with a high deposition rate as well. However, this is not the case, as will become clear later.

As can be seen in the graphs of Figures 2 and 3, the existence of negative EC and EE values was again verified, which means that the copper concentration in the electrolyte is increasing due to the dissolution of the porous matrix. When low current densities are applied and the bed thickness is increased, the dissolution effect becomes more and more accentuated.



Figure 2 - EC as a function of current density having the bed thickness as a parameter. q = 0.115 m/s.



Figure 3 - EE as a function of current density having the bed thickness as a parameter. q = 0.115 m/s.

An increase in the specific surface area by increasing the thickness of the fixed bed could contribute towards the possibility of operating the system with high current values and obtaining high current efficiency and with a shorter processing time, assuming at first that the electrical charges would be evenly distributed throughout the electrode, also providing an increase in the useful life of the electrode before it closes completely. However, as we can see through the analysis of the graph in Figure 2, an increase in the thickness of the bed makes it less and less efficient, therefore, it is more and more necessary to increase the applied current density for the bed to operate. in positive current and energy efficiencies.

At first, the increase in current density for beds with thicknesses of 2.0; 3.0 and 4.0 cm would allow, in addition to an increase in EC and EE, also an increase in the reaction rate, which could cause a highly desirable situation of high EC and EE combined with a high electrodeposition rate. However, for these bed thicknesses the EC reaches a maximum value that is still lower than the value found for a bed thickness of 1.0 cm.

It was again observed that most of the reaction occurred on the upper surface of the particles close to the counter electrode, which allows us to infer that it behaved practically like a flat electrode, except for the protuberance and roughness caused by the particles.

In view of this, increasing the thickness of the bed in order to prolong the operating time of the electrode before it closes is not possible, because regardless of the thickness of the electrode, the porous matrix will be blocked in the region close to the counter-electrode while the rest of the bed will have its porosity practically unchanged. Therefore, in view of these results, the most immediate way to increase the reaction rate while maintaining an adequate current density is by increasing the electrode diameter.

When working with current densities greater than 796  $A/m^2$ , a powdery deposit appeared, which became more and more intense as the applied current density increased. This deposit has bad consequences on the hydrodynamics of the system, causing the dust to accumulate in the pores and increasing the resistance to flow, and after a certain period of operation the electrolyte no longer flows through the bed.

#### Hydrodynamic Study

Figures 4 and 5 show the experimental results obtained regarding the pressure drop in the bed as a function of the flow velocity for the two current densities studied.

It can be seen in Figure 4 that the pressure drops as a function of the flow velocity is practically the same when we compare the two current densities applied, which means that once a certain mass of metal is deposited this will create a certain resistance to the flow that will determine a pressure drop that will depend on the permeability of the medium.

In the graphs in Figure 5, the adequacy of Forchheimer's quadratic equation to the system

can be observed, even when the flow rate was too small.



Figure 4. Pressure drop as a function of flow velocity.



Figure 5. Pressure drops in the bed as a function of flow velocity for a given process time. **a**) 318 A/m<sup>2</sup>; **b**) 477 A/m<sup>2</sup>.

As for the electrodeposition kinetics, this can be observed in the graph of Figure 6. An interesting fact that draws attention is that the deposition rate was practically constant, not being, therefore, influenced by the decrease in flow over time. Thus, the current efficiencies for the current densities of 318 and 477  $A/m^2$ 

were constant and their values were 94.2 and 98.2%, respectively.



Figure 6. Mass of electroprocessed copper as a function of operating time.

As for energy efficiency, it can be seen in the graph in Figure 7 that it slowly decreases throughout the process to a certain point where a sudden drop is observed, which occurs, in both cases, after approximately 75% of the total process time has already been completed. if passed. The total process time is defined as the elapsed time until the entire electrode is blocked and there is no more flow.



Figure 7. Energy efficiency as a function of operating time.

Once the values of pressure drop as a function of flow and concentration over time were known, it was possible, using Equations 3 and 4, to obtain the graphs in Figures 8 and 9, which correspond to the permeability and c factor as a function of electrode porosity.



Figure 8 Electrode permeability as a function of porosity.



Figure 9. Forchheimer c factor as a function of porosity.

It is verified that k and c were practically not influenced by the applied current density.

It was observed once again that also for 0.5cm electrode. the closure the that compromised its functioning occurred only on the upper surface close to the counter electrode, which would explain the rapid decrease in the permeability of the bed in the initial moment of the process. During the process, there is a large growth of the deposit in the vertical direction, therefore, the closing of the pores is not as intense and the decrease in permeability occurs more slowly.

As for the rapid increase in the c factor at the end of the process, this is due to the increase in inertial forces caused by the decrease in the fluid passage area through the electrode.

Once the kinetic and hydrodynamic behavior of the bed was known, functional relationships that could be applied to the design of electrochemical reactors that operate within the studied current densities values were sought. Figure 10 shows the decrease in porosity as a function of processing time.



Figure 10. Porosity as a function of time.

From Figure 10 it can be seen that it decreases linearly, that is,

$$\varepsilon(t) = \varepsilon_0 + f(i).t \tag{5}$$

where f(i) is the angular coefficient of the straight line formed, which depends on the applied current density, which in the case of the two studied here can be correlated by a straight line, resulting:

$$f(i) = 3.58 \times 10^{-5} - 5.088 \times 10^{-7}$$
. i (6)

Substituting Equation 6 in Equation 5 we get:

$$\varepsilon = 0.33 + [3.58 \times 10^{-5} - 5.088 \times 10^{-7} . i].t$$
 (7)

In order to establish the time that the system should work without great losses of efficiency, a criterion that is quite significant must be established.

Since the system operates at practically current efficiency (considering constant concentrations greater than 100 ppm) and regardless of the flow, then this parameter cannot be used. However, when we analyze energy efficiency, it is found that there is a point at a certain flow rate where energy efficiency suffers a sudden drop, causing energy consumption to increase too much, implying the economic unfeasibility of working with smaller EE (see Figure 7). In view of this, the criterion for establishing the operating time of the electrode was 75% of the total time necessary for its closure, that is,

$$t_{\rm op} = 0.75 \cdot t \tag{8}$$

Substituting Equation 8 in Equation 7 and equating the final porosity to zero (the electrode is completely blocked), it is then possible to obtain equation (9) and also the construction of the graph in Figure 11 that express the time in which the reactor must be operated depending on the current density applied to it, according to the pre-established criterion.

$$t_{\rm op} = \frac{-0.2475}{3.58'10^{-5} - 5.088'10^{-7} \cdot i} \tag{9}$$

where time is in minutes and current density is in  $A/m^2$ .



Figure 11. Operating time as a function of current density.

The maximum deviation of Equation 8 in relation to the operational time determined experimentally was 8.7% for  $i = 318 \text{ A/m}^2$  and the minimum deviation was 1.9% for  $i = 477 \text{ A/m}^2$ .

#### CONCLUSIONS

As conclusions of this work can be highlighted:

- It was found that the fixed bed is actually a reactor that can present high EC and EE when operated under some particular conditions: small thickness (less than 1.0 cm) and low current densities (equal to or less than  $477 \text{ A/m}^2$ );

- The decrease in the electrolyte flow due to the decrease in the porosity of the electrode did not cause a decrease in EC over the operating time. The EE remains at a practically constant level until a certain time when it begins to rapidly decrease due to the increase in the potential drop in the bed; - The rapid decrease in permeability at the beginning of the process is mainly due to the effect of the rapid deposition of metal in the initial moments on the surface of the electrode close to the counter electrode. During the process, it is verified that the deposit grows preferentially in the vertical direction (towards the counter-electrode), thus causing the permeability to decay more slowly. As for the increase in c factor at the end of the process, this is due to the increase in inertial forces caused by the decrease in the fluid passage area;

- It was found that it is interesting to operate the system until processing times corresponding to 75% of the total process time, since from then on energy efficiency becomes rapidly lower.

#### NOMENCLATURE

- c = Forchheimer's c factor (dimensionless);
- $C_i$  = component i concentration (ppm);
- C<sub>o</sub> = initial component i concentration (ppm);
- EE = energy efficiency (kg copper/kWh);
- EC = current efficiency (%);
- F= Faraday constant (96487 Coulomb/mol);
- $i = current density (A/m^2);$
- $k = bed permeability (m^2);$
- L = fixed bed thickness (cm);

 $M_i$  = ionic mass (63,54 g.mol<sup>-1</sup> for the copper);  $m_{io}^s$  = initial mass of copper ions in the electrolyte solution (kg);

- $\Delta m$  = electroprocessed mass in  $\Delta t$  (g);
- $\Delta P$  = pressure drop in bed (Pa- kg.m<sup>-1</sup>.s<sup>-2</sup>);
- q =fluid surface velocity (m/s);
- $T = temperature (^{o}C);$
- $\Delta t = time interval (s);$
- V = voltage drop in bed (volts);
- $V_L$  = total volume of fixed bed (m<sup>3</sup>);
- $z_i$  = number of electrons involved in the
- electrochemical reaction (for the copper, z = 2);
- $\mu$  = fluid viscosity (kg.m<sup>-1</sup>.s<sup>-1</sup>);
- $\rho$  = fluid density (kg/m<sup>3</sup>);
- $\epsilon$  = Fixed bed porosity (dimensionless);
- $\varepsilon_0$  = initial bed porosity (dimensionless);
- $\rho_{\rm m}$  = metal density (kg/m<sup>3</sup>);

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#### HYDRODYNAMIC CHARACTERIZATION OF THE VORTEX BED\*

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<u>Abstract</u> - This work aimed to study some hydrodynamic characteristics of the vortex bed in view of the limited availability of literature on the subject. Bed pressure drop curves were constructed for increasing and decreasing flows. The bed consisted of sand, copper and glass particles and the fluid used was water at room temperature. Five bed heights were used for each type of particle. A qualitative description of the behavior of this bed was carried out. From the curves obtained, it was possible to adjust empirical equations to predict the maximum pressure drop in the bed, the pressure drop in the vortex formation flow rate and the minimum velocity of vortex formation.

#### **INTRODUCTION**

The objective of this study of the vortex bed is its use in the treatment of diluted solutions containing heavy metals through electrochemical techniques. The conventional treatment of metal ions in dilute solutions generally requires a sequence of steps that cause the loss of hundreds of tons of metals per year and also serious environmental problems. studying Therefore, when the electrodeposition of heavy metals, the aim is to solve a problem that is both ecological. economic and The electrochemical process consisting of only one step, in which the metal is coated, provides great benefits, being able to combine reduction of implantation costs with greater efficiency.

Previous studies indicate that volumetric electrodes are highly suitable for this use. Initially, the studies were limited to fixed and fluidized beds, however, due to deficiencies presented by these, mobile bed electrodes were developed, among them, the *vortex bed electrode*. The option for this bed comes from studies carried out by Stankovic and Wragg (1984), Stankovic and Stankovic (1991) and Scott (1981, 1988) that indicate this equipment, together with the spouted bed, as promising in the recovery of heavy metals. Recently, Mello (1994) reported deficiencies presented by the spouted bed that would discourage the use of this bed in electrochemical applications, indicating the vortex bed as the best option. When using the latter in the study of recovery of heavy metals,

#### MATERIALS AND METHODS

The particles used to fill the bed were sand, copper and glass, whose physical properties are summarized in Table 1. The average diameters of sand and glass were obtained in a Tyler/Mesh system of sieves. To obtain the average diameter of the (cylindrical) copper particles, the diameter and height of a sample of particles were measured with a caliper, obtaining the average for both and, with these data, the diameter of the sphere of equivalent volume (dp). The specific mass of the particles was obtained by pycnometry with water. The fluid used to move the particles was water at room temperature.

| particle | diameter            | sphericity | specific                             |  |
|----------|---------------------|------------|--------------------------------------|--|
| particle | ulameter            |            | mass                                 |  |
|          | (10 <sup>3</sup> m) |            | 10 <sup>-3</sup> kg/m <sup>3</sup> ) |  |
| sand     | 1.83                | 0.80       | 2.602                                |  |
| copper   | 2.76                | 0.87       | 8.804                                |  |
| glass    | 0.84                | 1.00       | 2.502                                |  |

Table 1 - Physical properties of particles

To carry out this study, an acrylic vortex bed was constructed (Figure 1), measuring 35.0 x 15.0 x 3.5 cm with an internal angle of 60° and width of the entrance section of 0.5 cm. The fluid is introduced at the bottom of the bed. passing through a free region that aims to homogenize its movement, followed by a stainless-steel screen that aims to prevent the flow of particles. The circulation of the fluid was obtained through a centrifugal pump and its flow controlled by a gate valve. As a flow meter, a duly calibrated Venturi type meter was used and the pressure drop in the bed was obtained with a U-shaped manometer. The bed was initially filled with one of the types of particles up to one of the predetermined heights (measured from the imaginary point of intersection between the left and right walls at the base of the bed).

Starting from zero flow, increasing values (known) of fluid flow were fixed and, at each increase, the value of the pressure drop in the bed was obtained and a qualitative description of the behavior of the particles in the bed was carried out. Special attention was dedicated to the points of vortex formation and maximum pressure drop. After stabilization in the value of the pressure drop, from the vortex point, the flow rate was slowly decreased and the same procedure used for ascending flows was used. This methodology was employed for 5 different bed heights for each of the three particle types.

#### **RESULTS AND DISCUSSION**

# Qualitative description of the behavior of particles in the bed

Sand and glass particles -- At the lowest bed height; Sand and glass particles showed the worst behavior in the formation of the vortex, especially in the upper region of the bed, where a great difference in height was observed between the ascending and descending regions of the bed towards the sand, and the glass had behavior similar to the spout. In all tests, a much higher velocity was observed in the ascending region in relation to the descending one, probably due to the small difference between the specific masses of sand and glass in relation to that of water.

# *Typical sequence of vortex formation steps:*

Initially the bed remains fixed; and then a gradual increase in the pressure drop in the bed is observed.

This is followed by the appearance of particle movement at the bottom of the bed, when the pressure drop across the bed begins to decrease.

A preferential channel is then formed with upward movement, central for the sand and to the left for the glass, observing that from this point onwards the pressure drop in the bed remains approximately constant. When the glass was used, the preferential channel formed moved to the center and, later, to the right.

Then, an incipient vortex movement begins in the region to the right of the bed, with the other regions remaining stagnant.

This movement gradually expands its extension until a well-

established vortex movement is reached throughout the volume of the bed.

After the fully characterized vortex, the increase in flow only accentuates the existing height difference between ascending and descending regions. In the case of glass, the increase in flow was limited by the tendency for particle drag.

With the gradual decrease of the flow, the vortex returns to establish itself only in the region to the right of the bed, remaining the other regions stagnant.

In sequence, the stagnant region increases in extension, and consequently, the vortex movement tends to have its area of action restricted to an increasingly smaller region until resulting in the complete loss of characterization of the movement.

There remains, then, only one preferred ascending channel; in the center for sand and on the right when using glass, which then moves to the center.

Further decreases in fluid flow lead to less particle movement, which also initiates a decrease in bed pressure drop.

This decrease in particle movement progresses to complete bed stagnation.

*Copper particles* -- In the same way as observed for sand and glass particles, also in the case of copper particles the worst behavior occurred when using the lowest particle height with the bed at rest. Compared to the previous cases, its performance was considerably better.

In general, all experiments carried out with copper particles showed better behavior, with uniform vortex formation throughout the bed, without losing character in any of its regions.

The vortex motion did not show a large difference in velocity between the ascending and descending regions, and

apparently these regions contained similar volumes of particles.

The visual observation of the experiments showed that, for the different bed heights used, the movement of the particles inside the bed occurred in a very similar way.

Due to the better performance presented with the use of copper particles, a more detailed description of their behavior was decided. For a typical experimental run, its characteristic curve will be presented (figure 2) in parallel with the qualitative description of the points considered pertinent to the understanding of the vortex movement.

The experiment to be described used a bed height - for particles at rest - of  $9.91 \times 10^{-2}$  m, which corresponds to the fourth height (in ascending order) among the five used.

Figure 3 shows drawings that aim to illustrate the various stages described in the movement of particles inside a vortex bed, which were obtained from visual observation.

Qualitative description:

Increasing flows:

• Points 1⇔2: the bed remains fixed.

• Point 3: particle movement begins at the base of the bed.

• Point 4: the movement started at point 3 is extended.

• Point 5: Incipient vortex movement appears in the left region of the bed.

• Point 6: an internal vortex is formed in the region on the left (that is, that does not reach the upper part of the bed or the opposite end to which it is located) in approximately 20% of the bed volume (figure 3(a)). • Point 7: the vortex movement increases, reaching about 50% of the bed but remains internal (figure 3(b)).

• Point 8: the vortex movement expands, reaching almost the entire bed (figure 3(c)).

• Point 9: the vortex is established throughout the bed volume (figure 3(d)).

• point  $10 \Rightarrow 11$ : vortex movement continues throughout the bed, observing only an increase in particle velocity and consequent increase in pressure drop (figure 3(e)).

Decreasing flows:

• Point  $11 \Rightarrow 12$ : the vortex remains established but shows a gradual decrease in its speed.

• Point 13: particle accumulation begins in the bed, characterizing the end of the established vortex (figure 3(f)).

• Point 14: the vortex movement becomes internal only, limited to the left region of the bed (figure 3(g)).

• Point 15: the vortex movement loses intensity (figure 3(h)).

• Point 16: only an incipient vortex movement remains (figure 3(i)).

• point  $17 \Rightarrow 18$ : the movement of the particles is limited to the base of the bed without any vortex characteristic.

• Point 19: the only movement observed happens to be in the inlet channel of the bed.

• Point  $20 \Rightarrow 1$ : the bed is completely fixed.

Adjustment of empirical equations for the vortex bed

The characteristic curves obtained for sand, copper and glass are presented in figures 4. (a) (b) and (c), respectively.

From these curves (together with the observation of the bed) the values of flow and pressure drop in the bed were obtained when the maximum pressure drop and vortex formation were present.

Depending on the three types of particles and the five bed heights used, values were obtained for 15 points of maximum pressure drop and 15 points of vortex formation.

For empirical correlations that would allow the prediction of maximum bed pressure drop and pressure and velocity drop when in vortex formation, the following dimensionless numbers, grouping all the variables of interest, were used:

| $N_h = \frac{h}{h_0}$                                                                                     | $N_{\rho} = \frac{\rho_s - \rho_f}{\rho_f}$                                     |
|-----------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------|
| $N_{Ga} = \frac{\left(\phi \cdot d_p\right)^3 \cdot \left(\rho_f\right)^2 \cdot g}{\left(\mu_f\right)^2}$ | $N_{Re} = \frac{\left(\phi \cdot d_{p}\right) \cdot \rho_{f} \cdot v}{\mu_{f}}$ |
| $N_{\Delta Pm\acute{a}x} = \frac{\Delta P_{m\acute{a}x}}{\rho_{f} \cdot g \cdot h_{0}}$                   | $N_{\Delta Pv} = \frac{\Delta Pv}{\rho_f \cdot g \cdot h_0}$                    |

Through the numerical method, the following correlations were then obtained:

$$N_{\Delta Pmax} = 0.363 N_{Ga}^{0.17} N_{\rho}^{1.14} N_{h}^{1.40} N_{Re}^{-0.29}$$
 (1)

$$N_{\Delta Pv} = 1.296 N_{Ga}^{-0.15} N_{\rho}^{1.30} N_{h}^{1.21}$$
 (2)

$$N_{Rev} = 1.818 N_{Ga}^{0.57} N_{\rho}^{0.33} N_{h}^{0.02}$$
 (3)

The adjusted empirical equations showed good agreement between predicted and observed values, as shown in figure 5. The average relative error presented was 5.14%, 3.87% and 7.10%, respectively.

Equation (3) confirms the fact observed during the experiments that the dependence between the employed bed height and the minimum vortex velocity is small.

In general, the vortex movement was more adequate when the difference in solid-fluid density was more significant and the particles were larger (copper particles).

For bed heights equal to or lower than  $h_0$ , the behavior of the particles was uncharacterized (similar to that of a spouted bed) due to the fact that, for these heights, the characteristic asymmetry of the vortex bed does not influence the particles.

For the copper particles (cylindrical and larger), after the formation of the vortex movement, an increase in the pressure drop was observed as the flow rate was increased. This fact is probably due to the friction between the particles and between them and bed walls.

#### CONCLUSIONS

In general, the vortex movement was more adequate when copper particles were used.

For bed heights equal to or lower than h<sub>0</sub>, the behavior of the particles was uncharacterized.

As can be seen from equation (1), the value for the maximum pressure drops in the bed  $(\Delta P_{max})$  increases with increasing d<sub>p</sub>,  $\rho_s$  and h decrease with increasing v.

By equation (2), it is observed that the pressure drops when the vortex movement is formed ( $\Delta P_v$ ) increases with increasing  $\rho_s$  and h decreases with increasing dp. From equation (3), it is concluded that the minimum velocity of vortex formation  $(N_{Rev})$  increases with increasing d<sub>p</sub>,  $\rho_s$  and h.

#### NOMENCLATURE

- d<sub>p</sub>: particle diameter [L]
- g: gravitational acceleration [LT<sup>-2</sup>]
- h: height of particles at rest [L]
- h<sub>0</sub>: reference height (fig. 1(b)) [L]
- N<sub>Ga</sub>: Galilei number[dimensionless]
- Nh: dimensionless height

N<sub>∆Pmáx</sub>; maximum pressure drop [dimensionless]

N<sub>Re</sub>: Reynolds number[dimensionless]

 $N_{\Delta P \nu}$ : pressure drop at the vortex point [dimensionless]

N<sub>p</sub>: dimensionless specific mass

- $\Delta P_{máx}$ : maximum pressure drop in the bed [ML<sup>-</sup>  $^{1}T^{-2}$ ]
- $\Delta P_V$ : pressure drop at the vortex point [ML<sup>-1</sup>T<sup>-2</sup>]
- v: fluid velocity in the inlet section[LT<sup>-1</sup>]

Greek letters

φ: particle sphericity

 $\rho_f\!\!:$  specific mass of the fluid [ML^-3]

- $\rho_s$ : specific mass of particles [ML<sup>-3</sup>]
- $\mu_{f}$ : fluid viscosity [ML<sup>-1</sup>T<sup>-1</sup>]





Figure 1. Vortex bed used in the experiments: (a) Perspective view. (b) Schematic representation; where  $\alpha = 50^{\circ}$ ,  $\gamma = 70^{\circ}$  e h<sub>0</sub> = 2,71 cm.



Figure 2. Characteristic curve for vortex bed



Figure 3. Steps in the behavior of a vortex bed for flows: Increasing flow - 3(a) to 3(d) - and decreasing flow - 3(e) to 3(i).



Figure 4. Characteristic curves of the vortex bed: pressure drop (Pa) in the bed as a function of the flow rate ( $cm^3/s$ ) for sand **a**) copper **b**) and glass **c**) having the height of the bed (m) as a parameter,



Figure 5. Predictive ability of equations (1); (2) and (3)

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#### A SYSTEM FOR CARRYING OUT POTENTIAL MEASUREMENTS IN THREE-DIMENSIONAL ELECTRODES\*

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<u>Abstract</u> - In the 70's, several types of probes were developed, through which the metalsolution potentials inside porous electrodes were obtained. Aiming to overcome the problems presented by these existing probes, this work sought to develop a more agile and effective technique for building this type of probe, as well as obtaining a probe whose measurements obtained by it were accurate, reliable and reproducible. Experimental tests were performed and their accuracy was guaranteed. After some adjustments were made to the probe and the construction of a support for its movement and support, its use was extended to the vortex bed electrode, where it performed well. Preliminary data were obtained for this electrode and shown through three-dimensional surfaces in the form of overpotentials.

#### **INTRODUCTION**

Several three-dimensional electrode systems, used in the electrodeposition of heavy metals from dilute solutions, have been experimentally and theoretically studied in recent decades.

Due to the great need to understand the internal behavior of these systems, most of these experimental studies have investigated the metal-solution potential distribution inside electrochemical reactors. This is because the local electrochemical reaction depends on the local potential distribution. The efficiency of the process will depend on the success of this reaction, Ponte and Gubulin (1992).

The measurements of the metal-solution potentials are obtained through a probe introduced, at the top, inside the bed to be investigated.

Several types of probes have already been built and used in laboratory tests, among

them we have the probe developed by Coeuret and collaborators (1976), the one used by Huh and Evan (1987) and the one by Lee and collaborators (1995), the latter two being similar to the probe elaborated by Plimley and Wright (1984).

Aiming to overcome the problems presented until then in the elaboration and use of existing probes, such as: clogging of the internal hole in the lower part of the probe during experimental measurements, difficulties in the internal insulation of the metallic rod, fixation and isolation of the reference electrode support in the upper end of the probe stem, among others, this work sought to develop a more agile and effective technique for making this type of probe, as well as obtaining a probe whose acuity was guaranteed.

This recently developed probe is similar to the one previously described by Coeuret et al (1976). Its use, in addition to fixed and fluidized beds, was extended to the vortex bed, with some adaptations made to the probe and the elaboration of a support for its movement and support, which together made it possible to obtain some preliminary data on the distribution of potentials in the vortex bed electrochemical reactor, shown through three-dimensional graphs in the form of overpotentials.

#### MATERIALS AND METHODS

The probe used in this work is composed of two parts: a lower part, which is introduced into the bed, and an upper part, where there is a glass support to which the reference electrode is attached, as shown in Figure 1. One of the reasons why it is also called a composite probe.



Figure 1 - Probe and the Reference Electrode

The lower part consists of a stainlesssteel rod coated internally and externally with a heat-shrink material, resistant to acid attack. At its end is the sensitive element of the probe, which is an ogival-shaped copper tip, with dimensions close to that of a bed particle, containing a small central hole to allow ionic contact between the electrolyte solution and the saline solution of the reference electrode. This tip, when introduced into the bed, behaves like one of its particles, presenting similar potential fluctuations.

The probe rod works as a Luggin capillary, containing the saline solution of the

reference electrode inside. Due to its length, its upper region is coated with a 3.3 mm thick glass tube, in order to offer greater firmness and precision in locating the points inside the bed.

The reading and presentation of the values of the metal-solution potentials are made through a digital multimeter connected to the reference electrode and to a small exposed surface of the metal rod, located between the support and the glass tube.

When extending the use of this probe to the vortex bed electrochemical reactor, it was necessary to change its rectilinear format, introducing a 149° angle between the glass tube and the lower rest of the rod (see Figure 1). Thus, disturbances in the hydrodynamics of the bed were avoided when penetrating the interior of the bed, thus making it possible to carry out measurements of the potentials without altering the characteristic vortex movement of the particles in this bed.

Another adaptation pertinent to its use in the vortex bed electrochemical reactor, which is illustrated in Figure 1, is the presence of an acrylic disc that surrounds the upper end of the glass tube. This is part of the mechanical support made to move and support the probe. When incorporated in it, it allows the displacement of the probe in the direction of the current flow through its rotation movement.

This mechanical support, illustrated in Figure 2, is made of acrylic and consists of three parts: a rectangular base resting on the top of the bed, responsible for moving the probe along the width of the bed; a second piece responsible for movement along the height of the bed, whose shape and length is the same as the probe rod and lastly, the disk fixed to the probe rod, already mentioned, whose immobilization is carried out by a U-shaped piece containing a threaded screw that when properly fitted and threaded (see Figure 2) prevents any rotational movement by the probe.

In Figure 3 we have an overview of the vortex bed electrochemical reactor with the probe mechanical support at the top, and the probe fitted together with the reference electrode.







- probe mechanical support
- probe reference electrode

#### Figure 3 - Vortex bed electrochemical reactor, together with the probe and its mechanical support.

The vortex bed and the experimental unit used to obtain preliminary measurements of the metal-solution potential, in this type of reactor, were the same as those presented in a previous work, Ponte and Gubulin (1992).

where the kinetic behavior of this bed was verified in the electrodeposition of copper ions in dilute solutions. The reference electrode used in all the tests was the saturated mercurous sulfate electrode.

#### Methodology developed for making the probe

The technique developed and tested for making the probe consists of a series of steps described below.

#### 1st Step: Internal and external coating of the metal rod.

Starting from a stainless-steel metal rod, the internal lining is first made. This is made with an outer diameter heat shrink material  $(\phi_{\text{ext}}=1.46 \text{ mm})$  close to the internal diameter  $(\phi_{int}=1.2mm)$  of the metal rod. Initially, this material is cut to the same length as the probe rod and left in an oven at 100°C for four minutes, where it acquires a certain flaccidity. Then it is stretched until it reaches a smaller diameter, enough to penetrate the stainless-steel tube, an epoxy and polymercaptan-based glue is applied over its entire external surface and quickly inserted into the tube. Once this is done, the set, stainless steel tube and internal coating, is heated in an oven for a few minutes, so that the coating relaxes, thus ensuring good adhesion to the internal walls. Care must be taken that the heat shrink material exceeds the metal rod by about 0.5 mm at one end and 1 cm at the other (see Figure 4a),

internal Once the insulation is completed, the external coating begins with the same material used previously, with a larger diameter ( $\phi_{ext}=3,00$ mm;  $\phi_{int}=2,33$ mm). The same glue used previously is passed all over the outside of the stainless-steel tube and then inserted inside the heat shrink material. Next, the entire assembly is heated in an oven at 100°C for three minutes, so that the coating contracts and adheres to the stainless steel. This outer coating is not done on the entire surface of the metal rod. 3.5 cm away from the end with the greatest amount of excess internal coating, leave about 2 cm of stainless steel exposed to allow electrical contact, as shown in Figure 4b.

Once this is done, the probe rod is coated with the glass tube from the exposed metallic area to the lower part of the probe that will not come into contact with the bed particles (see Figure 4c).

#### 2nd Step: Fixing the reference electrode support

After an interval of ten hours, the fixation of the reference electrode glass support begins. At the end close to the electrical contact region, apply the same type of glue already mentioned and insert the glass support. Let it dry until it is perfectly fixed and then, with the help of a syringe, this glue is injected inside until it covers approximately 0.5 cm of its spare internal lining, taking care not to clog it. it (see Figure 1). Once this is done, the probe is immobilized in a vertical position until it is dry and sealed.

#### 3rd Step: Fitting the copper tip

First, approximately 2 mm of the external coating of the lower end of the probe is cut and the exposed stainless steel is sanded well, in order to remove excess glue and allow perfect electrical contact between the metal rod and the copper tip. Then, the tip is fitted to the probe under pressure, as shown in Fig. 4d, and an epoxy-based resin is passed around it in order to isolate possible exposed areas of the metal rod during its fixation. Finally, the copper tip is sanded.



### Figure 4 - Illustrative drawings of the steps of making the probe.

#### Experimental tests carried out on the probe

Qualitative background tests were carried out in order to prove the isolation of the probe and to verify if there were changes in the values of the local potentials measured before and after the presence of the probe in areas not cathodically protected. This is because, according to Germain and Goodridge (1976), copper particles, when in the presence of areas not cathodically protected, dissolve, as well as the copper deposited on them, forming an oxide layer on their surface resulting from the reaction of dissolved copper. with the oxygen present in the solution. The sensitive element of the probe, behaving like one of the particles, would probably also create this oxide layer on its surface in the presence of such zones,

In the first test, a copper plate was immersed in an electrolytic solution containing 0.08M of copper sulfate and 0.1M of  $H_2SO4$  and its equilibrium potential was measured with the aid of a Luggin capillary coupled to a saturated mercurous sulfate electrode. Next, the probe was immersed in this same solution and the equilibrium potential of the copper tip was obtained.

For the second test, several tests were carried out in an acrylic cuvette, containing two copper plates, one functioning as a cathode and the other as an anode, both connected to a stabilized source, and an electrolytic solution with 1M of  $C_uSO_4$  and 0.1M H<sub>2</sub>SO<sub>4</sub>. The current supplied to the system was constant and the values kept between 0.04 and 0.12A.

For each analyzed current value, the following procedure was used: initially, the tip was immersed in the solution and the equilibrium potential was measured. Then the probe tip was sanded and the source was turned on. After the system reached equilibrium, the metal-solution potential was measured, firstly at the cathode by approaching and successively touching the current feeder, and then at the anode, also measured by approaching and touching the counter electrode. The potential values were noted and the readings repeated, always taking care to sand the tip before starting the measurement on the cathode. Then the same procedure was performed, only first on the anode and then on the cathode. This done, other measurements with the same experimental conditions were performed at the cathode and then at the anode, and vice versa,

#### **RESULTS AND DISCUSSIONS**

In the test carried out to verify the perfect insulation of the probe, the values of the equilibrium potentials obtained, both by the copper plate and by the probe's copper tip, were equal to  $-370 \text{ mV} (\pm 2\text{mV})$ , similarity through which the reliability of the values obtained by the probe was ensured.

As for the reproducibility of the measurements obtained by the probe in the cathode zones before and after its presence in dissolution regions, we have in table 1 the values of the metal-solution potentials obtained for one of the analyzed currents, I=0.04A, for the three different measurement conditions: first at the cathode and then at the anode, sanding the probe tip before starting the measurement at the cathode; then starting at the anode and then at the cathode, also sanding the tip before measuring again at the anode, and finally at the cathode and anode, alternately, without sanding the probe tip.

| solution for $I = 0.04A$ . |   |                      |      |      |
|----------------------------|---|----------------------|------|------|
| 1st condition              | 1 | E <sub>AC</sub> (mV) | -367 | -370 |

Table 1 - Values of metal potentials

| 1st condition    | 1 | $E_{AC}(mV)$ | -367 | -370 | -372 |
|------------------|---|--------------|------|------|------|
| $E_{eq}$ =-345mV | 2 | $E_{CE}(mV)$ | -306 | -308 | -309 |
| 2nd              | 1 | $E_{CE}(mV)$ | -309 | -312 | -306 |
| $E_{eq}$ =-350mV | 2 | $E_{AC}(mV)$ | -397 | -410 | -405 |
| 3rd              | 1 | $E_{AC}(mV)$ | -395 | -390 | -406 |
| $E_{eq}$ =-355mV | 2 | $E_{CE}(mV)$ | -309 | -313 | -306 |

It can be seen that the values close to the cathode and anode remained practically the same in each of the experiments, regardless of whether the copper tip was sanded or not, or whether the contact was made with the anode first and then with the cathode. For the other analyzed currents, this behavior was also maintained, that is, no alteration was perceived between the potential values obtained near the cathode before and after the contact of the probe with the anode. Although nothing influenced these measurements, at the end of the experiment, it was observed that the current feeder had a thin layer of pink deposits, while the counter electrode had a reddish-brown film. With these results and observations, it was concluded that there may be formation of copper oxide in the dissolution areas, when present, but this, as it is possibly a porous oxide film, presents an inexpressive interference on the values of the metal-solution potentials provided by the probe. This is because the reactions between copper and copper are more favorable than the reactions between copper oxide and copper.

Preliminary experiments performed on a 3.5 cm thick vortex bed electrode for an electrolyte solution containing 0.5 mol/l H<sub>2</sub>SO4 and 2 g/l of CuSO<sub>4</sub>, ei = 991.41 A/m2, demonstrated that the overpotential values obtained from the difference between the local metal-solution potential and the equilibrium potential measured with the probe, are in accordance with the predicted by the literature, as shown in Figure 5.





More negative overpotentials are found close to the counter electrode in the bed region where the particles have a downward movement and their porosity is very low. This is explained by the low resistivity of the dispersed phase in this region, which means that "the path of least resistance" from the cathode to the anode is through the particles, thus resulting in an increased probability of these reactions occurring in the bed region close to the anode.

#### CONCLUSIONS

The probe developed proved to be reliable and its measurements reproducible, thus ensuring its perfect use in carrying out potential measurements in electrodes in porous beds.

Preliminary measurements, carried out on the vortex bed electrode, proved to be in agreement with the results predicted by the literature.

#### NOMENCLATURE

ELV: vortex bed electrode

E<sub>AC</sub>: potential measured on the power supply E<sub>CE</sub>: potential measured on the counter electrode I: electric current applied to the system i: applied current density  $\phi_{ext}$ : external diameter

 $\phi_{int}$ : internal diameter

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#### REMOVAL OF COPPER IONS FROM DILUTE SOLUTIONS IN A PULSED BED ELECTRODE\*

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<u>Abstract</u> - This work presents a new conception of particulate electrode, the pulsed electrode, which was used in the removal of copper ions. This reactor operates in a fluid (electrolyte) flow regime that varies so as to characterize the electrode sometimes as a fixed bed, sometimes as a fluidized bed, thus uniting the main advantages of both. The performance of the reactor was evaluated using the central composite design, from which empirical models were obtained for two important response variables in the operation of this class of reactors, energy consumption and current efficiency, as a function of four independent variables considered pertinent to the study: electric current applied to the reactor, frequency of flow pulses, concentration of sulfuric acid and concentration of copper ions present in the composition of the electrolyte. Results show that the pulsating electrode compared to a fluidized electrode, under similar experimental conditions, presents a significant increase in current efficiency, without producing the agglomeration of the porous medium characteristic of the fixed bed electrode.

#### **1. INTRODUCTION**

Safe handling of polluting industrial waste is one of the biggest society. challenges facing modern Pollution through heavy metals such as copper, lead, mercury, nickel and zinc come from a wide variety of industries and most of these industries, when using some type of treatment, employ chemical treatment (precipitation), with large generation of highly metal concentrate. Modern environmental legislation tends to prioritize processes involving the reduction and minimization of waste, as well as their recycling. In this panel, electrochemical technologies will play an increasingly important role in providing society with efficient means of protecting the environment.

Among the existing electrochemical technologies, we highlight the use of electrochemical reactors with particulate electrodes Silva and Gubulin, (1996) which, due to their large specific surface area and the high mass transfer rates obtained, become ideal for the recovery of metals in dilute solutions, which are controlled by the metal ion diffusion process Rajeshwar and Ibanez, (1997).

In the development of particulate electrodes, three configurations stand out: the fixed bed electrode, the fluidized bed electrode and the circulating bed electrode. The studies of these reactors pointed to the presence of some limitations when using them in the recovery process of heavy metals present in liquid effluents. These limitations that sometimes appear in one reactor configuration, sometimes in another are mainly: existence of an internal distribution of overpotentials, poor conductivity of the dispersed phase, sintering of the porous medium, lack of mathematical adequate models. difficulties when scaling up Coeuret, (1992). The relationship between these deficiencies and the type of electrode to be used can be seen in Table 1.

Table 1. Limitations present in threedimensional electrodes

| alactrada tura        | fixed bed | fluidized bed | circulating bed |
|-----------------------|-----------|---------------|-----------------|
| electrode type        | electrode | electrode     | electrode       |
| Distribution of       | v         | v             | v               |
| overpotentials        | Λ         | Λ             | Λ               |
| poor conductivity     |           | Х             |                 |
| Sintering             | Х         |               |                 |
| Absence of models     |           |               | Х               |
| Difficult to scale up |           |               | Х               |

These difficulties led Coeuret and Paulin (1988) to develop an alternative three-dimensional electrode, called the *pulsed electrode*. What draws attention in this study is not the presentation of new а reactor configuration, but the use of an innovative operating mode in an already known equipment, which consisted of a fixed bed of cylindrical geometry with current and electrolyte flows. parallel. The electrolyte flow was admitted into the reactor through two valves, one of which was electrically controlled, which was adjusted by the operator so that, at regular intervals, it would allow an

increase in flow in the system, thus placing the bed in a state of fluidization. The reactor assumed a hybrid character, sometimes acting as a fixed bed, sometimes acting as a fluidized bed.

The present work extends the original conception of Coeuret and Paulin (1988) now using a rectangular geometry electrode with perpendicular electric current and electrolyte flows and, with the aid of auxiliary devices, such as frequency inverters and programmable logic controllers, proposes a reactor, also innovative and extremely versatile, capable of immediate scale-up.

In the evaluation of this reactor, the factorial design of experiments was used, specifically the central composite design, which, from relatively few experimental points, allows the adjustment of second-order empirical models [Myers and Montgomery, 1995].

For the study in question, the response variables chosen were current efficiency (EC) and energy consumption (EC) and the independent variables, four in number, were the current applied to the electrochemical cell (I), the frequency of the pulses of flow admitted to the reactor (P) and the concentration of sulfuric acid (Cac) and copper sulfate (Ccu) in the composition of the electrolyte.

### 2. MATERIALS AND METHODS

# 2.1 Reactor and systems supplying electricity and flow pulses

The reactor was completely made of acrylic and its dimensions are  $38.0 \times 10.0 \times 5.0$  cm. The current feeder and the counter electrode consist, respectively, of a copper plate and a lead plate.

As particulate electrode, copper particles were used in the form of cylinders with a diameter and length equal to 1.0 mm. To avoid direct contact of charged particles with the counter electrode, it was coated with a polyamide screen, which served as a diaphragm.

The electrolyte totaled a volume of 40 dm<sup>3</sup> and was constituted by the mixture of deionized water, copper sulfate and sulfuric acid, in such quantities as to provide the concentrations of sulfuric acid and copper ions required by the factorial design. It was pumped from the reservoir to the bottom of the reactor and returned from the top by gravity.

The electrical energy was supplied through a current source operating galvanostatically.

The system that enabled the variable flow regime, which characterizes the pulsating bed, is composed of a frequency inverter and a programmable logic controller coupled to the centrifugal pump.

#### 2.2 Experimental planning

According to the usual procedure in the use of factorial planning, the independent variables were coded, from a relationship of the type:

$$x_{i} = \frac{x_{i}^{*} - x_{i}^{*}(0)}{x_{i}^{*}(1) - x_{i}^{*}(0)}$$
(1)

where:

xi = real value of the coded variable;

xi\* = real value of the variable in uncoded form;

 $xi^{*}(0) =$  intermediate value of the variable in uncoded form;

 $xi^*(1) = variable value in uncoded form corresponding to the value encoded in 1.$ 

Table 2 brings the correspondence between coded and noncoded values as well as the experimental limits used in obtaining the models, in whose variation range they are valid.

Table 2. Values assumed by the variables during the experiments

|                          | Codification |     |     |     |     |
|--------------------------|--------------|-----|-----|-----|-----|
|                          | -2           | -1  | 0   | 1   | 2   |
| C <sub>ác</sub><br>(M)   | 0            | 0.3 | 0.5 | 0.7 | 0.9 |
| C <sub>cu</sub><br>(g/l) | 0            | 0.7 | 1.1 | 1.6 | 2   |
| I(A)                     | 4            | 5   | 6   | 7   | 8   |
| P (*)                    | 17           | 100 | 183 | 266 | 349 |

\*(number of pulses/30 min)

The factorial design chosen was the central composite design, which allows, from relatively few experimental points, the adjustment of a second-order empirical model as follows:

$$y_{i} = b_{o} + \sum_{i} b_{i} . x_{i} + \sum_{i} \sum_{j} b_{ij} . x_{i} x_{j} + \sum_{i} b_{ii} . x_{i}^{2}$$
(2)

The experiments were carried out according to the planning matrix shown in Table 3, where each line represents the conditions under which each of the experiments was carried out, in a total of thirty-six.

Table 3. Planning Matrix

| Point | Cac | Ccu | I  | Р  |
|-------|-----|-----|----|----|
| 1     | -1  | -1  | -1 | -1 |
| 2     | 1   | -1  | -1 | -1 |
| 3     | -1  | 1   | -1 | -1 |
| 4     | 1   | 1   | -1 | -1 |
| 5     | -1  | -1  | 1  | -1 |
| 6     | 1   | -1  | 1  | -1 |
| 7     | -1  | 1   | 1  | -1 |
| 8     | 1   | 1   | 1  | -1 |
| 9     | -1  | -1  | -1 | 1  |
| 10    | 1   | -1  | -1 | 1  |
| 11    | -1  | 1   | -1 | 1  |
| 12    | 1   | 1   | -1 | 1  |
| 13    | -1  | -1  | 1  | 1  |
| 14    | 1   | -1  | 1  | 1  |
| 15    | -1  | 1   | 1  | 1  |
| 16    | 1   | 1   | 1  | 1  |
| 17    | -2  | 0   | 0  | 0  |
| 18    | 2   | 0   | 0  | 0  |
| 19    | 0   | -2  | 0  | 0  |
| 20    | 0   | 2   | 0  | 0  |
| 21    | 0   | 0   | -2 | 0  |
| 22    | 0   | 0   | 2  | 0  |
| 23    | 0   | 0   | 0  | -2 |
| 24    | 0   | 0   | 0  | 2  |
| 25    | 0   | 0   | 0  | 0  |
| 26    | 0   | 0   | 0  | 0  |
|       |     |     |    |    |
| 36    | 0   | 0   | 0  | 0  |

2.3 Experimental procedure

The following steps were then performed for each of the 36 experimental points:

- Preparation of electrolytic solution from calculated amounts of sulfuric acid, copper sulfate and deionized water.

- Assembly of the electrochemical reactor with the addition of a known amount of copper particles.

- Preparation of the electricity supply system, setting a value of electric current to be applied to the reactor.

- Adjustment of the system supplying flow pulses at a given pulse frequency.

- Experimental run itself, with the monitoring of the voltage drop presented by the reactor through a digital multimeter.

After this procedure, the reactor was emptied and the particles weighed,

resulting in values obtained experimentally for the electrodeposited mass on the particles that constituted the particulate bed and for the average voltage difference in the cell during the experimental run.

As for the variable frequency of flow pulses, the following should be highlighted: during the experimental run (30 minutes), the period in which the electrode remained in the fluidization state was fixed at 3 seconds for all experiments and the period in bed state fixed assumed the following values: 2.15s; 3.75s; 6.85s; 15.00s; 102.90 s, resulting in the pulse frequency shown in Table 2.

#### **3. RESULTS ANALYSIS**

With the values of electrodeposited mass and the average voltage in the reactor were calculated, using Eq. (3) and from Eq. (4), respectively, the current efficiency (CE) and energy consumption (EC) values.

$$CE = \frac{100 \cdot z_i \cdot F \cdot dm}{M_i \cdot I \cdot dt}$$
(3)

$$EC = \frac{2.78 \times 10^{-4} \cdot V \cdot I \cdot dt}{dm}$$
(4)

where:

dm - electrodeposited mass [g]

dt - time during which current is applied to the reactor [s]

F-Faraday constant [94487 A.s/mol]

I - electrical current applied to the reactor [A]

Mi - ionic mass of the species involved [63.55 g/mol]

zi - number of electrons involved in the electrochemical reaction

V - voltage drop in the reactor [V]

The models were adjusted through the Least Squares Method and the regression coefficients can be found in Table 4, where the terms considered not significant were already excluded from the model (with a significance level of 93%).

Regression model coefficients term EC CE 78.68 Constant 3.41 3.9 -0.7 C<sub>ác</sub> C<sub>cu</sub> \_ \_ 2.29 0.1 Ι Ρ -1.63 0.24  $C_{\acute{a}c}^{2}$ -0.810.3  $C_{cu}^{2}$ -0.99  $\mathbf{I}^2$ \_ - $\mathbf{P}^2$ -0.82 \_ Các.Ccu \_ \_ Các.I 1.07 \_ Các.P \_ \_ C<sub>cu</sub>.I \_ \_

Table 4. Regression Analysis

The analysis of variance for the responses under study can be seen in Table 5.

1.38

1.45

\_

\_

C<sub>cu</sub>.P

I.P

Table 5. Analysis of Variance for the response variable RV

| RV | R <sup>2</sup> | Re-<br>gres-<br>sion<br>mean<br>square | Error<br>mean<br>square | Fc    | Ft<br>(99.9%) |
|----|----------------|----------------------------------------|-------------------------|-------|---------------|
| CE | 0.82           | 78.96                                  | 6.11                    | 12.92 | 4.64          |
| EC | 0.89           | 4.06                                   | 0.063                   | 64.44 | 6.07          |

The adjustment of the empirical models showed that, for the current efficiency, the independent variables affect this response in a complex way, including the presence of interaction terms. As for energy consumption, it showed a simpler behavior, without the presence of interactions and being greatly influenced by the acid concentration variable.

The squared multiple correlation coefficients  $(R^2)$  of 0.82 and 0.89 obtained for the current efficiency and energy consumption models, respectively, can be considered acceptable in view of the wide range of variation of the variables used in obtaining the models.

# 3.1 Comparison with the fluidized bed electrode

The equipment used in the study in purposely auestion was built-in dimensions similar to those found in Silva and Gubulin (1996), who used a fluidized bed electrode. and subjected to experimental conditions as close as possible to those used by the authors in order to allow comparison of the results.

In the work by Silva and Gubulin (1996), bed thickness was a variable under study and, therefore, the model obtained was a function of this variable. To make the comparison with the pulsating electrode, the encoded value 1 (corresponding to 3.0 cm) was used in the model obtained for the fluidized electrode, so that the thickness of the two reactors was the same.

For this thickness value, the highest current efficiencies for the fluidized bed electrode are obtained for the highest values of acid concentration and current (+2 coded). The largest values for the current efficiency as the copper ion concentration decreases assuming the coded values of 2, 0, -2 are then respectively 82.69%, 75.27% and 78.17%.

For the pulsed electrode, under the same conditions of acid concentration and electric current (+2 coded), the model for current efficiency becomes a function only of the number of pulses and the copper concentration. Copper concentration assuming the same coded values of 2, 0, -2 results in three models for current efficiency that are functions only of the number of pulses (P). By deriving these functions in order to obtain the values of P that would provide the for the maximum value current efficiency, the values of P were obtained: 2; 0.77 and -0.91 which resulted, respectively, in values of 92.92%, 92.59% and 88.82% for the current efficiency. It can be observed, then, that they are notably superior to those obtained when the reactor operates only in a fluidization regime.

#### 4.CONCLUSIONS

The joint use of a frequency inverter and a programmable logic controller proved to be adequate for operating the pulsed electrode, consisting of a versatile arrangement capable of an eventual reactor scale-up, where the flow pulse supply system would not need to be exchanged.

The pulsed electrode operating under experimental conditions close to those of a fluidized electrode provided a significant improvement in the values obtained for the current efficiency, without presenting at any moment the agglomeration (sintering) of the porous medium, typical of the fixed bed electrode.

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